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Ultrafast Dynamics of Cp*M(CO)$_2$ (M = Ir, Rh) in Solution: The Origin of the Low Quantum Yields for C−H Bond Activation

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Abstract: Using picosecond transient absorption spectroscopy we have examined the dynamics of Cp*Ir(CO)$_2$ (Cp* = C$_5$Me$_5$) in cyclohexane and Cp*Rh(CO)$_2$ in *n*-pentane solution at room temperature following 295-nm UV excitation. A transient absorption with an instrument limited risetime was observed for Ir from 440 to 740 nm and for Rh from 500 to 650 nm. Each transient can be well fit to a biexponential decay consisting of a fast component of 2−3 ps and a slower component of 30−40 ps. These transients are attributed to excited state absorptions. Taking into account independent femtosecond IR studies of the ground state recovery and our data, we suggest that most excited state molecules relax through nondissociative excited states, decaying to the ground state without the loss of CO. These results offer an explanation for the low C−H bond activation quantum yields observed on preparative irradiation of Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$.

Introduction

Since the discovery that certain d^8 organometallic compounds such as Cp*Ir(CO)$_2$ lead to intermediates that activate or break the carbon−hydrogen bonds of alkane solvents following UV irradiation, this class of molecules has been intensely studied.[1] Much of the work has been aimed at elucidating the details of the reaction mechanism. Because of the clear structural information available by monitoring the carbonyl stretching absorptions of these compounds, most studies have concentrated on the 2000-cm^{-1} region of the infrared. Kinetic and spectroscopic experiments carried out in the gas phase,[2] low-temperature matrices,[3] and in liquid noble gases[4] have revealed that a single new IR absorption is produced directly after excitation. In the gas-phase experiment, Wasserman et al. observed the transient absorption of the monocarbonyl species and its subsequent decay in approximately 1 μs as the C−H activated product formed. These results clearly indicate a dissociative mechanism in which the first step of the reaction is the photoinitiated loss of CO.

Despite this progress, however, the individual steps of the mechanism have not yet been directly observed in room temperature alkane solution. Two important characteristics of the reaction have together hindered detection of the intermediates: (i) the extremely rapid reaction rate and (ii) the low quantum yield for C−H activation (reported to be ∼1%).[5,6] Specifically, the reaction has proven too fast to be resolved by microsecond and nanosecond studies while the yield is too low to generate a concentration of intermediates large enough to detect with current ultrafast systems. This fact has recently been confirmed by an ultrafast infrared experiment by Heilweil.[7]

While the low quantum yield has hindered the study of the reaction mechanism in Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$, studies of dicarbonyl(tris(3,5-dimethylpyrazolyl)hydridoborato)rhodium [Tp*Rh(CO)$_2$] irradiation reported a considerably larger quantum yield of 30%.[8] We are currently conducting a femtosecond infrared study of this molecule in alkanes and have found that the quantum yield for this system is in fact large enough to allow us to probe the C−H bond activation mechanism directly. The results of these experiments will be published elsewhere.

In this paper we report our recent study on the origin of the low quantum yield for the C−H activation reaction of Cp*M(CO)$_2$ in alkanes. In light of the strong evidence for the CO dissociation pathway and the extreme reactivity of coordinatively unsaturated organometallic intermediates, the low quantum yield probably originates in the primary photophysical processes that take place *before* the M−CO bond is broken. The excited state dynamics then play a critical role in the subsequent photochemistry by determining the branching ratio between the dissociative and nondissociative reaction pathways. The existence of lower lying excited states below the strong MLCT band is evident in

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(10) With the same pump power, the neat solvent scans have a bigger signal than the iridium complex at long times. This is because more UV photons are available to excite the solvent molecule in the neat scans than in the Cp*Ir(CO)$_2$ solution due to the absorbance of the complex itself. The solvent scan is thus scaled to obtain the same value at long time based on the result from the IR experiment that almost all the excited Cp*Ir(CO)$_2$ returns to the ground state in 40 ps. This scaling procedure is justified since both the solvent signal alone and the total signal were measured to be linearly dependent on pump power. Although the solvent signal is thought to result from two-photon ionization of solvent molecules, the presence of a two-photon process does not necessarily guarantee a quadratic power dependence of the solvent signal due to the non-Gaussian beam shape. This was shown by earlier absorption studies in xenon using the same experimental setup.[18]

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the UV/vis absorption spectrum of these compounds and has been demonstrated by wavelength-dependent measurements of the C−H activation quantum yield.[6] In an effort to investigate the dynamics of these excited states and how they affect the quantum yield for CO loss, we have performed transient visible absorption spectroscopy on room temperature solutions of Cp*Ir$(CO)_2$ in cyclohexane and its congener Cp*Rh$(CO)_2$ in *n*-pentane solution with 1 ps time resolution.

Experimental Section

The laser apparatus used to carry out the picosecond pump-probe experiments has previously been described in detail.[9] Briefly, 1-ps, 10-μJ pulses at 295 nm were used to excite the sample (concentration ~ 1 mM) and transient absorption signals were measured by using 10 nm fwhm band-pass filters at selected probe wavelengths (440−740 nm) from a continuum generated in a water cell. In the Rh experiments, pump power was attenuated to avoid signals originating from the solvent. In the Ir experiments, however, the small signal size necessitated the use of the fairly strong pump powers. In order to eliminate the resulting solvent contribution to the observed signal for the Ir complex, a neat cyclohexane solvent scan was taken immediately preceding the sample scan. This scan was then subtracted from the overall signal.[10]

Cyclohexane and pentane were purchased from Fisher Scientific Co. and were of spectrometric grade. The Cp*Rh$(CO)_2$ complex was purchased from Strem Chemicals and was used as received while the Ir complex was prepared according to the literature.[11]

Results and Discussion

After excitation into the M → CO CT bands of the Ir and Rh complexes at 295 nm, transient absorptions are observed at each wavelength probed from 440 to 740 nm for Ir (Figure 1) and from 500 to 650 nm for Rh (Figure 2). A representative long time scale trace for Rh (Figure 3) shows that on the 100 ps time scale, the signal returns nearly to the baseline.[10] The data are summarized in Tables 1 and 2. All of the transients consist of instrument-limited (1.5 ps) rises followed by biexponential decays. The best fits to the data yield a fast component which decays in 2−3 ps and a slower component which decays in 30−40 ps. Within our signal to noise the time constants are similar at all wavelengths probed while the amplitudes of the fast components appear to be larger at redder wavelengths. While the low signal-to-noise ratio of the Rh data does not allow a quantitative statement to be made concerning the recovery of the signal, it clearly returns to within a few percent of its original value by 100 ps (Figure 3). This recovery is consistent with both the earlier IR results[7] and the quantum yield measurements.[8]

Neither the reactant Cp*Ir$(CO)_2$ nor the product Cp*Ir(CO)(R)(H) absorb significantly in the 440−740-nm range we probed. Therefore, any transient absorptions detected at these wavelengths correspond to new intermediate species generated by photoexcitation. In addition, because we do not observe any wavelength dependence of the decay time constants, these transients cannot be due to the vibrational cooling of the hot parent molecule or photoproduct.[12a,b] Since we do not know how large the extinction coefficient is for the new species, we must consider the possibility that the transients are a result of the loss of CO to form a monocarbonyl intermediate despite the low quantum yield. The instrument-limited rise times are certainly consistent with the time scale for CO loss observed in other metal carbonyls. For example, CO dissociation in $M(CO)_6$ (M = Cr, Mo, W) has been observed to occur on the 300 fs time scale.[13] However, considering the time scales of the decays (see following paragraphs) and results from previous IR experiments,[7,14] the behavior of the transients is inconsistent with that expected for a monocarbonyl. Such pathways are (1) recombination with CO to reform the parent molecule and (2) reaction with the solvent.

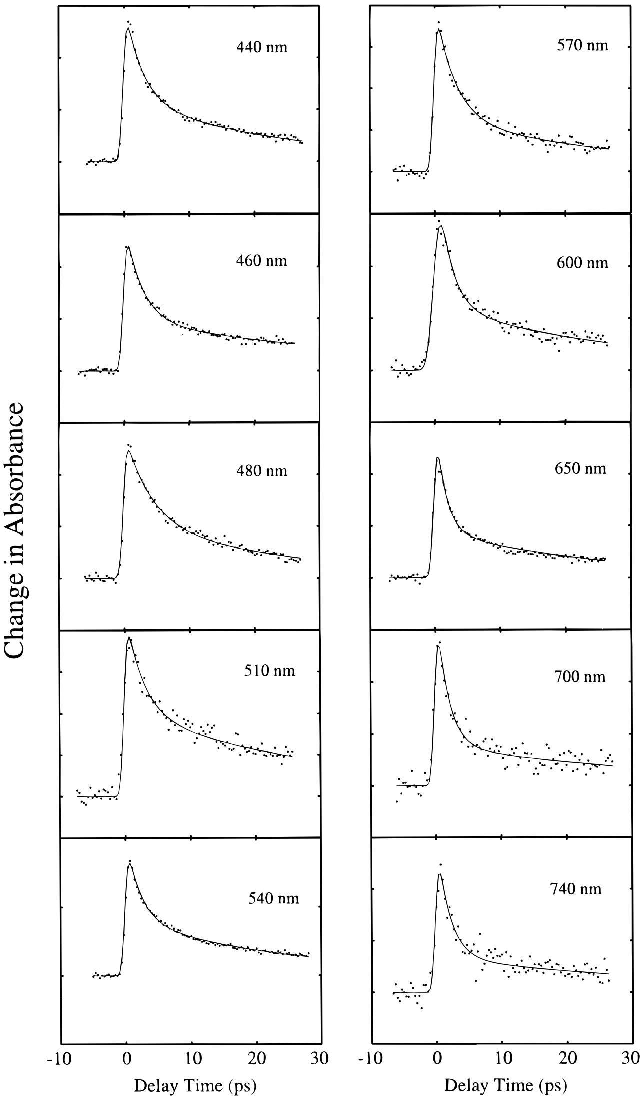

Figure 1. Transient absorption dynamics for Cp*Ir$(CO)_2$ in room temperature cyclohexane at various probe wavelengths. Data points are shown along with solid lines representing fits to biexponentials convolved with a Gaussian instrument function. The fitting parameters are summarized in Table 1.

We can rule out the possibility of CO recombination on the basis of the time scales of the decays. One way recombination may occur is via a diffusion process, which at millimolar concentrations would take place in microseconds, orders of magnitude slower than we observe. The other possibility is geminate recombination. This could occur if the photolyzed CO is not able to escape the solvent cage before recombining with the monocarbonyl fragment to regenerate the parent species. From previous experiments probing this process, the time scale for geminate recombination is known to be on the order of 100

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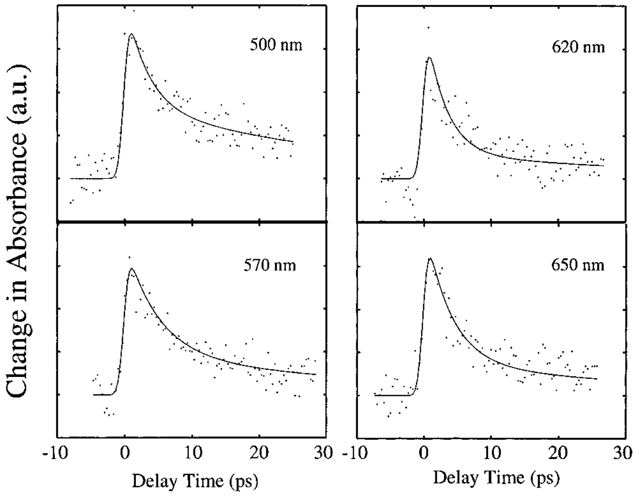

Figure 2. Transient absorption dynamics for Cp*Rh(CO)$_2$ in room temperature *n*-pentane at various probe wavelengths. Data points are shown along with solid lines representing fits to biexponentials convolved with a Gaussian instrument function. The fitting parameters are summarized in Table 2.

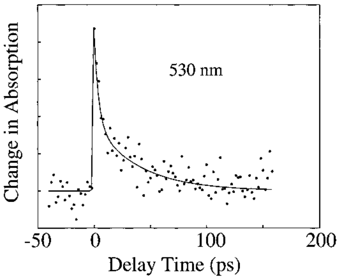

Figure 3. Representative longer time transient absorption dynamics for Cp*Rh(CO)$_2$ in room temperature *n*-pentane at 530 nm. This trace shows that the signal returns nearly to the baseline in approximately 100 ps.

Table 1. Summary of Iridium Data

λ (nm)	τ_1 (ps)	C_1 (%)	τ_2 (ps)	C_2 (%)	λ (nm)	τ_1 (ps)	C_1 (%)	τ_2 (ps)	C_2 (%)
440	2.6	61	24	39	570	3.0	68	30	32
460	2.6	66	35	34	600	2.0	70	30	30
480	4.0	61	25	39	650	1.5	71	30	29
510	2.7	54	33	46	700	1.8	78	40	22
540	2.3	59	25	41	740	2.0	77	40	23

Table 2. Summary of Rhodium Data

λ (nm)	τ_1 (ps)	C_1 (%)	τ_2 (ps)	C_2 (%)
500	3.3	60	37	40
530	5.0	53	40	47
570	5.0	73	40	27
620	3.0	84	40	16
650	4.8	84	38	16
530 (long scan)	4.0	58	40	42

fs to 1 ps—significantly faster than the decays we recorded.[15] Therefore, we conclude that the transients are not due to the recombination of CO with a monocarbonyl fragment.

In the recent femtosecond IR study of Cp*M(CO)$_2$ (M = Ir, Rh) in *n*-hexane by Heilweil,[7] UV excitation at 289 nm was found to lead to a bleach of the parent molecule CO stretching bands. The bleach recovers with a 40 ps time constant, indicating the reformation of the parent molecules. No detectable amount of C−H activated product is observed. From this observation, we can conclude that the visible transients we see for the Ir and Rh complexes are not due to the reaction of a monocarbonyl intermediate with the solvent.

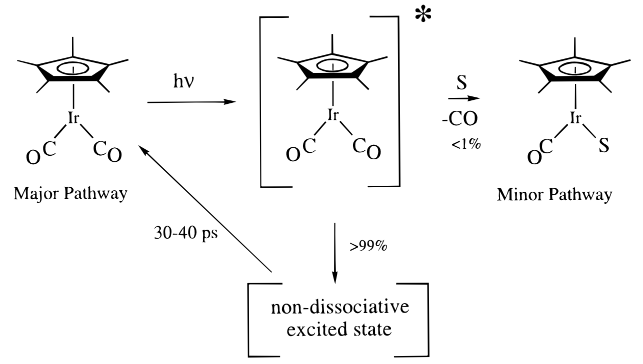

Figure 4. Proposed reaction scheme for Cp*M(CO)$_2$ in room temperature alkane solution. After initial excitation by a UV photon, most (~99%) of the metal complexes decay quickly to a non-dissociative excited state leading directly back to the ground state in 30−40 ps. The other 1% of the excited molecules lose a CO, leaving a coordinatively unsaturated intermediate capable of C−H activating the surrounding solvent. This accounts for the low quantum yield observed for formation of the C−H activated product, Cp*M(CO)(R)(H).

In addition, the energy barrier for C−H bond activation has been determined from the experiments in liquid noble gases to be on the order of 6 kcal/mol.[16] Using a simple Arrhenius description, we can estimate how long it should take for the C−H activated product to form, corresponding to the time scale of the decay of a monocarbonyl. Using a pre-exponential factor of 1×10^{11} s^{-1} and an energy barrier for metal insertion into the C−H bond of 6.0 kcal mol^{-1},[16b,c] the C−H activated product should form with a half-life on the order of 200 ns. This is several orders of magnitude longer than the time we measured, again implying that the transients are not reacting with the solvent to form the C−H activated product.

Ruling out the generation of a monocarbonyl species as the origin of the visible transients, we attribute our result to the first direct observation of a short-lived nondissociative excited state due to UV excitation of Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$. This finding is important because it provides an explanation for the low quantum yields for C−H activation by these complexes. Namely, after excitation by a UV photon, most molecules end up in one or more excited states that do not lead to CO loss. As a result of populating these states, the reactive coordinatively unsaturated species is never generated in most molecules. Instead, these molecules relax to the ground state within 40 ps. This scheme is shown in Figure 4. Furthermore, these observations support the results of the ultrafast IR study[7] which discussed the possibility of similar excited states to explain the bleach recovery in the parent CO stretches of Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$ following UV excitation.

Since the transition at 295 nm contains mainly M−CO* charge transfer character,[17] the nondissociative excited state involved is most likely a lower-lying state that is strongly coupled to the M−CO* CT state. This is supported by the static absorption spectra of these molecules in alkane solutions, each of which show weak and broad absorption from 350 to 500 nm

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indicating that there are lower lying states below the strong metal to CO charge transfer band at 290 nm for Ir and 315 nm for Rh. Wavelength-dependent quantum yield measurements of Si−H activation by Cp*Rh(CO)$_2$ have found that the quantum yield for this reaction decreases by an order of magnitude when the excitation wavelength is changed from 313 to 458 nm.[6] This reduced quantum yield indicates that the low-lying state accessed by excitation at 458 nm has significantly less CO dissociation character. At this point, the exact nature of the excited state is still not known, although there have been some tentative assignments. Based on their wavelength-dependent quantum yield measurement, Lees and co-workers suggest that excitation into these low-lying states leads to a η^5 to η^3 ring slippage in the molecules, which can then undergo rapid reversible ring slippage to relax back to the ground state.[5,6] While it is possible that the 40-ps transient we observe corresponds to this ring-slipped intermediate, our data only allow speculation concerning this issue. In addition, Pradella and co-workers have suggested that these excited states also have substantial M−Cp* antibonding character.[17] They based this assignment on the surprising results of a recent study of the photolysis of Cp*Rh(CO)$_2$ in hexane solution in which they found that at $\lambda > 380$ nm the reaction pathway was consistent with the breaking of the Rh−Cp* bond.

It should also be noted that the fast component observed in our experiment was not identified in the IR study.[7] At early times the transient IR spectrum is broad and structureless due to the anharmonic coupling between the CO stretches and highly populated low-frequency modes.[14] This broadening, in addition to an experimental artifact present at early times,[14] may have obscured the fast transient in the IR spectrum. It is possible that this fast component is a result of the decay of the excited state to the ground state. This process would then produce a vibrationally excited ground state molecule in 2−3 ps. It is also possible that the short component is a result of the absorption of an initially generated excited state that relaxes in 2−3 ps into a longer-lived excited state which decays in 30−40 ps. This model would be favored if there is a wavelength dependence of the relative amplitude of the fast and slow components. Although it appears that the relative amplitude of the short component is larger toward redder wavelengths, the signal-to-noise ratio of our data is not large enough to distinguish between these two possibilities. Future experiments probing the parent molecule absorption in the UV will provide an answer to this question.

Conclusion

Examination of the visible transient absorptions of Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$ in room temperature solution has allowed us to directly observe the excited electronic state responsible for the low C−H activation quantum yield. These results elucidate the pathway taken by the majority of Cp*Ir(CO)$_2$ and Cp*Rh(CO)$_2$ molecules that absorb a UV photon: they decay back to ground state within 30−40 ps through nondissociative short-lived excited states. We will hopefully gain further insight into the excited state dynamics of these interesting organometallics after we can compare our current results to those arising from planned experiments on both the highly efficient C−H activating Tp*Rh(CO)$_2$ and the non C−H activating but highly dissociative CpCo(CO)$_2$ species.

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