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(η^6-Anisole)(η^2-benzene)dicarbonylchromium(0): an intermediate in the photochemical carbonyl substitution of (η^6-anisole)tricarbonylchromium(0) in benzene

Shigero Oishi
Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556 (U.S.A.)

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Abstract

The photochemical carbonyl substitution of (η^6-anisole)$Cr(CO)_3$ has been investigated by laser flash photolysis. Both transient spectra and second-order rate constants for the reactions of transients with nucleophiles are found to be extremely variable depending upon solvents used. The coordination of benzene to the transient in cyclohexane forms the transient in benzene, indicating two discrete chemical species: (η^6-anisole)$Cr(CO)_2$ and (η^6-anisole)$Cr(CO)_2$(η^2-benzene). The latter type of transient was observed also for fluorobenzene and mesitylene, leading to the assignment of a weak band in the visible region as η^2-arene → Cr charge transfer. The existence of (η^6-arene)$Cr(CO)_2$(η^2-arene$'$) may throw light on what have been described as solvent effects in organometallic reactions.

Introduction

A carbonyl of (η^6-arene)$Cr(CO)_3$ is well known to be photochemically substituted by various nucleophiles [1]. (η^6-Arene)$Cr(CO)_2$ has been suggested as an intermediate, and this does not conflict with the results of quantitative studies: quantum efficiencies in alkane and arene solvents are almost identical with each other [2–4].

$$(\eta^6\text{-arene})Cr(CO)_3 \xrightarrow{h\nu} (\eta^6\text{-arene})Cr(CO)_2 + CO \qquad (1)$$

$$(\eta^6\text{-arene})Cr(CO)_2 + L \rightarrow (\eta^6\text{-arene})Cr(CO)_2L \qquad (2)$$

Transient spectra observed by means of laser flash photolysis, however, are found to be extremely variable depending upon the solvents used [5*]. We describe here

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* Reference numbers with asterisks indicate notes in the list of references.

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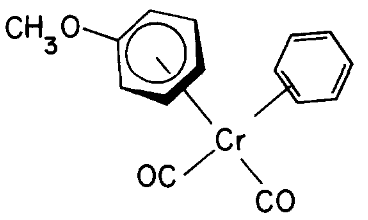
the kinetic and spectroscopic natures of transients and claim the existence of (η^6-arene)Cr(CO)$_2$(η^2-arene′) as an intermediate in arene solvents, where arene′ originates from the solvent.



(η^6-anisole)Cr(CO)$_2$(η^2-benzene)

Results and discussion

Cyclohexane or benzene solutions of (η^6-anisole)Cr(CO)$_3$ (1.0 m*M*) were deaerated by bubbling argon through, and then subjected to pulsed-laser photolysis at 337 nm using a nitrogen laser (3 mJ/pulse and 8 ns of pulse width). Differential absorption spectra at 50 ns after the excitation pulse are shown in Fig. 1. Distinct differences can be seen throughout the region observed. As the lowest energy band of (η^6-anisole)Cr(CO)$_3$ assigned as a Cr → arene charge transfer band is significant only at wavelengths shorter than 425 nm [6], these spectra can be thought of as the exact absorptions of the transients. Assuming that quantum yields for the generation of the transients are unity, ϵ_{630} for **1** and ϵ_{590} for **2** are determined as 310 and 240, respectively, by a comparative method using benzophenone [7]. The assumption is considered proper by the fact that quantum efficiency of the carbonyl substitution by *N*-n-dodecylmaleimide is reported as unity [3]. Essentially similar solvent differences in transient spectra could be observed also in the case of (η^6-benzene)Cr(CO)$_3$ or (η^6-mesitylene)Cr(CO)$_3$, though a simple comparison as above was disturbed by the presence of Cr → arene CT bands at longer wavelengths.

In the presence of pyridine as a nucleophile, these two different spectra changed to an identical spectrum, which is the spectrum of the final product, (η^6-anisole)Cr(CO)$_2$Py [2]. Second-order rate constants for the reaction in cyclohexane and benzene obtained at 510 nm by the change of pyridine concentration (0.012–0.12 *M*) differ by a factor of 40, as shown in Table 1. We believe that the differences in rate constants are great enough to suggest that the reactions of two discrete chemical species are being observed. Indeed, when mixtures of cyclohexane and benzene (0.07–0.43 *M*) were used as solvents, we could observe the change of **1** to **2**: the second-order rate constant of the reaction was determined at 460 nm as 4.0×10^7 M^{-1} s^{-1}. This means that **1** is converted into **2** within ~ 2 ns in benzene alone as a solvent.

The observations can be consistently explained by assuming **1** as (η^6-anisole)Cr(CO)$_2$ and **2** as (η^6-anisole)Cr(CO)$_2$(η^2-benzene). The modes of coordination of two arenes in **2** must be distinct from each other, because the photochemical substitution of arene in (η^6-arene)Cr(CO)$_3$ was reported to be not so efficient [4]. In other words, the interconversion between (η^6-arene)Cr(CO)$_2$(η^2-arene′) and (η^2-arene)Cr(CO)$_2$(η^6-arene′) may explain the photochemical substitution of arene if a rather high energy barrier is assumed [8].

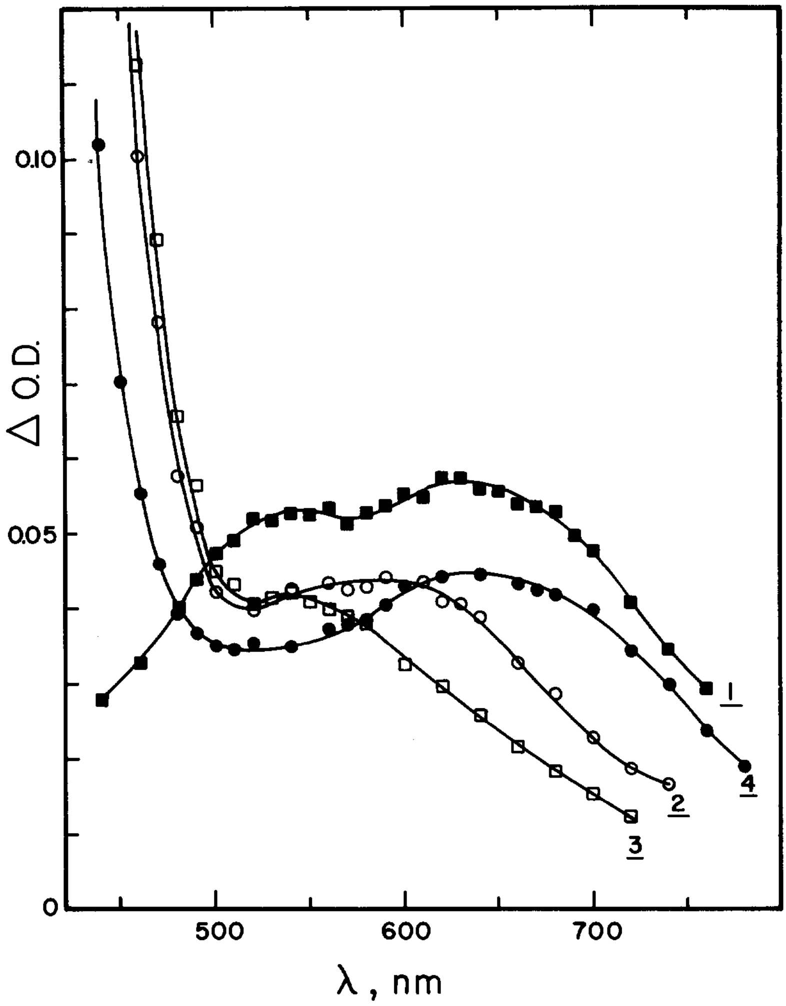


Fig. 1. Transient differential absorption spectra of (η^6-anisole)Cr(CO)$_3$ (1.0 m*M*) in cyclohexane (**1**), benzene (**2**), fluorobenzene (**3**), and mesitylene (**4**), observed at 50 ns after the laser pulse (337 nm). Each point plotted is obtained by the average of at least four shots and normalized by referring the intensities of benzophenone triplet absorption measured before and after the experiments.

Table 1

Second-order rate constants for the reaction of the transients with nucleophiles

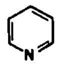
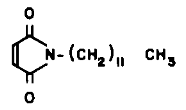
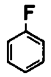
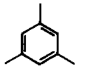
L \ Solvent	Cyclohexane	Benzene
	2.9×10^{7} $M^{-1}\,s^{-1}$	7.4×10^{5}
	4.1×10^{7}	7.9×10^{5}

Table 2

Second-order rate constants for the reaction of the transient in cyclohexane (**1**) with arenes, and absorption maxima of the resultant species

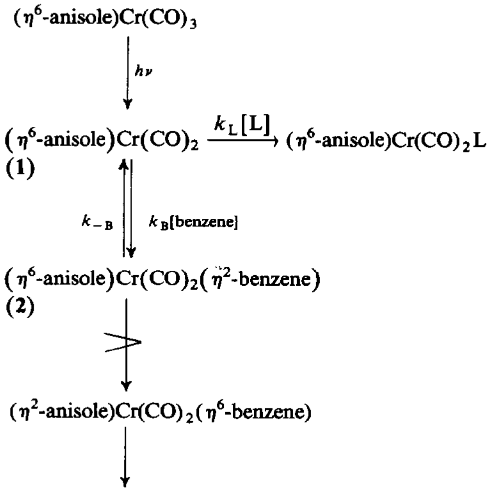
Arene			
k_2 M^{-1} s^{-1}	1.4×10^7	4.0×10^7	5.0×10^6
Absorption Maximum nm	540	590	630

By the application of the steady-state treatment to the system after the excitation pulse ($k_B[B] \gg k_L[L]$), we can obtain the equation:

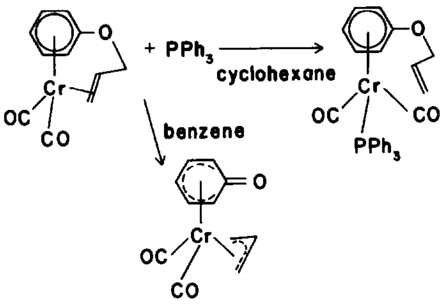
$$\frac{d[P]}{d\,t} = \frac{k_{-B}}{k_B[B]} \cdot k_L[L][\mathbf{2}] = \frac{k_{-B}}{k_B[B]} \cdot k_L[L]\{[P]_\infty - [P]\}$$

where [P] stands for the concentration of a substitution product. The apparent rate constant obtained in benzene (Table 1), therefore, consists of the real coordination rate constant (k_L) and the factor concerning to the equilibrium between **1** and **2** ($k_{-B}/(k_B[B])$). The apparent great differences in the rate constants for cyclohexane and benzene are due to the latter part. The real coordination rate constant (k_L) itself cannot be considered to be influenced such a great extent by these two solvents, because of the similar viscosities.

Transient spectra in fluorobenzene and mesitylene were measured (Fig. 1), and second-order rate constants for the coordination of these arenes to **1** were determined in cyclohexane solution (Table 2). The fact that the absorption maximum shifts to longer wavelengths with increasing electron density of η^2-arene suggests



Scheme 1



Scheme 2

that the absorption contains η^2-arene → Cr CT transitions in its character. A smaller rate constant for fluorobenzene than for benzene can be explained by the idea that donation of electrons from η^2-arene to Cr is more important than back-donation in making the η^2 coordination bond. A smaller rate constant for mesitylene may be due to steric hindrance caused by three methyl substituents [9]. This kinetic and spectroscopic evidence unambiguously suggests the existence of (η^6-arene)$Cr(CO)_2$-(η^2-arene′) where arene′ originates from arene solvents.

In conclusion, the photochemical carbonyl substitution of (η^6-arene)$Cr(CO)_3$ in arene solvents proceeds via a four-step process; initial photochemical generation of coordinatively unsaturated (η^6-arene)$Cr(CO)_2$, immediate coordination of arene′ (solvent) to give (η^6-arene)$Cr(CO)_2$(η^2-arene′), regeneration of (η^6-arene)$Cr(CO)_2$ by the dissociation of arene′, and coordination of L to give (η^6-arene)$Cr(CO)_2L$. Though the intervention of (η^6-arene)$Cr(CO)_2$(η^2-arene′) has almost no effect as far as we see quantum yields of the photochemical carbonyl substitution by pyridine or *N*-n-dodecylmaleimide, this type of species is thought to play an important role in organometallic reactions, e.g., in the following case where reaction modes depend on solvents [10,11] (Scheme 2).

Immediate formation of a η^2-benzene complex may prevent the reaction of PPh_3 with a coordinatively unsaturated species generated by dissociation of the olefinic part, thus making another reaction mode predominant.

A question of whether (η^6-arene)$Cr(CO)_2$ is coordinated by an alkane, as is thought to occur with $Cr(CO)_5$ [12], remains open. The interaction, however, is not expected here, since it is thought to arise from an extreme deficiency of electron density on Cr caused by coordination of five carbonyls.

Experimental

Materials. (η^6-Anisole)$Cr(CO)_3$ was prepared according to Fischer et al. [13]. (η^6-Benzene)$Cr(CO)_3$ and (η^6-mesitylene)$Cr(CO)_3$ were purchased from Strem Chemicals, Inc. and Aldrich Chemical Co., respectively. Complexes were purified by vacuum sublimation. Spectrophotometric grade cyclohexane and benzene (Aldrich Chemical Co.) were further purified by treatment with sulfuric acid, filtration through an alumina column, and distillation from $LiAlH_4$. Fluorobenzene and mesitylene were purchased from Aldrich Chemical Co. and purified with an alumina column and distillation.

Laser flash photolysis. A Molectron UV-400 nitrogen laser was used for excitation. A right-angle optical system using a 10-mm cell was employed for the excitation-analysis set-up. The kinetic spectrophotometer and data collection system are described elsewhere [14]. Samples were deaerated by bubbling with argon for 20 min or by several freeze-pump-thaw cycles after transfer of solvent from a reservoir, containing $LiAlH_4$, using a vacuum line. Second-order rate constants were obtained from the plots of pseudo-first order rate constants vs. the concentrations of nucleophiles or arenes.

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