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Photochemical synthesis of arenetricarbonylchromium(0) complexes: scope and limitations

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Abstract

Two photochemical methods for the preparation of arenetricarbonylchromium(0) complexes are described. The first involves irradiation of a solution of hexacarbonylchromium(0) and arene in THF at room temperature with a medium pressure mercury lamp. In the second a suspension of hexacarbonylchromium(0) in THF is irradiated in the same way and the arene then added. The yields are generally lower than those obtained by the usual thermal methods, but there is advantage in the milder reactions conditions.

Introduction

Tricarbonylchromium(0) complexes of a number of cyclophanes have been reported [1]. Most of these complexes were made in the conventional fashion by heating the cyclophane with $Cr(CO)_6$ or a suitable derivative. This approach, is only practicable however, if the cyclophane possesses sufficient thermal stability.

The thermal stability of [*n*]paracyclophanes decreases rapidly as the bridge is shortened. While [7]paracyclophane [2] and [6]paracyclophane [3] are thermally stable, [5]paracyclophane, generated by irradiation of its precursor 1,4-pentamethylene Dewar benzene, decomposes above 0 ° C [4]. Introduction of electron-withdrawing groups on the aromatic ring slightly improves the thermal stability [5], but no compound of this type has been isolated. The transformation of [5]paracyclophane into a tricarbonylchromium complex is expected to increase the thermal stability and allow isolation of this compound as a metal-complexed ligand, and possibly also furnish a derivative suitable for X-ray crystal structure determination. As the known methods for the preparation of tricarbonylchromium complexes [6] were too severe for survival of the sensitive [5]paracyclophane, we tried to develop a milder, photochemical approach.

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The methods of synthesizing arenetricarbonylchromium complexes were reviewed [6,7]. The most widely used method is that discovered by Mahaffy and Pauson [8a], in which the arene and $Cr(CO)_6$ are stirred in refluxing dibutyl ether for 40 h. Several workers have modified this procedure by using highly reactive intermediates such as (triamine)tricarbonylchromium(0) [9] or (triacetonitril)tricarbonylchromium (0) [10]. Although these modifications allow use of milder reaction conditions (2 h in refluxing THF or dioxane) they are more time consuming, since they involve the synthesis and purification of the reactive intermediates; moreover, the conditions are still much too severe for [5]paracyclophane.

There have been only a few investigations of use of photochemical approach. As long ago as 1969, Strohmeier and Müller reported that irradiation of $Cr(CO)_6$ in THF yielded a pentacarbonyltetrahydrofuranchromium(0) complex that could be used to synthesize pentacarbonylmonophosphinechromium(0) complexes [11]. Deckelmann and Werner synthesized benzene- and mesitylene-tricarbonylchromium(0) by irradiating the arene and $Cr(CO)_6$ in high vacuum at 20–50 ° C [12]; they pointed out the advantage of this procedure for thermally sensitive compounds. Christiani et al. used a combination of a thermal and a photochemical method by irradiating a refluxing solution of [2,2]paracyclophane and $Cr(CO)_6$ in ligroin at 100 ° C [13]; the molybdenum and tungsten complexes were obtained similarly. Pannell et al. also used a combination of a photochemical and thermal procedure, involving irradiation of a refluxing solution of dibenzo-18-crown-6 and $Cr(CO)_6$ in THF/2,2,4-trimethylpentane (1/1), to make the corresponding tricarbonylchromium complex [14].

We describe here a photochemical route to arenetricarbonylchromium(0) complexes which can be used at room temperature; to our knowledge, such a mild procedure has not been reported before. The new approach has so far been examined in only a preliminary way and the reaction conditions have been optimized only for the anisole complex.

Results and discussion

Two variations of the photochemical complexation reaction were investigated. In method A a solution of arene (ArH) and $Cr(CO)_6$ (ratio 15/1) in degassed THF was irradiated for 40 h at room temperature. In method B the arene was added to a photolysed solution of $Cr(CO)_6$ in THF. As can be seen from Table 1, method A generally gave the better results.

Most striking is the difference in the case of the benzoic ester derivatives, which do not react at all by method B. It is noteworthy that during the formation of **7**, large amounts of **1** were formed (up to 50%). This photochemical decarboxylation reaction did not take place in the case of **8** and **9**, and its origin is unclear.

In the case of the halobenzenes only method B was successful, although the yields were very low; raising the reaction temperature slightly to 40 ° C increased the yields of **4** and **5**. Method A gave unidentified black material. The reason for this is the photochemical instability of **4** and **5**, as shown by the following experiments. The free halobenzenes were found to be stable when irradiated under the conditions of method A in the absence of $Cr(CO)_6$. In contrast, **4**, obtained by method B, upon irradiation gave black decomposition products, which were probably identical to those formed in method A.

Table 1

Yields of arenetricarbonylmetal compounds $ArH(CO)_3M(0)$

Product			Yield (%)		
$ArH(CO)_3M$	Arene (ArH)	Metal (M)	Method A [a]	Method B	Thermal [b]
1	C_6H_6	Cr	50	25	89 [b]
2	C_6H_5OMe	Cr	40	24	85 [b]
3	$C_6H_5NMe_2$	Cr	21	23	85 [b]
4	C_6H_5Cl	Cr	0	5(10) [c]	64 [b]
5	C_6H_5F	Cr	0	$<1(6)$ [c]	90 [b]
6	$p\text{-}C_6H_4Me_2$	Cr	26	21	94 [b]
7	C_6H_5COOMe	Cr	19 [e]	0	89 [b]
8	$p\text{-}MeC_6H_4COOMe$	Cr	15	–	79 [d]
9	$o\text{-}C_6H_4(COOMe)_2$	Cr	29	0	–
10	C_6H_5OMe	W	24	–	25 [f]

[a] See Text. [b] Taken from ref. [8a]. Reaction temperature 40 ° C. [d] Taken from ref. 8b. [e] A 1/1 mixture of **1** and **7** was obtained. [f] Taken from ref. 16.

Method A is also applicable to other metal carbonyls, as can be seen from table 1, entry 10.

The results presented in Table 1 are from nonoptimized experiments. Optimization was examined only in the case of **2** in method B (Table 2). The results show that prolonged irradiation does not significantly increase the yield (entries 1 and 2). An excess of the aromatic compound, which is normally used in the thermal complexation, is not required (entries 2 and 3), but excess of $Cr(CO)_6$ is beneficial (entries 3 to 6). Particularly important for the potential complexation of difficultly-accessible and sensitive small cyclophanes is the observation that reasonable yields may be obtained (calculated for the minor component) even in dilute solutions with an excess of $Cr(CO)_6$ (entries 4 and 5).

The course of the photochemical formation of the tricarbonylchromium(0) complexes can be suggested in the light of the observation that when a suspension of $Cr(CO)_6$ in degassed THF is irradiated, bubbles of CO are immediately evolved. This was noted previously by Strohmeier who also reported that the first molecule

Table 2

Effect of the reaction conditions on the yield of **2** from procedure B [a]

Entry	$Cr(CO)_6$ (mmol)	Anisole (moles per mole of $Cr(CO)_6$)	Irradiation time (h)	Reaction time (h)	Yield [b] (%)
1	4.5	15	40	20	20
2	4.5	15	70	20	25
3	4.5	1	40	20	24
4	4.5	1/2	40	20	30
5	4.5	1/4	40	20	51
6	9.0	1	40	20	33

[a] All reactions were carried out in 80 ml of THF at room temperature (see Experimental). [b] Based on the reactant used in the smaller amount.

of CO was lost most readily [11]. We believe that prolonged irradiation eventually leads to a triple fission of the chromium–CO bonds, and in the presence of THF this leads to a $Cr(CO)_3(THF)_3$ complex, although such a complex seems not to have been identified in solution. The photolysed solutions probably also contain other complexes $Cr(CO)_{6-n}(THF)_n$; that CO loss from $Cr(CO)_6$ produces coordinatively highly unsaturated chromium species in the gas phase is well documented [15]. Our method therefore probably involves the in situ generation of a highly reactive THF-analogue of the triamine and triacetonitrile compounds, which has the advantage of being more reactive in the formation of arene complexes.

Conclusions

Although the yields are not as high as those from the thermal methods, the advantage of the direct photochemical formation of arenetricarbonylchromium(0) complexes lies in the much milder reaction conditions. This makes the reaction useful in the case of thermally labile compounds; the in situ preparation of a highly reactive precursor makes the method less time consuming as well.

The two methods can probably be extended to the synthesis of other metal carbonyl complexes, as is exemplified by the synthesis of anisoletricarbonyltungsten (**10**). A major disadvantage for general application is the low reactivity of the haloarenes, which might possibly be overcome by using slightly higher reaction temperatures in method B.

The application of the new, milder method for the preparation of a tricarbonylchromium(0) complex of [5]paracyclophane and similar strained arenes is under investigation.

Experimental

^1H NMR spectra were recorded on a Bruker WM 250 spectrometer at 250.13 MHz or a Bruker WH 90 spectrometer at 90 MHz. Melting points are uncorrected. All solvents were deoxygenated by immersion for 20 min in an ultrasonic bath. The irradiations were carried out with a water-cooled Hanau TQ 150 medium pressure mercury lamp under N_2 in a photochemical reactor described by Jaouen and Simonneaux [18]. Medium pressure column chromatography was performed on a Jobin–Yvon-miniprep with pentane/EtOAc (9/1) as the eluent on silicagel 60 (40 mesh).

Method A, general procedure

A stirred suspension of 1 g (4.5 mmol) of $Cr(CO)_6$ and 67.5 mmol of arene in 80 ml of THF was irradiated for 40 h at room temperature. CO evolution was more vigorous in the beginning of the reaction. The THF was distilled off under reduced pressure. The residue was dissolved in pentane/EtOAc (9/1) and chromatographed on a short silica column. From the eluted solutions, the solvents and remaining arene were evaporated under reduced pressure to leave the products. In the case of **9**; purification was by medium pressure column chromatography (silica; pentane/EtOAc (9/1)). In each case the main fraction was recrystallized from pentane. Details of yields and physical properties are given in Tables 1 and 3, respectively.

Table 3

^{1}H NMR spectral data and melting points for compounds **1**–**10**

Compound	m.p. (°C)	^{1}H NMR data [a]
1	159–160 (lit 159–160 [8])	5.33(s, 6H)
2	84–85 (lit 86–87 [17])	5.56 (dd, *J* 6.3,6.0Hz, 2H, H(3,5)), 5.13 (d, *J* 6.3 Hz, 2H, H(2,6)), 4.89 (t, *J* 6.0 Hz, 1H, H(4)), 3.74 (s, 3H, OCH$_3$).
3	144–145 (lit 145–146 [17])	5.60 (dd, *J* 6.2, 7.2 Hz, 2H, H(3,5)), 4.85 (t, *J* 6.2 Hz, 1H, H(4)), 4.80 (d, *J* 7.2 Hz, 2H, H(2,6)), 2.90 (s, 6H, CH$_3$).
4	103 (lit 102–103 [17])	5.45 (bs, 2H, H(3,5)), 5.43 (s, 2H, H(2,6)), 5.03 (m, 1H, H(4)).
5	118–19 (lit 122–124 [17])	5.53 (dt, *J* 3.1, 6.1 Hz, 2H, H(3,5)), 5.35 (dd, *J* 6.0, 6.1 Hz, 2H, H(2,6)), 4.87 (dt, *J* 2.7, 6.1 Hz, 1H, H(4)).
6	98–99 (lit 99–100 [17])	5.26 (s, 4H), 2.14 (s, 6H)
7	93–95 (lit 97–98 [17])	6.10 (d, *J* 6 Hz, 2H, H(2,6)), 5.6–5.1 (m, 3H, H(3,4,5)), 3.91 (s, 3H, OCH$_3$) [b]
8	*c*	5.60 (AA′BB′ system, δ(A) 6.10, δ(B) 5.10, *J*(AB) 7.0 Hz, *J*(A′B) 0, 4H, H(2,3,5,6)), 3.85 (s, 3H, OCH$_3$), 2.26 (s, 3H, CH$_3$) [b]
9	*c*	5.53 (AA′BB′ system, *J*(AB) ca. 6 Hz, *J*(AB′) ca. 2 Hz, 4H, H(2,3,4,5)), 3.90 (s, 6H) [b]
10	100 (decomp)	5.64 (dd, *J* 6.2,6.2 Hz, 2H, H(3,5)), 5.34 (d, *J* 6.2 Hz, 2H, H(2,6)), 5.03 (t, *J* 6.2 Hz), 1H, H(4)), 3.70 (s, 3H, OCH$_3$).

[a] CDCl$_3$, 250.1 MHz, 295 K. [b] CDCl$_3$, 90 MHz, 295 K. [c] Sublimation caused partial decomposition so a m.p. could not be obtained.

Method B, general procedure

A stirred suspension of 1 g (4.5 mmol) of Cr(CO)$_6$ in 80 ml of THF was irradiated at room temperature for 40 h, 67.5 mmol of arene were then added, and stirring was continued for another 20 h. Work-up was as described for method A.

Both methods were also performed on half scale with the same result.

Method B, optimisation procedure

A stirred suspension of 1 g (4.5 mmol) of Cr(CO)$_6$ in 80 ml of THF was irradiated at room temperature for 40 h. Anisole was then added (for amounts see Table 2) and stirring was continued for another 20 h. Work-up was as described for method A.

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