

LOWEST EXCITED STATES REORDERING IN (ARENE)M(CO)₃, WHERE M = Cr or W, COMPLEXES

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ABSTRACT

A series of electronic spectral changes was observed when (arene)M(CO)₃ complexes (where arene = benzene, chlorobenzene, phenyltrimethylsilane, acenaphthene, mesitylene, and M = Cr or W) were irradiated with 313 nm light in benzene solution at 298 K in the presence of excess pyridine. These photolysis were neatly leading to the formation of (arene)M(CO)₂(py) without any interference from further net photoreaction or thermal reaction on the same time scale. The lower photoreactivity was exhibited by acenaphthene complex. The influences of ring substituents in these complexes and of entering ligands on their photoreactions are discussed in detail with respect to reordering of their electronic states.

Keywords: photolysis, arene metal tricarbonyl, excited states reordering

INTRODUCTION

The class of arene metal carbonyl complexes has gained a great deal attention since the beginning of their syntheses. A number of studies on photoreactivity of (arene)M(CO)₃ complexes have been reported. Irradiation of (arene)M(CO)₃ complexes in solution containing excess ligand (L) lead to formation of (arene)M(CO)₂L complexes. Variety of ligands has been employed, such as N-n-dodesilamide [1], 1-pentene [2], and pyridine [3]. In addition, these complexes or their derivatives, have extensively investigated in a number of applications as catalyst [4-6], antitumor agents [7], and asymmetric homogeneous hydrogenation [8]

It has been established that the photoinduced loss of CO was the primary path. The quantum yield of reaction was found close to unity. The reaction was also found wavelength independent; no excitation wavelength dependence on the quantum yield value was observed [3]. This suggests the existence of a single relaxed reactive excited state which can be populated efficiently from upper excited state. Wrighton et al. reported that the efficiency of the benzil or biacetyl sensitized reaction was considerably less than the direct irradiation reaction, i.e. without the presence of any sensitizer [9]. They suggested that this difference was due to variations in the singlet and triplet state reactivities.

The presence of the suspected ligand field (LF) and metal to arene charge transfer (MArCT) excited states in the lowest absorption energy band of (arene)M(CO)₃ complexes [10] has made it possible to reorder the relative position between these two excited states and relate this phenomenon to the photoactivity of these complexes. This study reports the reordering of

the lowest energy band of (arene)M(CO)₃, where M = Cr or W, complexes upon irradiation in the presence of different ligands.

EXPERIMENTAL SECTION

Equipment and Materials

Irradiation source for photolysis is obtained from a high pressure mercury arc 200W (Ealing Electrooptic). All IR spectra were recorded on Perkin-Elmer 283B in CDCl₃ solvent using KBr discs, and NMR spectra were obtained as solution in CDCl₃ or CS₂ from Bruker AM 360, using tetramethylsilane (TMS) as internal standard. All electronic spectra were obtained from UV-Vis spectrophotometer (HP 8450A), as solution in appropriate solvents.

Chromium hexacarbonyl was purchased from Aldrich Chemical Co. and used without further purification. The solvents used for electronic absorption studies and photolysis were photrex grade (J.T. Baker Chemical Co.) and used without further purification. All other solvents for synthesis of (arene)M(CO)₃ complexes were purchased from Aldrich Chemical Co. as reagent grade and used without further purification. The benzene, chlorobenzene, phenyltrimethylsilane, methanol, dichloromethane, chloroform, pyridine, piperidine, trimethylphosphine, dan N,N'-dimethylaniline, and isooctane were obtained from Aldrich Chemical Co. and were further purified using procedures described by Perrin et al. [11]. All other materials were purchased from Aldrich Chemical Co. as reagent grades and used without further purification. The tungsten complex, i.e. (mesitylene)W(CO)₃, were

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obtained from Strem Chemical Co. and used as purchased.

Synthesis

In general, the chromium tricarbonyl complexes were synthesized by refluxing the same amount of moles of chromium hexacarbonyl and appropriate aromatic ligands in inert solvent for 9 - 48 hours depending on the arene ligands. The mixtures were then filtered using alumina column, followed by rotatory evaporation, and recrystallization. The complexes are obtained in the form of robust solids which have color ranging from yellow to orange. They are relatively stable in air at room temperature.

Photolysis

Irradiation of the complexes in the presence of excess ligands in benzene solution was conducted using filter which blocked all wavelengths but 313 nm for a total 15 minutes. The progress of the photoreaction was monitored by observing the electronic absorption spectral sequence, in situ, every three minutes time interval.

RESULT AND DISCUSSION

A characteristic feature of arene metal tricarbonyl complexes is the presence of a relatively intense broad band with λ_{max} in the region 310 – 350 nm of their electronic spectra. These lowest electronic absorption bands are typically not solvent sensitive [10] and have been known to be photochemically reactive.

When the $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_3$ complex was irradiated with 313 nm light in benzene solution at 298 K in the presence of excess py, a series of spectral changes were observed corresponding to the formation of $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_2(\text{py})$ (see Figure 1).

It can be seen from Figure 1 that the isosbestic points at 301 and 354 nm are preserved during the reaction, ruling out further net photoreaction or thermal reaction of $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_2(\text{py})$ on the same time scale. The decreasing band at 318 nm was followed by the appearance of a broad, structureless band which has λ_{maks} at ~ 478 nm. This new band is assigned to be a metal to $\pi^*\text{py}$ charge transfer transition as the entering py ligand has a low-lying π^* orbital [3]. Spectral data of the other complexes investigated are listed in Table 1.

It is widely believed that a ligand field (LF) transition causes a labilization with respect to metal-ligand bonding [12]. Hence, the high quantum yield of $(\text{arene})\text{Cr}(\text{CO})_3$ is inferred to be caused by a low-lying LF excited state. However, variation of the efficiency quantum yield found in these complexes indicates that the nature of the low-lying excited state can be altered considerably. Referring to Table 1 it can be said that

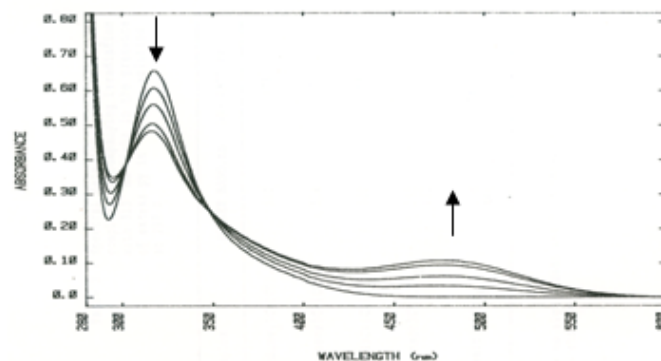


Figure 1. Electronic absorption spectral sequence observed following irradiation of $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_3$ in the presence of excess py in benzene at 298 K at three minutes time interval.

Table 1. Spectral data for $(\text{arene})\text{M}(\text{CO})_3$ complexes accompanying irradiation with 313 nm light in the presence of excess py in benzene solution at 298 K.

Complex	New Band, λ_{maks} (nm)
$(\text{PhSiMe}_3)\text{Cr}(\text{CO})_3$	478
$(\text{benzene})\text{Cr}(\text{CO})_3$	475
$(\text{PhCl})\text{Cr}(\text{CO})_3$	455
$(\text{acenaph})\text{Cr}(\text{CO})_3$	a
$(\text{mesit})\text{W}(\text{CO})_3$	~ 476

Notes:

a = no significant reaction observed

s = shoulder

substituents on the ring influence photoreactivity. Electron donating substituents result in increase the reaction yield; the $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_3$ complex has the highest yield, determined from increasing intensity at 478 nm. Although mesitylene has electron donating substituent the yield for $(\text{mesitylene})\text{W}(\text{CO})_3$ is lower. This difference might be attributed to variation in the singlet and triplet state reactivities; it is widely known that singlet state is more reactive than triplet [9]. So, the tungsten complex, that is dominated more by triplet excited state, shows a lower yield.

In addition, $(\text{PhCl})\text{Cr}(\text{CO})_3$ complex shows less photoactive as compared to $(\text{PhSiMe}_3)\text{Cr}(\text{CO})_3$ complex, on the basis of new growing band of its UV-Vis spectra. It indicates that the electron withdrawing substituent (such as chloro) reduces photoreactivity of the molecules [2].

Pyridine has a low-lying π^* orbital which can stabilize the $(\text{arene})\text{M}(\text{CO})_2(\text{py})$ complexes. Investigation was continued to observe the effect of other ligands which do not have low-lying orbitals such as piperidine (pip), triphenylphosphine (PPh_3), and $\text{N,N}'$ -dimethylaniline (DMA) on perturbing electronic structure of $(\text{arene})\text{M}(\text{CO})_3$ complexes. Under similar experimental conditions employed in the py study only disappearance of the 320 nm bands of tricarbonyls

parent compounds was observed. Apparently, the photoproduct was produced, i.e. (arene)M(CO)₂L complexes, where L = pip, PPh₃, or DMA) but it rapidly decomposed thermally and photochemically within the reaction time scale. This can be argued by realizing that the substitution of CO from the parent compound by a ligand which has a weaker strength in the spectrochemical series causes destabilization of the substituted compound [12]. Also, the proposed lowest LF excited state of this photoproduct is itself a highly unstable state with respect to loss of ligands.

Excited States Reordering

The results of photolysis on (arene)M(CO)₃ complexes indicates that there is ligand field (LF) transition in the range of 310 – 320 nm energy. This transition overlaps with and covered by metal to arene charge transfer (MArCT) transition [10]. Since the lowest MLCT excited state has not been believed to cause labilization with respect to the metal – ligand bonding, it would be expected that the reactivity of (arene)M(CO)₃ complexes is substantially reduced when metal to arene charge transfer is going to the lowest excited state. This unreactivity, in fact, was observed for (acenaphthene)Cr(CO)₃ complex. Additionally, the MArCT excited state exhibits electron delocalization throughout the molecule upon excitation [10].

The proposed reordering of excited state schemes for (arene)M(CO)₃ complexes is illustrated in Figure 2. Figure 2(a) represents M = Cr and arene = benzene, chlorobenzene, or phenyltrimethylsilane, and M = W and arene = mesitylene. Figure 2(b) represents M = Cr and arene = acenaphthene. The heavy horizontal lines denote thermally equilibrated excited states. The wiggly lines indicate nonradiative processes and the light

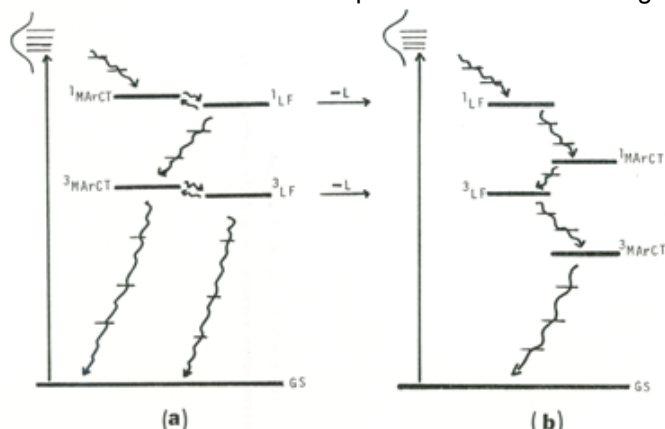


Figure 2. Excited state schemes for (arene)M(CO)₃ complexes, where (a) M = Cr, or W and arene = chlorobenzene, benzene, phenyltrimethylsilane, or mesitylene, and (b) M = Cr and arene = acenaphthene

horizontal lines represent a few of successive complex-solvent cage energy as the vibrationally excited states relax.

The mixing of the LF and MArCT excited states in (arene)M(CO)₃ complexes is illustrated in Figure 2(a). The order of these excited states can not be resolved precisely and can only be speculated that the LF state is somewhat lower in energy than the MArCT excited state on the basis of the high photoreactivity of these (arene)M(CO)₃ complexes. On the other hand, the (acenaphthene)Cr(CO)₃ complex clearly has lowest MArCT excited state (Figure 2b) as this complex exhibits a dramatically different absorption spectrum and is virtually unreactive photochemically. The triplet excited states are represented in these schemes in recognizing the mixing of singlet and triplet states in these molecules.

CONCLUSION

The yields of photosubstitution reactions of (arene)M(CO)₃ complexes with a number of entering ligands are influenced by the nature of aromatic ring. When the ring has no low-lying π^* orbital the LF state is the lowest, and electron donating substituents on the ring tend to enhance their photoreactivities. On the other hand, the photoreactivity of the complex is greatly reduced when the MArCT state shifts to the lowest excited state, such as in the case of (acenaphthene)Cr(CO)₃ complex in which there is low-lying π^* orbital.

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