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Evidence for a Carbonyl-Containing Intermediate in the 308-nm Photolysis of *trans*-$RhCl(CO)(PMe_3)_2$

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Time-resolved infrared absorption spectroscopy is used to monitor the events during the first ~100 μs following 308-nm photolysis of *trans*-$RhCl(CO)(PMe_3)_2$ (**I**) in a C_6D_6 or Decalin solution. Upon photolysis, the intensity of the carbonyl stretching absorption of **I** decreases and a new C–O stretching absorption (**A**) appears at 2006 cm^{-1} in C_6D_6 (2013 cm^{-1} in Decalin). Within ~100 μs, **A** disappears concurrently with partial regeneration of **I** and oxidative addition of a solvent C–D (C–H) bond. Our observation of the prompt formation of a carbonyl-containing intermediate contrasts with prior observations that photolysis at longer wavelengths leads solely to dissociation of CO from **I**. The implications of the observation of **A** for the understanding of the mechanisms of photocatalytic reactions of **I** are discussed.

Introduction

The square-planar complex *trans*-$RhCl(CO)(PMe_3)_2$ (**I**) is a known photocatalyst for processes such as carbonylation[1,2] and transfer dehydrogenation[2,3] of alkanes, and consequently, its photochemistry has been of considerable interest. While these studies have provided a great deal of insight into the mechanisms of the reactions of **I**, to our knowledge, the only reports to have appeared in the literature of *direct* solution measurements of the transient unstable species that act as reaction intermediates in the chemical processes arising from photolysis of **I** are those published by Ford and co-workers. Their initial investigation,[4] which used time-resolved UV−vis spectroscopy to observe the events following flash photolysis ($\lambda_{irr} > 330$ nm) of **I**, concluded that the primary photolytic process is loss of CO, followed by either recombination to regenerate the parent or activation of a solvent molecule. About a decade later, the Ford group performed an elegant study of the fast photochemistry of *trans*-$RhCl(CO)(PR_3)_2$ (R = Me, Ph, *p*-tolyl) on time scales ranging from milliseconds down to picoseconds.[5] They showed that, for **I**, photolysis at $\lambda_{irr} = 355$ nm leads to prompt (within 1 ns) formation of an intermediate (identified as $RhCl(PMe_3)_2(solv)$ where solv = a molecule of solvent) that oxidatively adds a solvent C−H bond on a time scale of ~100 μs. No evidence for a CO-containing intermediate leading to C−H oxidative addition was found.[6]

The present study was motivated by the observation[7] that the product distribution of the photocatalytic reactions of **I** has a remarkable dependence on the photolysis wavelength

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(6) They did report the existence of a weak transient absorption at 2023 cm^{-1} following photolysis of $RhCl(CO)(PPh_3)_2$ but did not further discuss the nature of this species; in this case (unlike the photolysis of **I**), the 2023-cm^{-1} absorbance could arise from a Rh−H stretch of an orthometalated intermediate.

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(λ_{irr}): when $\lambda_{irr} = 308$ nm, benzene carbonylation is much more efficient than cyclooctane dehydrogenation, while at $\lambda_{irr} = 351$ nm, the relative efficiencies are reversed.[7b] We felt that it is reasonable to hypothesize that this wavelength dependence might be due to the formation of different reaction intermediates, presumably due to excitation into different metal-to-ligand charge-transfer transitions that place different amounts of electron density on the different ligands.[8] Moreover, earlier work in our laboratory had provided evidence that the microsecond-scale kinetics following UV irradiation of Vaska's complex, *trans*-IrCl(CO)(PPh$_3$)$_2$, depend on the photolysis wavelength.[9,10] Given the known dependence of the photochemistry of complexes such as **I** on λ_{irr}, we felt that it would be interesting to investigate the fast (μs) photochemistry of **I** when $\lambda_{irr} = 308$ nm rather than 355 nm.

Experimental Section

The spectrometer in our laboratory has been described in detail elsewhere, so only a brief description will be given here.[11] A room-temperature solution of **I** (typically (1−3) × 10^{-3} mol L^{-1}) flows through an 0.5-mm path length CaF$_2$ IR cell, where it is photolyzed (unless otherwise specified, under Ar) by the 308-nm pulsed output of a XeCl excimer laser (~20 ns pulse^{-1}, ~100 mJ pulse^{-1}, repetition rate typically 3 Hz). The events during the ~100 μs following the photolysis pulse are monitored by using time-resolved IR (TRIR) absorption spectroscopy, with either a Step-Scan FTIR (S^{2}FTIR) spectrometer or a tunable CW Pb-salt diode laser as the IR source. **I** was synthesized according to literature procedures,[1g] and its purity was verified by NMR spectroscopy and mass spectrometry. C$_6$D$_6$ was obtained from Cambridge Isotopes Laboratories (99.6 atom % D) and distilled from Na/benzophenone. Because of the expense of the solvent, for some runs, previously used C$_6$D$_6$ was redistilled; no evidence for impurities in the redistilled solvent was found. Anhydrous Decalin (decahydronaphthalene, mixture of cis and trans isomers, 99+%) was obtained from Aldrich and used without further purification.

Results and Discussion

Typical S^{2}FTIR results for photolysis of **I** in C$_6$D$_6$ are shown in Figure 1. At the flash (to within the instrumental response time of ~50 ns), the absorbance of the C−O stretch of **I** (1956 cm^{-1}) decreases, and a new absorbance (due to a species we shall call **A**) appears at 2006 cm^{-1}. Because of the low output of our IR laser above 2000 cm^{-1} combined with the low absorbance of **A** (Figure 1), we were unable to perform detailed laser-based TRIR measurements of the kinetics of **A**. These laser experiments are consistent with the formation of species **A** within <50 ns of the photolysis; the S^{2}FTIR experiments establish definitively that it is formed within 1 μs of the flash. The absorbance due to **A** then disappears over the subsequent ~100 μs (with first-order kinetics and a room-temperature rate constant $k_{obs} \sim 10^4$ s^{-1}).

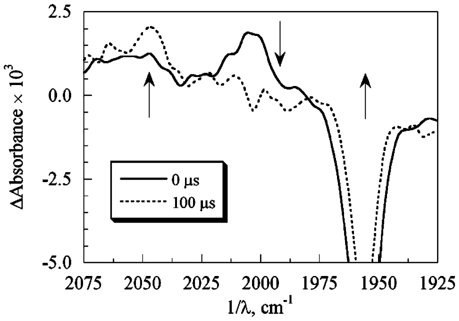

Figure 1. S^{2}FTIR difference spectra obtained at <1 μs (solid line) and 100 μs (dashed line) following 308-nm photolysis of a 1 mM solution of **I** in C$_6$D$_6$ under Ar.

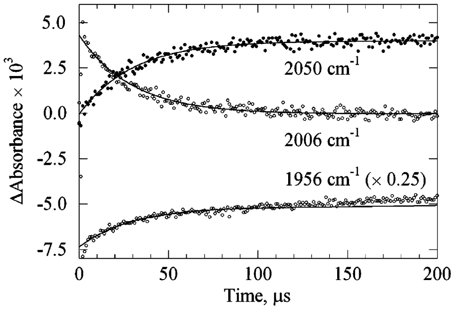

Figure 2. Absorbance changes (×10^{-3}) as a function of time following 308-nm photolysis of a 3.5 mM solution of **I** in C$_6$D$_6$ at 2050, 2006, and 1956 cm^{-1} (the last divided by 4). The solid lines are exponential fits to the data with $k_{obs} = 34\,000$ s^{-1}.

Simultaneously with the disappearance of **A**, two processes are observed: a new absorbance (species **B**) grows in at 2050 cm^{-1} with a time dependence equal within experimental error to that of the decay of the absorbance due to **A**, and partial recovery of the C−O stretch of **I**. Typical time-dependent absorptions following photolysis of **I** in C$_6$D$_6$ at wavelengths corresponding to absorbances of **A**, **B**, and **I**, obtained by successive measurements of the peak intensities in the time-resolved spectra, are shown in Figure 2. We did not observe any dependence of k_{obs} on the laser photolysis power, which was varied from 70 mJ pulse^{-1} (the minimum for which we were able to obtain a measurable transient signal) to 140 mJ pulse^{-1} (the maximum output of our excimer laser). No further reactions are observed on the time scale of the experiment.

In addition to the above experiments in C$_6$D$_6$, we also made some measurements of the photolysis of **I** in Decalin.[12] The results were qualitatively similar to those observed in C$_6$D$_6$: at the flash, the C−O stretch of **I** (1961 cm^{-1}) decreases with the simultaneous appearance of a new C−O stretch (**A′**) at 2013 cm^{-1}. The intensity of **A′** decreases over ~100 μs with simultaneous growth of a new band (**B′**) at 2030 cm^{-1}. **B′** appears to be less stable than **B**: while the absorbance due to **B** reaches a maximum and then remains constant on the time scale of the experiment (Figure 2), the

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(12) We could not use C$_6$H$_6$ as the solvent because of its strong absorbance at 1950 cm^{-1}.

absorbance due to **B′** begins to decay ~120 μs after the photolysis flash. Photolysis of **I** in a 50:50 (v/v) mixture of C_6D_6 and decalin yields both **B** and **B′**, but the relative intensities of the two absorptions appear in a 7:1 ratio.

Attempts to intercept the intermediate by adding an additional ligand to the solution were complicated by the tendency of **I** to react thermally with CO or PR_3 to form a five-coordinate $RhCl(PMe_3)_2(CO)L$ complex. For L = CO, this complex regenerates **I** upon photolysis, but for $L = PR_3$ (R = Me or Bu), photolysis of the five-coordinate complex yields an IR-silent intermediate (presumably $RhCl(PR_3)_3$) rather than **A**. In fact, in the presence of excess PR_3, the regeneration of **I** is actually slower in the presence of excess PR_3 than in the absence of added ligand, presumably because regeneration of **I** from $RhCl(PR_3)_3$ requires exchange of a phosphine ligand.

We assign the absorbance of **B** to the C−O stretch of the previously identified[1f,5] C−D activated product $Rh(Cl)(CO)(PMe_3)_2(C_6D_5)(D)$ (**II**) and that of **B′** to the analogous C−H activation product of the reaction with decalin. The assignment is consistent with the formal oxidation of the Rh atom that takes place during the reaction. In addition, the relative amounts of **B** and **B′** in the competition experiment and the lower stability of **B′** are consistent with the long-known preference for aromatic over aliphatic C−H activation by transition-metal complexes.[13]

The absorbance of **A** at 2006 cm^{-1} (and of **A′** at 2013 cm^{-1}) is most plausibly explained as the C−O stretch of a carbonyl-containing intermediate. Given that the C−H activation appears to proceed via **A** (see below), we believe that the most likely structure for **A** is a five-coordinate "**I**−solvent" complex in which there is a significant metal−C−H interaction. Similar stable five-coordinate Rh(I) complexes of the form $RhClL_4$ are known.[14] The proposed solvated intermediate might be accessible via an excited triplet state of **I** (^{3}**I**), which is calculated[15,16] to be quasi-tetrahedral ($\angle$Cl−Rh−C ~ 108°; $\angle$P−Rh−P ~ 155°). The difference of several reciprocal centimeters in the C−O stretching frequencies of **A** and **A′** may indicate that this species has significant metal−solvent interaction. The C−O stretching frequencies of solvated "$W(CO)_5$" in C_6H_6 and decalin differ by several reciprocal centimeters,[17] consistent with the change in frequency of **A** in the two solvents. These differences do not *prove* that **A** is five-coordinate, however, because the wavelength of the C−O stretching absorption of **I** itself also differs by several reciprocal centimeters from solvent to solvent.

Another possible structure for **A** is the high-energy cis isomer of **I**, the C−O stretch of which has been calculated to be significantly blue-shifted relative to that of **I** and to which a 2012-cm^{-1} peak observed following photolysis of **I** in a Nujol glass matrix has been attributed. Other possibilities for **A** seem to be much less likely. For example, density functional theory calculations indicate that the C−O stretch of ^{3}**I** is very close in frequency to that of the ground state,[15,16] making it unlikely that **A** is ^{3}**I**. Our failure to observe acceleration of the regeneration of **I** in the presence of excess PR_3 implies that **I** is not "$RhCl(CO)(PMe_3)$" produced by photolytic loss of PMe_3 from **I** either. Note that while our experiment cannot distinguish among these possible structures for **A**, the kinetic arguments that follow do not depend on which (if any) of them is correct.

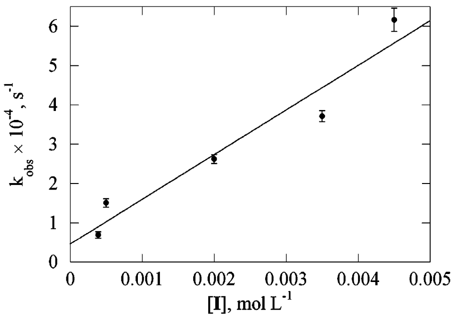

Figure 3. Room-temperature first-order rate constant k_{obs} ($\times 10^{-4}$) for the decay of the absorption of **A** in C_6D_6 (measured at 2006 cm^{-1}) as a function of the concentration of **I**. The solid line is a least-squares linear fit to the data points. Error bars represent 1σ uncertainties.

As shown in Figure 2, the appearance of **II** and a component of the regeneration of **I** occurs with the same rate constant (to within experimental error) as the disappearance of **A**, implying that the two are both formed directly from **A**. These reactions alone cannot account for all of the observed kinetics, however. Experiments in which we varied the concentration range of **I** over the range of $(0.4-3.5) \times 10^{-3}$ mol L^{-1} reveal that k_{obs} depends linearly on [**I**] (Figure 3). The dependence of k_{obs} on [**I**] indicates that, in addition to production of **II**, there must be at least one other process involving **A** in which it reacts with a second species containing Rh. Furthermore, in addition to the 100-μs process, a second component to the regeneration of **I** occurring over milliseconds can be seen in the trace shown in Figure 2. Regeneration of Vaska's complex following UV photolysis occurs on a millisecond time scale as well,[9,10] and we have previously presented evidence that it occurs via a dimeric intermediate.[10] We see no evidence for any other carbonyl-containing species in our experiment, but given the relative amounts of "fast" and "slow" regeneration, it is not out of the question that a dimeric intermediate is present but at concentrations too low to provide a measurable ($> \sim 10^{-3}$ au) absorbance change. Ford and co-workers have also suggested the possibility of regeneration of **I** and its analogues via a dimeric intermediate. The linear fit to the values of k_{obs} (Figure 3) implies a second-order rate constant for this process of $(1.1 \pm 0.2) \times 10^7$ L mol^{-1} s^{-1}. This value is similar to second-order rate constants for such processes as the formation of the dimeric intermediate that eventually leads to regeneration of Vaska's complex ($\sim 6 \times 10^7$ L mol^{-1} s^{-1})[10] and the dimerization of the tricoordinate intermediate $RhCl(PPh_3)_2$ (4×10^7 L mol^{-1} s^{-1}).[9a] Thus, the [**I**] dependence of k_{obs} and the "slow" component of the regeneration of **I** can be explained if 308-nm photolysis of

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(17) These measurements were made on the same S^2FTIR apparatus as that used for the experiments described in the present report.

I produces, in addition to **A**, the formally tricoordinate "$RhCl(PMe_3)_2$" product of CO dissociation.[18] Direct recombination of **A** with CO would compete with reaction of **A** with the (spectroscopically invisible in our system) tricoordinate $RhCl(PMe_3)_2$ to form a dimer that regenerates **I** by recombination with CO on a longer time scale.

Conclusions

While some ambiguities do remain, we can, nonetheless, make several definite conclusions regarding the 308-nm photolysis of $RhCl(CO)(PMe_3)_2$ (**I**). Our results demonstrate that 308-nm photolysis of **I** yields an intermediate (**A**) that contains a carbonyl ligand and, furthermore, that the subsequent oxidative addition of a solvent C−H bond to the metal center arises from a reaction that involves this intermediate. Furthermore, these observations may help to explain the wavelength dependence of the product distribution in the photocatalytic reactions of **I**. If the excitation of **I** is done at a wavelength appropriate for the formation of **A**, then carbonylation will be more efficient because the intermediate already contains a carbonyl ligand. If, on the other hand, the excitation is done at a wavelength that leads to carbonyl dissociation, the efficiency of carbonylation will be decreased relative to that for dehydrogenation, which does not require the presence of CO. In addition, one might expect that, if the C−H activation step from the "$RhCl(PMe_3)_2$" intermediate is sufficiently rapid, recombination with the electron-withdrawing CO ligand would be further disfavored because of the formation of an intermediate in which the Rh atom has formally been oxidized. Further experiments and calculations are underway to try to resolve the remaining ambiguities in the structure and kinetics of **A**.

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(18) ΔA for loss of **I** upon photolysis is ~4 times greater than that for the formation of **A** (Figure 1). Because the molar extinction coefficients for the C−O stretches in the two species should be similar, the large difference in ΔA may be further evidence that photolysis of **I** produces an IR-silent species in addition to **A**.