Photochemistry of $Cr(CO)_4(bpy)$ (bpy = 2,2′-Bipyridine) Studied by Time-Resolved Infrared Spectroscopy

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Received May 15, 1996[⊗]

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Published on September 17, 1996 on http://pubs.acs.org | doi: 10.1021/om960369q

*Summary: Employing time-resolved IR spectroscopy, we have demonstrated that, following photolysis of $Cr(CO)_4$(bpy) (**1**) in CH_2Cl_2, the only detectable photoproduct on the 50 ns time scale is the solvated CO-loss intermediate fac-$Cr(CO)_3(bpy)(CH_2Cl_2)$ (**2**); this intermediate is formed following either MLCT (532 nm) or LF (355 nm) excitation. The rate of the back-reaction of **2** with CO has been measured ($k_2 = 7.1(\pm 0.5) \times 10^6\ M^{-1}\ s^{-1}$); in the presence of PPh_3, the intermediate **2** reacts to produce fac-$Cr(CO)_3(bpy)(PPh_3)$ (**3**) exclusively ($k_2 = 1.0(\pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$). From UV/visible flash photolysis data, we conclude that this intermediate **2** is probably produced on a ps/sub-ps time scale.*

Introduction

There has been considerable interest in the photophysics and photochemistry of $M(CO)_4$(α-diimine) (M = Cr, Mo, W) complexes.[1−11] Following early work[9] by Wrighton and Morse on $W(CO)_4$(bpy) (bpy = 2,2′-bipyridine), Manuta and Lees[6] performed extensive quantum yield studies on the photosubstitution of $M(CO)_4$(α-diimine) (M = Cr, Mo, W; α-diimine = bpy 4,4′-bpy, phen (phen = phenanthroline), 4-Me-phen, 5-Me-phen, 5-Ph-phen, 5-Cl-phen and 5-NO_2-phen). Irradiation into either LF or MLCT absorption bands led to substitution, but the quantum yield decreased considerably for the latter. They concluded that either the MLCT state is very weakly photoactive or a low-lying ^{3}LF state, close in energy to the MLCT state and in thermal equilibrium with it, is responsible for the long-wavelength photochemistry.

Photosubstitution of $M(CO)_4$(α-diimine) by phosphines (PR_3) leads to *fac*-$M(CO)_3(PR_3)$(α-diimine) final products.[10] Balk *et al.* concluded[11] from resonance Raman studies on a series of $M(CO)_4$(α-diimine) complexes that the MLCT excited state is delocalized over the *cis* carbonyls and suggested that it is this delocalization which is responsible for the long-wavelength photochemistry. Further photochemical studies[4] on similar species led to the conclusion that Cr complexes behave differently from complexes of Mo and W, with the first stage for Cr being photodissociative. A detailed study of the excitation wavelength dependence of quantum yields of $Cr(CO)_4$(bpy) photosubstitution led Víchová *et al.* to suggest[2] that CO dissociation of the axial CO group occurs from the excited vibrational levels of a ^{1}MLCT state on a sub-ps time scale. On excitation in the MLCT region (532 nm) they detected a short-lived transient with a lifetime (τ) of *ca* 50 ps, and they assigned this to the vibrationally relaxed ^{1}MLCT excited state. A longer lived (τ ≫ 10 ns) intermediate was also detected and assigned to the ^{3}MLCT state. This longer-lived species was the only transient detected on LF (355 nm) excitation.

In this paper we investigate the time-resolved IR spectra of $Cr(CO)_4$(bpy) in CH_2Cl_2 solution which were measured in order to unravel the nature and the stereochemistry of its primary photoproduct and also in an attempt to detect the putative ^{3}MLCT state. We show hereinafter that the only detectable photoproduct observed on the 50 ns time scale is *fac*-$Cr(CO)_3$(bpy)(CH_2Cl_2), which is probably produced on a ps/sub-ps time scale. We have also measured the rates of reaction of this intermediate with CO and PPh_3.

Results and Discussion

Figure 1a shows the ν(CO) FTIR spectrum of $Cr(CO)_4$(bpy) (**1**) in dichloromethane in the presence of 2 atm of argon. Figure 1 also shows time-resolved infrared (TRIR) spectra of this solution obtained 250 ns after (b) visible (532 nm) and (c) UV (355 nm) photolysis. It is clear that, upon both 532 and 355 nm excitation, there is loss of parent bands and generation of identical new spectral features, except that the spectral changes following 532 nm excitation are *ca.* 10× smaller than those resulting from 355 nm irradiation. This difference

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Vlček, A., Jr.; Víchová, J.; Hartl, F. *Coord. Chem. Rev.* **1994**, *132*, 167−174.

(2) Víchová, J.; Hartl, F.; Vlček, A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 10903−10910.

(3) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39−112.

(4) (a) Wieland, S.; Reddy, K. B.; van Eldik, R. *Organometallics* **1990**, *9*, 1802−1806. (b) Wen-Fu, F.; van Eldik, R. *Inorg. Chim. Acta* **1996**, *250*, in press.

(5) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 2154−2160.

(6) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 1354−1359.

(7) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825−3828.

(8) Lindsay, E.; Vlček, A., Jr.; Langford, C. H. *Inorg. Chem.* **1993**, *32*, 2269−2275.

(9) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405−420.

(10) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem. Acta* **1979**, *34*, 267−274.

(11) Balk, R. W.; Snoek, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015−3021.

(12) Another possibility is dechelation of the bpy ligand. Although such an intermediate would be expected to have four ν(C−O) bands, it is possible that only three would be observed. However, replacing one of the nitrogen ligands with a solvent molecule would result in an *upward* shift in ν(C−O) bands. Furthermore the kinetic behavior displayed by the intermediate, under CO and Ar atmospheres, make it unlikely that **2** is the dechelated intermediate.

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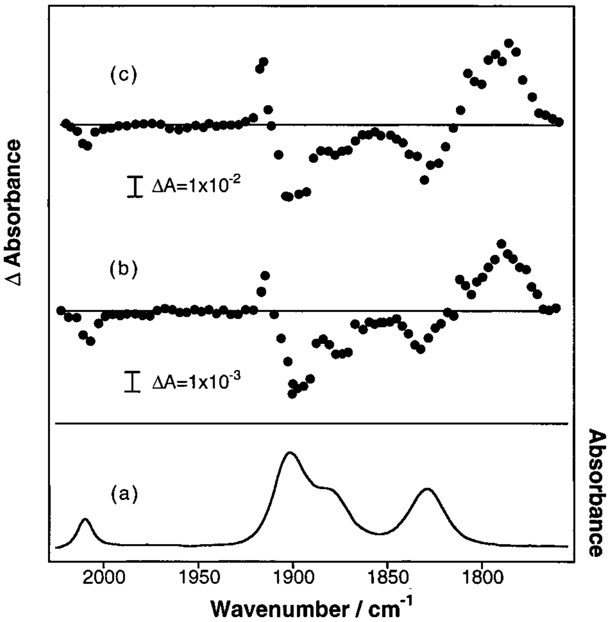

Figure 1. (a) FTIR spectrum (Perkin-Elmer System 2000 spectrometer) of $Cr(CO)_4(bpy)$ in CH_2Cl_2 (1×10^{-3} M). TRIR spectra of $Cr(CO)_4(bpy)$ in CH_2Cl_2 (1×10^{-3} M), in the presence of 2 atm of Ar, obtained 250 ns after the flash, following (b) 532 nm and (c) 355 nm excitation. Data points plotted downward indicate loss of parent; data points plotted upward indicate generation of new species.

is consistent with quantum yield measurements[2] for the photosubstitution of **1** by PPh_3, where the quantum yield changed by a similar amount between these two wavelengths. The three new transient bands, at *ca.* 1915, 1809, and 1786 cm^{-1}, all decay at the same rate and are tentatively assigned to the CO-loss product $Cr(CO)_3(bpy)(CH_2Cl_2)$ (**2**).[12] The *downward* shift in ν(C−O) bands, relative to the parent absorptions, is characteristic[13] of solvated 16-electron intermediates generated by photodissociation of CO; if **2** was an MLCT excited state, then an *upward* shift in ν(C−O) bands would be expected.[14] It should be noted that although the spectra in Figure 1b,c were recorded at 250 ns, the rise-time of the peaks due to **2** is instrument limited and no other transient was observed from 50 ns upward.

The assignment of the photogenerated transient absorptions to the CO-loss product is supported by examining the kinetics under a CO atmosphere. Figure 2 shows the decay of **2** and the corresponding regrowth of parent, under Ar and CO atmospheres. It is evident that the rates are increased in the presence of CO. Under 2 atm of CO the observed rate of decay of **2** is $1.3(\pm 0.3) \times 10^5$ s^{-1} and the rate of regeneration of **1** is $1.2(\pm 0.3) \times 10^5$ s^{-1}, which are the same within experimental error. We estimate[15] the second-order rate constant for the reaction of **2** with CO to be $7.1(\pm 0.5) \times 10^6$ M^{-1} s^{-1}.

There are two possible structural isomers of **2**, *mer* and *fac*. Each of these has three ν(C−O) bands in the infrared; howver isomers of this type have rather different spectra.[16] The major difference lies in the intensity of the high-frequency a_1 ν(C−O) bands, for *fac* isomers it is relatively strong whereas for *mer* isomers it is very weak. A further difference lies in the separation and intensities of the two lower frequency bands. For *fac* isomers the bands are both of medium intensity and relatively close, ca. 20 cm^{-1}, whereas for *mer* isomers the higher frequency band is much more intense and the separation of the two bands is nearer 50 cm^{-1}. Figure 1 shows immediately that the TRIR spectrum of **2** exhibits all of the features expected for a *fac* isomer. The high-frequency band is relatively strong,[17] separated from the strong low-frequency feature by *ca.* 115 cm^{-1}. The latter TRIR absorption is broad, composed of two bands some 23 cm^{-1} apart. Moreover a closely analogous complex[18] to the intermediate is *fac*-$Cr(CO)_3(bpy)(CNEt)$, which has bands at 1910, 1805, and 1782 cm^{-1}, compared with the intermediate's bands at 1915, 1809, and 1786 cm^{-1}. We conclude that the intermediate is the *fac* isomer of $Cr(CO)_3(bpy)(CH_2Cl_2)$ (**2**).

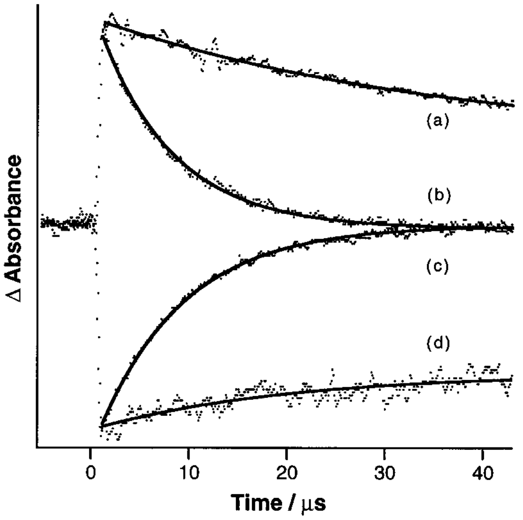

Figure 2. Time-resolved kinetic traces obtained following excitation (355 nm) of $Cr(CO)_4(bpy)$ in CH_2Cl_2 (1×10^{-3} M), at 1913 cm^{-1} (traces a and b) and 1901 cm^{-1} ((c) and (d)) in the presence of 2 atm of Ar ((a) and (d)) and 2 atm of CO ((b) and (c)). The solid lines are exponential fits through the data points. The traces have been auto scaled; *i.e.* the absorptions have been scaled for presentational purposes.

It is known[2,6] that the photoreaction of **1** with PPh_3 yields *fac*-$Cr(CO)_3(bpy)(PPh_3)$ (**3**) as the only product. When this reaction was followed using TRIR, the bands assigned to **2** were detected immediately after the flash, which is consistent with a dissociative first step. These bands decayed to produce **3** *directly*, Figure 3. The rate of decay of **2** ($k_{obs} = 1.8(\pm 0.5) \times 10^4$ s^{-1}) and the rate of growth of **3** ($k_{obs} = 2.2(\pm 0.5) \times 10^4$ s^{-1}) allow the estimation of the second-order rate constant, for the reaction of **1** with PPh_3, to be $1.0(\pm 0.5) \times 10^7$ M^{-1} s^{-1}); this experiment does not of course distinguish between dissociative or associative mechanisms for this second thermal stage.

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(13) Poliakoff, M.; Weitz, E. *Adv. Organmet. Chem.* **1986**, *25*, 277−316.

(14) George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977.

(15) To the best of our knowledge the solubility of CO in CH_2Cl_2 has not been reported. We have therefore assumed that the solubility of CO in $CHCl_3$ is similar to CH_2Cl_2, and we have used this to calculate k_2: Cargill, R. W. *Solubility Data Series, volume 43, Carbon monoxide*, 1st ed.; Pergamon Press: London, 1990; p 246.

(16) Stor, G. J.; Morrison, S. L.; Stufkens, D. J.; Oskam, A. *Organometallics* **1994**, *13*, 2641−2650.

(17) The high frequency a_1 ν(C−O) band is the most intense after computer subtraction of the parent, $Cr(CO)_4(bpy)$, absorptions.

(18) Connor, J. A.; Overton, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2397−2402.

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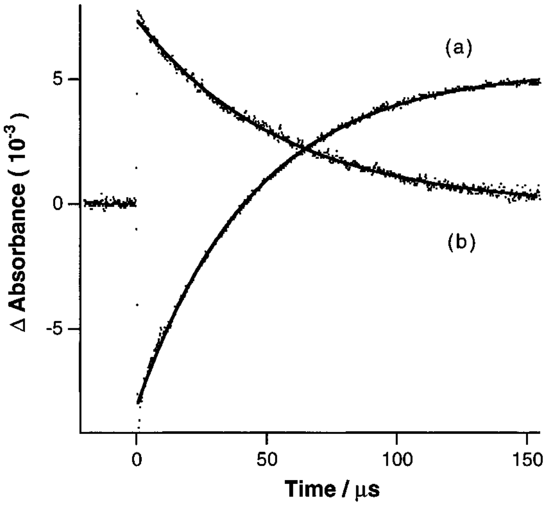

Figure 3. Time-resolved kinetic traces showing (a) the growth of *fac*-$Cr(CO)_3(bpy)(PPh_3)$ at 1909 cm^{-1} and (b) the corresponding decay of *fac*-$Cr(CO)_3(bpy)(CH_2Cl_2)$ at 1919 cm^{-1}, following photolysis (355 nm) of $Cr(CO)_4(bpy)$ in CH_2Cl_2 (1×10^{-3} M), in the presence of PPh_3 (1.6×10^{-3} M). The highest frequency band of *fac*-$Cr(CO)_3(bpy)(PPh_3)$, centered at 1910 cm^{-1}, overlaps with the parent band at 1902 cm^{-1}. As a result, the kinetic trace recorded at 1909 cm^{-1} initially shows a depletion.

Nanosecond time-resolved UV/vis absorption spectra of $Cr(CO)_4(bpy)$ measured in a toluene solution after 532 nm (7 ns pulse) excitation show a broad transient absorption that overlaps with the bleached ground-state absorption and extends to longer wavelengths, above 630 nm; see Figure 4. This transient absorption is fully developed immediately after the excitation pulse. Its lifetime decreases with increasing CO concentration, being only *ca.* 2 μs in CO saturated toluene. This kinetic behavior shows that the visible transient absorption belongs to the CO-loss product, formulated by analogy with the TRIR-characterized intermediate **2** as *fac*-$Cr(CO)_3(bpy)(toluene)$ (**4**).

Comparison of the ns spectrum of the intermediate **4**, Figure 4, with the visible spectrum obtained earlier[2] on the 30 ps−10 ns time scale indicates that the long-lived[2] ($\tau \gg 10$ ns) transient is actually the CO-loss intermediate **4**, instead of the ^{3}MLCT excited state to which it was originally assigned. Very similar long-lived transient absorptions observed[2] by ps spectroscopy in other solvents (CH_2Cl_2, pyridine, THF) may thus be attributed to similar species, *fac*-$Cr(CO)_3(bpy)(solvent)$. Very fast ($\ll$30 ps, presumably sub-ps) formation of these species, revealed by the ps studies[2] is fully in line with the ultrafast (sub-ps) character of the dissociation of the CO ligand, deduced primarily[1,2] from the dependence of the photochemical quantum yield on the excitation wavelength varied over the region of the MLCT absorption.[19] By analogy the long-lived species produced on a sub-ps time scale by LF excitation[2] is also assigned to the solvated intermediate.

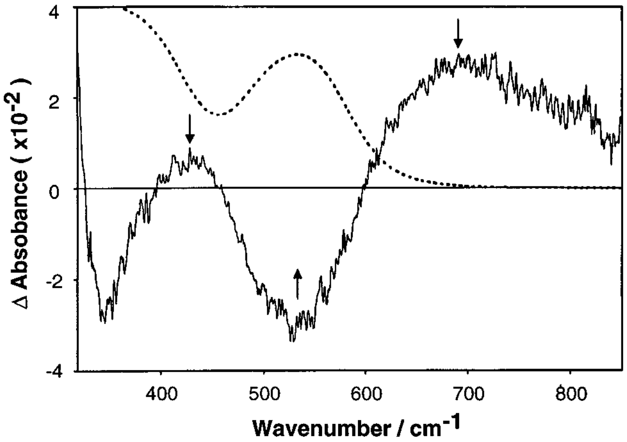

Figure 4. Transient absorption spectrum obtained 15 ns following 532 nm excitation of $Cr(CO)_4(bpy)$ in a CO-saturated toluene solution, shown together with a ground-state absorption spectrum (dashed curve).

In conclusion, the nanosecond TRIR study of $Cr(CO)_4(bpy)$ has shown that the only photoproduct present in CH_2Cl_2 solution, on a time scale of 50 ns and longer, is *fac*-$Cr(CO)_3(bpy)(CH_2Cl_2)$ regardless of the excitation wavelength. No evidence for a long-lived ^{3}MLCT excited state or any other photoproducts such as the *mer* isomer or the dechelation product $Cr(CO)_4$(bpy-*N*)(CH_2Cl_2) was found. Visible transient absorption spectra obtained on ns and ps time scales, assigned in accordance with the TRIR results, indicate that *fac*-$Cr(CO)_3(bpy)(CH_2Cl_2)$ is probably the primary photoproduct of $Cr(CO)_4(bpy)$, formed on a ps/sub-ps time scale after either MLCT (532 nm) or LF (355 nm) excitation. This uncertainty arises because we cannot completely exclude the possibility that CO-loss occurs from the equatorial position to give the *mer* intermediate with the same UV/visible absorption spectrum (although this is unlikely[16]) as the *fac* intermediate, into which it converts in $\ll$50 ns. With this caveat it appears that *fac*-$Cr(CO)_3(bpy)(solvent)$ is formed by a rather selective photodissociation of the axial Cr−CO bond of the $Cr(CO)_4(bpy)$ molecule, independent of the nature (LF, MLCT) of the initial optical excitation.

Experimental Section

The Nottingham TRIR apparatus has been described in detail elsewhere.[20] Briefly, it consists of a pulsed UV/vis source, a Nd:YAG laser (Quanta-Ray GCR-11; 355 or 532 nm, 7 ns pulse), to initiate photochemical reactions, and a CW IR laser (Mütek IR diode laser; MDS 1100), to monitor the transient IR absorptions. The change in IR transmission at one particular IR frequency is measured following excitation, and IR spectra are built up on a "point-by-point" basis by repeating this measurement at different IR frequencies.

UV flash photolysis experiments were carried out at the University of Amsterdam. Solutions of $Cr(CO)_4(bpy)$, in toluene (*ca.* 2×10^{-4} M) in a 1 cm quartz spectral cell, were excited by a Nd:YAG laser (Spectra Physics GCR-3, 532 nm, 7 ns, 20 mJ pulse). A 450 W high-pressure Xe lamp with a Müller-Elektronik MSP05 pulser was used as a probe beam. The excitation and probe beams were focused perpendicularly on the sample. After passing the sample, the probe light was

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(19) The short-lived species (τ *ca.* 50 ps) produced on MLCT excitation[2] was assigned to the ^{1}MLCT vibrationally relaxed state. The present experiments are consistent with this assignment, although the assignment to a ^{3}MLCT state cannot be excluded. Picosecond TRIR measurements could confirm the charge-transfer nature of this species: Turner, J. J.; George, M. W.; Johnson, F. P. A.; Westwell, J. R. *Coord. Chem. Rev.* **1993**, *125*, 101−114.

(20) (a) Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, B. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2083−2092. (b) George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551−560.

(21) Stiddard, M. H. B. *J. Chem. Soc.* **1962**, *4*, 4712−4715.

transferred by an optical fiber to a EG&G 1234 spectrograph equipped with a 150 mm^{-1} grating and a 250 μm slit, resulting in 6 nm resolution, and detected by a MCP-gated diode array detector (EG&G 1421). The data were analyzed by an EG&G 1460 OMA III console provided with a 1302 fast pulser and EG&G FPG/05 gate pulser with a gate of 10 ns.

$Cr(CO)_4$(bpy) was synthesized according to the literature procedure[21] and recrystallized from a CH_2Cl_2−isooctane mixture under a nitrogen atmosphere. CH_2Cl_2 (Aldrich HPLC grade) and toluene (Aldrich) were distilled over CaH_2 and Na wire, respectively, prior to use.

Acknowledgment. We acknowledge the EU Scientific Network “Organometallic Photochemistry”, COST Action D4, the EPSRC (GR/H63296), and Perkin-Elmer Ltd. for financial support. We thank Dr. B. D. Rossenaar (Univeristy of Amsterdam) for help with the UV/visible flash photolysis measurements. We are especially grateful to Prof. D. J. Stufkens for helpful discussions and allowing us to carry out UV flash photolysis measurements in Amsterdam.

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