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LASER FLASH PHOTOLYSIS OF A CHROMIUM CARBENE COMPLEX: PENTACARBONYL(1,3-DIMETHYL-4-IMIDAZOLIN-2-YLIDENE)CHROMIUM(0)

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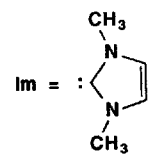
ABSTRACT

Photoreactions of $Cr(CO)_5(Im)$ (Im = 1,3-dimethyl-4-imidazolin-2-ylidene) have been investigated by laser flash and continuous photolysis. Quantum yields for the disappearance of $Cr(CO)_5(Im)$ in benzene under Ar or CO were very low, although transients observed by laser flash photolysis reacted rapidly with CO. This suggests that photodissociation of the carbene ligand is very minor. The laser flash photolysis at 337 nm in benzene (B) gave a transient (λ_{max} = 630 nm), which converted to the second transient (λ_{max} = 455 nm) within ~100 ns. The kinetic studies of these transients revealed that the first one is a 'free' coordinatively unsaturated species ($Cr(CO)_4(Im)$) and the second one carries a solvent molecule as a ligand ($Cr(CO)_4(Im)(B)$). From the comparison of $Cr(CO)_4(Im)$ and $Cr(CO)_5$, apparently lower reactivity of $Cr(CO)_5$ was found to be due to the strong coordination of a solvent molecule. The Im ligand neutralizes the deficit of electron density on Cr. A simple synthesis of $Cr(CO)_5(Im)$ was also described.

INTRODUCTION

It is well established that the photoreactions of metal carbonyls start with photodecarbonylation.[1] In the case of group 6 metal carbonyls, the coordinatively unsaturated species so generated captures a solvent molecule immediately, and other reactions such as the substitution of the solvent molecule follow.[2–4] Although carbene ligands have formal similarities to carbonyl in the sense that there are only six valence electrons on carbon, there have been few studies concerning the photoreactions of metal carbene complexes. Öfele and Herberhold have reported the photoreactions of a Fischer-type carbene complex: the irradiation of pentacarbonyl(1,3-dimethyl-4-imidazolin-2-ylidene)chromium(0) ($Cr(CO)_5(Im)$) in THF gave $Cr(CO)_4(Im)_2$ in 8% yield.[5] Free carbene Im seems to be suggested as an intermediate of the dismutation.



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Considering its rigorous conditions, namely, 4 h of irradiation with a 450 W high-pressure mercury lamp at the boiling temperature of THF, the primary photoreactions can hardly be deduced from this synthetic study. We have investigated the photoreactions of $Cr(CO)_5(Im)$ by means of laser flash photolysis, intending to look at whether the free carbene (Im) can be generated by photolysis, equation (1a), and what effect the Im ligand will produce in the behavior of $Cr(CO)_4(Im)$ if decarbonylation is the primary process, equation (1b).

$$Cr(CO)_5(Im) \xrightarrow{h\nu} Cr(CO)_5 + Im \quad (1a)$$

$$\text{or } Cr(CO)_4(Im) + CO \quad (1b)$$

EXPERIMENTAL

Materials

$Cr(CO)_6$ was purchased from Aldrich Chemical Co. and was used without further purification. Pyridine (Aldrich, Gold label) was distilled and dried with molecular sieves of 4Å. Benzene (Fischer Scientific, Spectranalyzed grade) was purified with usual sulfuric acid treatments, distillation, and an alumina column, and stored on molecular sieves of 4Å. THF (American Burdick & Jackson) was purified just before the experiments by distillation under Ar from the benzophenone ketyl solution. Acetonitrile (Aldrich, Spectrophotometric grade) was purified with distillation from P_2O_5. Acetone (Fischer, Spectranalyzed grade) was distilled and dried on molecular sieves of 4Å.

Synthesis of $Cr(CO)_5(Im)$

$Cr(CO)_6$ (4·4 g, 20 mmole) and 1,3-dimethylimidazolium iodide (4·5 g, 20 mmole) were dissolved with acetone (100 ml) in a 250 ml flask. The solution was deaerated by bubbling argon, aqueous NaOH (2·5 g, 62·5 mmole, in 3·5 ml of water) was added, and the solution was kept overnight at 50 °C. After the evaporation of acetone and water under vacuum, the flask was heated to 120 °C for 30 min. Some part of the product sublimated to the reflux condenser. The sublimate and the residue in the flask were charged on a silica gel column and eluted with benzene. The pale yellow product was further purified with sublimation at 80 °C under high vacuum Yield: 2·4 g, 42%. Found: C, 41·69; H, 2·82; N, 9·89%. Calcd. for $C_{10}H_8CrN_2O_5$: C, 41·68; H, 2·80; N, 9·72%. M.p., MS, UV, IR, and NMR were in good agreement with those reported in the literature.[6]

Laser flash photolysis

A Molectron UV-400 nitrogen laser was used for excitation (337 nm, 3 mJ/pulse, 8 ns of pulse width). A right-angle optical system using a 10-mm cell was employed for the excitation-analyzing set-up. All measurements were carried out at ambient temperature (24 ± 1 °C) and were the results of averages of at least four laser pulses. The estimated uncertainties in the rate constants obtained are ±20%. Details of the kinetic spectrophotometer and data collection system are described elsewhere.[7–9] Samples were degassed by several freeze-pump-thaw cycles and stirred for 20 min under a given pressure of CO (Linde, Research grade) to be equilibrated. Concentrations of CO in benzene were calculated from the value (7·54 mM at

1 atm and 25 °C) in the literature.[10] For the experiments using pyridine as a ligand, samples were deaerated by bubbling argon (Linde, Ultra high purity grade) for 20 min and pyridine was added with a micro-syringe.

Continuous photolysis

An optical train for irradiation consisted of 500 W high-pressure mercury arc lamp installed in an Oriel lamp housing (#66060), a secondary focusing lens (f = 250 mm), 12 cm of aqueous $CuSO_4$ (0·2 M) filter, a monochromator (Bausch & Lomb), and a vacuum photodiode detector (Oriel, #7052) which was calibrated by ferrioxalate actinometry.[11] Benzene solutions of $Cr(CO)_5(Im)$ (0·49 mM) were deaerated by bubbling Ar or CO and irradiated by the 366 nm line (~6·3 × 10^{-8} einstein s^{-1}) with stirring. The decrease in absorption at 351 nm was used for calculating quantum yields.

RESULTS AND DISCUSSION

Benzene solutions of $Cr(CO)_5(Im)$ (1·6 mM) were deaerated by several freeze-pump-thaw cycles and equilibrated with 1 atm of CO, then subjected to laser flash photolysis at 337 nm. Figure 1a shows typical decay and growth traces observed at 630 and 455 nm, respectively. A differential spectrum at a given time can be composed by the collection of corresponding

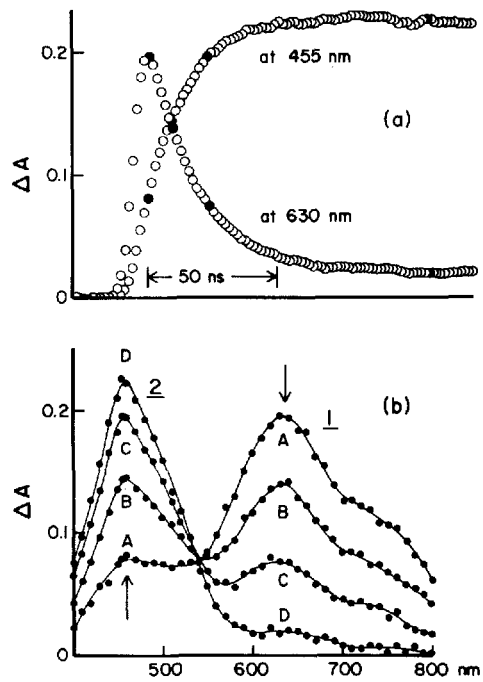


Figure 1. Laser flash photolysis of $Cr(CO)_5(Im)$ (1·6 mM) in benzene under CO (1 atm). (a) Typical decay (630 nm) and growth (455 nm) traces. Solid circles were sampled for spectra. (b) Time-resolved differential spectra. A, B, C, and D correspond to 0, 9·3, 23 and 109 ns after the pulse, respectively

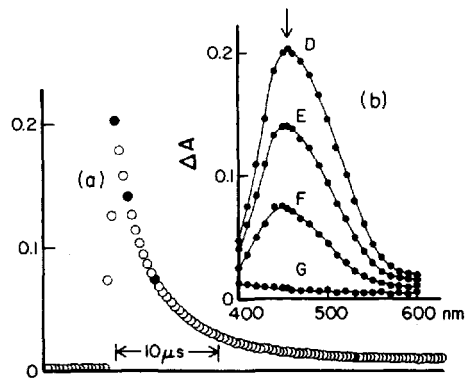


Figure 2. (a) The decay trace of the peak D at 455 nm, following to Figure 1. Solid circles were sampled for spectra. (b) Time-resolved differential spectra. D, E, F, and G correspond to 0·1, 1·2, 3·9, and 23·4 μs after the pulse, respectively

points from traces observed for various wavelengths. Figure 1b shows time-resolved differential spectra up to ~100 ns after the laser pulse. Spectrum A immediately after the pulse had an absorption peak at 630 nm and converted to Spectrum D (λ_{max} = 455 nm), obeying first-order reaction kinetics. Spectrum D, in turn, disappeared within ~15 μs (Figure 2). First-order reaction kinetics can be applied also to this disappearance.

The spectral change under vacuum was similar to the above observation, except that Spectrum A decayed more slowly and Spectrum D was larger in absorption intensity. This indicates that the reaction of species **1** (Spectrum A) with CO competes with the conversion to the transient **2** (Spectrum D). The species **2** disappeared more slowly under vacuum and obeyed second-order reaction kinetics ($t_{\frac{1}{2}}$ = ~25 μs), suggesting that the species **2** also reacts with CO. Under a CO atmosphere, pseudo-first-order reaction kinetics was realized because of the presence of excess CO. On the other hand, under vacuum, the presence of the same amount of CO as **2** made the reaction second-order.

In the case of laser flash photolysis of $Cr(CO)_6$ under the same conditions as Figure 1 and 2, free $Cr(CO)_5$ was not observed. Instead, the spectrum even just after the pulse was due to the species coordinated by benzene ($Cr(CO)_5(B)$), λ_{max} = 460 nm).[12] $Cr(CO)_5(B)$ shows almost no decay in the time range of Figure 2. If the Im ligand photodissociates from $Cr(CO)_5(Im)$, $Cr(CO)_5(B)$ must be observed. Because both **1** and **2** reacted rapidly with CO, neither of these can be $Cr(CO)_5(B)$. Indeed, quantum yields for the disappearance of $Cr(CO)_5(Im)$ were measured as low as 0·004 and 0·006 under Ar and CO, respectively.

Laser flash photolysis of $Cr(CO)_5(Im)$ in coordinating solvents such as THF, acetone, and acetonitrile gave similar spectra to **2** (λ_{max} = 450, 430, and 400 nm, respectively) even just after the pulse, and these spectra did not change up to ~700 μs. The spectrum corresponding to **1** was not observed.

These observations stated above can be most rationally explained by the idea that **1** is a free coordinatively unsaturated species ($Cr(CO)_4(Im)$), and **2** carries a benzene molecule as a ligand ($Cr(CO)_4(Im)(B)$). The coordination of THF, acetone, or acetonitrile to **1** is so fast that this reaction is completed within the duration of the laser pulse.

The second-order rate constant for the reaction of **1** with CO (k_{CO}) was determined in benzene as 8·0 × 10^9 M^{-1} s^{-1} from the plots of pseudo-first-order decay rates of **1** vs. the

concentrations of CO. The value implies that this reaction is almost diffusion-controlled and is of reasonable magnitude for a free coordinatively unsaturated species.[2]

$$\underset{\mathbf{1}}{Cr(CO)_4(Im)} + CO \xrightarrow{k_{CO}} Cr(CO)_5(Im) \quad k_{CO} = 8{\cdot}0 \times 10^9\ M^{-1}\ s^{-1} \tag{2}$$

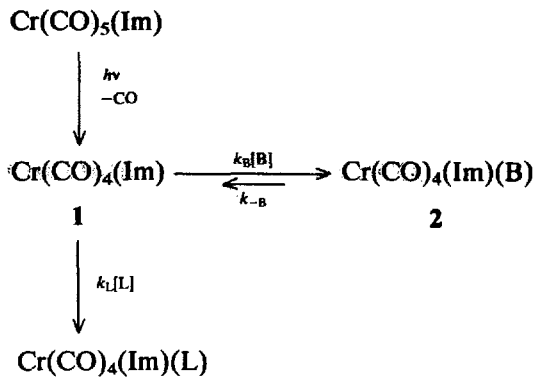
From the number of photons measured by referring to the concentration of benzophenone triplet, the concentration of CO formed by the pulse can be estimated as less than $1{\cdot}7 \times 10^{-4}$ M. So, using the value of k_{CO} obtained above, the value of $k_{CO}[CO]$ amounts to less than $1{\cdot}4 \times 10^6\ s^{-1}$, which is smaller than the decay of **1** under vacuum ($1{\cdot}3 \times 10^7\ s^{-1}$) by one order of magnitude. Therefore, the decay of **1** under vacuum is attributable almost completely to solvent coordination ($k_B[B]$). The k_B value is calculated as $1{\cdot}2 \times 10^6\ M^{-1}\ s^{-1}$ by using 11·2 M as [B].

$$\underset{\mathbf{1}}{Cr(CO)_4(Im)} + B \xrightarrow{k_B} \underset{\mathbf{2}}{Cr(CO)_4(Im)(B)} \tag{3}$$

The pseudo-first-order decay rate of **2** in benzene in the presence of excess CO did not correlate linearly with the concentration of CO; saturation was observed at higher [CO]. Thus, a direct substitution mechanism, equation (4), should be excluded.

$$\underset{\mathbf{2}}{Cr(CO)_4(Im)(B)} + CO \not\longrightarrow Cr(CO)_5(Im) + B \tag{4}$$

The dissociative mechanism as illustrated in Scheme 1 can explain the kinetic behavior of **2**.



Scheme 1

In Scheme 1, most of **1**, generated by the photodecarbonylation, converts swiftly to **2** by the coordination of benzene ($k_B[B]$) in the time range of Figure 1. **2**, in turn, supplies a small amount of **1** according to the equilibrium ($k_{-B}/(k_B[B])$ and the supplied **1** reacts with CO to disappear in the time range of Figure 2. For the disappearance of **2**, the steady state approximation ($d[\mathbf{1}]/dt = 0$) can be applied because of low concentration of **1**, and equation (5) is obtained.

$$\frac{d[\mathbf{2}]}{dt} = \frac{-k_{-B}k_L[L]}{k_B[B] + k_L[L]}[\mathbf{2}] \tag{5}$$

If $k_B[B] >> k_L[L]$ holds, equation (5) can be simplified to equation (6).

$$\frac{d[2]}{dt} = -k_{app}[L][2] \tag{6}$$

where

$$k_{app} = \frac{k_{-B}}{k_B[B]} k_L \tag{7}$$

The second-order rate constant (k_{app}), obtained from the plots of pseudo-first-order rate constants (k_{ps}) vs. [L], contains the term of the solvent coordination equilibrium, even if a linear part of the plots is used ($k_B[B] >> k_L[L]$).[2,12,13] In this study, k_{app} and k_{-B} were obtained from the plots of $1/k_{ps}$ vs. $1/[L]$ based on equation (9), as shown in Figure 3.

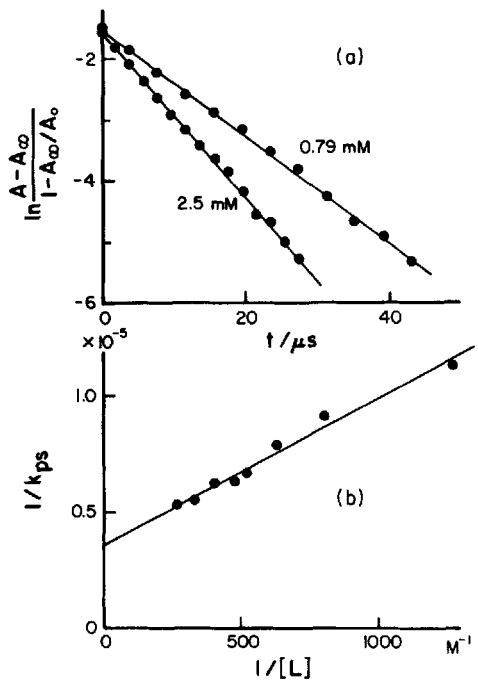


Figure 3. (a) Typical pseudo-first-order kinetic plots for the decay of **2** under various concentrations of CO. (b) Plots of $1/k_{ps}$ vs. $1/[L]$ based on equation (9)

$$k_{ps} = \frac{k_{-B}k_L[L]}{k_B[B] + k_L[L]} \tag{8}$$

$$\frac{1}{k_{ps}} = \frac{1}{k_{app}}\frac{1}{[L]} + \frac{1}{k_{-B}} \tag{9}$$

Since the concentration of CO could not be increased, the reaction of $Cr(CO)_5(B)$ with CO was too slow to measure its rate. In order to compare the kinetic behavior of $Cr(CO)_5$ and

Table 1. Comparison of kinetic behavior of $Cr(CO)_5$ and $Cr(CO)_4(Im)$

	k_{app} M^{-1} s^{-1}		k_{-B} s^{-1}	k_B M^{-1} s^{-1}	$\frac{k_{-B}}{k_B[B]}$
	L = CO	L = py			
$Cr(CO)_5$	$<10^{5}$[a]	$1{\cdot}2 \times 10^{5}$	$9{\cdot}8 \times 10^{4}$[b]	$>1{\cdot}1 \times 10^{7}$[d]	$<9 \times 10^{-4}$[e]
$Cr(CO)_4(Im)$	$1{\cdot}5 \times 10^{8}$	$4{\cdot}9 \times 10^{8}$	$2{\cdot}7 \times 10^{5}$[c] $2{\cdot}3 \times 10^{5}$[b]	$1{\cdot}2 \times 10^{6}$	$2{\cdot}0 \times 10^{-2}$

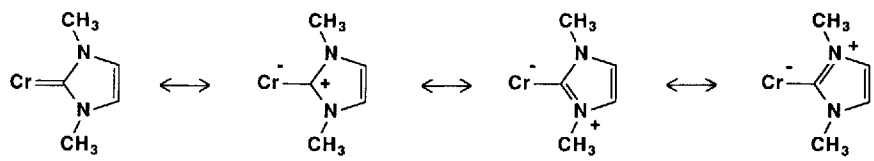
[a] Estimated from the fact that $Cr(CO)_5(B)$ does not decay up to ~1 ms under 1 atm of CO, namely, $1/(k_{app}[CO]) >> 10^{-3}$ s.
[b,c] Determined from the plots based on equation (9) for py and CO as L, respectively.
[d,e] Estimated from the fact that the generation of $Cr(CO)_5(B)$ is complete within the laser pulse duration, namely $1/(k_B[B]) << 8 \times 10^{-9}$ s.

$Cr(CO)_4(Im)$, the values of k_{app} and k_{-B} determined by using pyridine as a ligand are shown in Table 1.

By substituting the values of k_{app}, k_{-B}, and k_B in equation (7), k_{CO} for the system of $Cr(CO)_4(Im)$ and CO can be calculated as $7{\cdot}5 \times 10^{9}$ M^{-1} s^{-1}, in good agreement with the value obtained above ($8{\cdot}0 \times 10^{9}$ M^{-1} s^{-1}) from the dependence of the decay of **1** upon [CO], suggesting the appropriateness of Scheme 1.

The value of k_{app} for $Cr(CO)_4(Im)$ is larger than that for $Cr(CO)_5$ by 10^3 times. As can be seen from the value of $k_{-B}/(k_B[B])$, this is not due to k_L but to the term of solvent coordination equilibrium. Because of the extreme reactivity of $Cr(CO)_5$, it captures a solvent molecule immediately. The $Cr(CO)_5(B)$ so generated is very favorable in the solvent coordination equilibrium. In the case of $Cr(CO)_4(Im)$, because of decreased reactivity due to the Im ligand, free $Cr(CO)_4(Im)$ could be observed as a transient. $Cr(CO)_4(Im)(B)$ is also favorable in the equilibrium, but not to such an extent as the case of $Cr(CO)_5(B)$. The apparent rate constants for substitution (k_{app}) reflect stability of the solvent coordinated transients rather than true reactivity of the free species (k_L).

If the coordination of Im to Cr is considered by the following resonance structures, where (b) and (a) correspond to a donating and back-donating bond formation respectively, the donating bond formation is stabilized by the delocalization of electrons represented as (c) and (d). The formally empty p orbital of C_2 carbon is stabilized more efficiently by nitrogen $2p$ orbitals than metal $3d$ orbitals lying in higher energy levels.[14]



(a) (b) (c) (d)

Consequently, the Im ligand is not so electron-withdrawing as CO. The extreme reactivity of $Cr(CO)_5$ is due to the significant deficit in electron density on Cr caused by five carbonyls. Substitution of one carbonyl by Im neutralizes the electron-deficiency on Cr and decreases the

reactivity: free $Cr(CO)_4(Im)$, **1**, could be observed in benzene. Stabilization brought about by the coordination of benzene to $Cr(CO)_5$, is, of course, greater than that due to the coordination of benzene to $Cr(CO)_4(Im)$, because an electron-donating benzene ligand compensates the more significant electron-deficiency of $Cr(CO)_5$. This explanation is consistent with the observed equilibrium.

The expected generation of free carbene Im in the primary photolytic process of $Cr(CO)_5(Im)$ has been revealed to be very minor. In the synthetic work done by Öfele and Herberhold, $Cr(CO)_4(Im)_2$ may be formed via thermal reactions of $Cr(CO)_4(Im)$ (Solvent), accumulated in the solution with removal of photogenerated CO by boiling. Indeed, they reported later that the thermal reaction of $Cr(CO)_5(Im)$ in the presence of tricyclohexylphosphine gave the same product.[15]

The synthesis of $Cr(CO)_5(Im)$ described here is based on the nucleophilic attack of a hydroxide ion on a carbonyl carbon,[16] being easier than the reduction process of $Cr(CO)_6$ by pyrophoric C_8K. Although the reaction conditions were not optimized, yields were rather satisfactory, considering the simple procedure.

ACKNOWLEDGEMENT

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