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Sub-Picosecond IR Study of the Reactive Intermediate in an Alkane C−H Bond Activation Reaction by $CpRh(CO)_2$

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Summary: The reactive intermediate in a cyclohexane C−H bond activation reaction by $CpRh(CO)_2$ has been identified as the cyclohexane solvate η^5-$CpRh(CO)(C_6H_{12})$ by sub-picosecond infrared spectroscopy.

The photochemistry of transition-metal complexes, such as $CpM(CO)_2$ (M = Rh, Ir), capable of undergoing oxidative addition with alkane carbon−hydrogen bonds has been studied intensely.[1,2] This type of reaction is traditionally thought to begin by the initial dissociation of a ligand from the electronically saturated (18-electron) metal complex to form an electronically unsaturated (16-electron) intermediate. It is now well-established (see below) that this reactive intermediate rapidly forms a complex (or solvate) with an alkane molecule, and in a subsequent step, one of the C−H bonds in this complexed alkane undergoes oxidative addition at the metal center.[1,2] The first steps of this reaction have been identified by experiments in the gas phase,[3] liquefied noble gases,[4] and low-temperature matrixes.[5] However, the detailed mechanism of the subsequent bond activation step is not well understood, due to the difficulties in characterizing short-lived alkane complex intermediates.

Recently, a C−H oxidative addition reaction was studied by ultrafast time-resolved spectroscopy.[6,7] This involved a complete time-resolved IR spectroscopic study of the C−H bond activation reaction of $Tp^*Rh(CO)_2$ ($Tp^* = HB{-}Pz_3^*$, Pz^* = 3,5-dimethylpyrazolyl), shown in Figure 1c, in room-temperature alkane solution covering a time range from a few femtoseconds to milliseconds.[6] Several reactive intermediates in the overall C−H bond activation process were identified, and the corresponding reaction rates of various steps were determined. Two sequentially formed intermediates were detected, one of which was an η^2-$Tp^*Rh(CO)(alkane)$ complex in which a pyrazolyl−Rh bond has been cleaved.

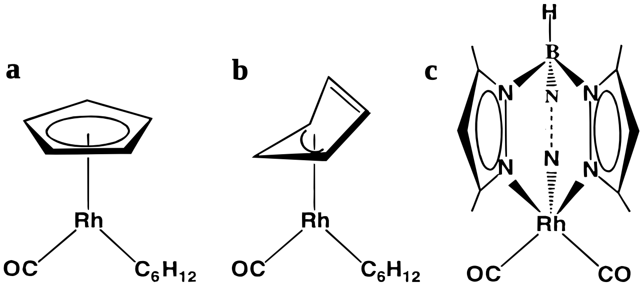

Figure 1. Structures of (a) η^5-$CpRh(CO)(C_6H_{12})$, (b) η^3-$CpRh(CO)(C_6H_{12})$, and (c) $Tp^*Rh(CO)_2$.

The above results raise the possibility that additional ligand detachment, rather than simple CO loss, might also be involved in C−H bond activation involving other organometallic compounds, especially the much-studied complexes $Cp^*M(CO)_2$ or $CpM(CO)_2$ ($Cp^* = C_5Me_5$).[8,9] In these systems, such intermediates could be generated by partial decomplexation of the Cp or Cp* ring in the initially generated monocarbonyl solvate to give solvates of “ring-slipped” η^3-CpRhCO, as shown in Figure 1b.

So far, only the highly methyl-substituted Cp* dicarbonyls have been subjected to ultrafast spectroscopic investigation. Unfortunately, due to their very low quantum yields for CO dissociation, the reactive intermediates involved in C−H bond activation reactions formed from $Cp^*M(CO)_2$ have not been observed in these studies in room-temperature alkane solutions.[10,11] The smaller yield was attributed to the generation of nondissociative excited states which relax back to the ground state in less than 40 ps. In this communication, we report the first ultrafast study of the photochemistry of the related unmethylated complex $CpRh(CO)_2$. A higher quantum yield for CO loss in this molecule compared to the Cp* analogue has enabled us to observe the reactive intermediate directly and follow the time course of its reactions up to 1 ns. This molecule serves as an excellent system in which to study metal−alkane interactions because its relative simplicity is more

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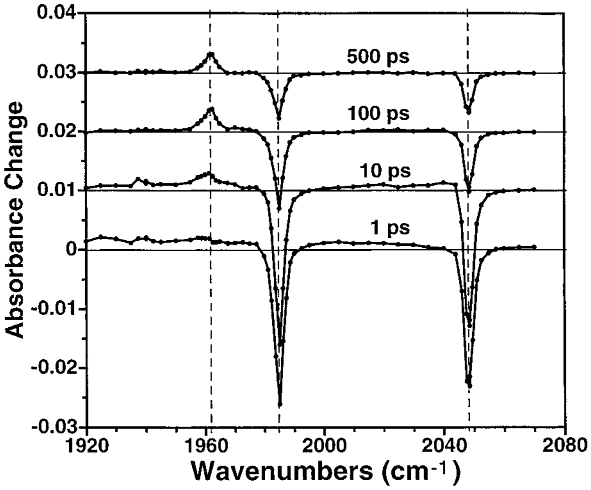

Figure 2. Transient IR spectra of $CpRh(CO)_2$ in cyclohexane after 267 nm photolysis. The spectra at different delay times have been displaced vertically for comparison.

amenable than the permethylated system or $Tp^*Rh(CO)_2$ to high-level electronic structure calculations.[12–14]

The 1 kHz sub-picosecond tunable IR spectrometer[15] used for this study has a 150 fs time resolution and a tunable IR probe wavelength from 1 to 10 μm. A flowing cell (250 μm path length) containing $CpRh(CO)_2$ in cyclohexane was pumped by a 3 μJ photolysis pulse with a FWHM of ca. 100 fs at 267 nm, and the subsequent IR spectral changes in the CO stretching mode region were recorded as a function of time for up to 1 ns. After passing through the sample, the probe IR pulses are dispersed in a monochromator to obtain a 2 cm^{-1} spectral resolution. The pump and probe beam diameters at the sample are 350 and 250 μm, respectively. The relative polarization of the pump UV and probe IR beams was set at 54.7° to ensure that the measured absorbance change was due to population dynamics only. $CpRh(CO)_2$ was synthesized according to a published procedure[16] and fully characterized by conventional spectroscopic methods. The sample solution (ca. 10 mM concentration) was kept under dry N_2 and continuously flowed through an airtight cell to ensure that each laser pulse probed a fresh volume of sample.

Shown in Figure 2 are the transient IR difference spectra obtained upon irradiation of $CpRh(CO)_2$ in cyclohexane recorded at 1, 10, 100, and 500 ps after the 267 nm photolysis pulse. The negative peaks at the frequencies corresponding to the parent CO stretching bands of 1985 and 2048 cm^{-1} indicate the depletion of parent molecules due to photolysis. A single new band at 1963 cm^{-1} grows in, suggesting the formation of only one transient solvate.[17] After photolysis, the recovery of the bleach at the parent CO bands indicates the partial reformation of the parent molecules. Shown in Figure 3 are the kinetics measured at the parent absorption bands (panels b and c) and the new product band at 1963 cm^{-1} (panel a). The bleach recovery kinetics are well fit to a single-exponential recovery time of 55 ± 5 ps. For the new product band, the kinetics can be well fit by an exponential rise time of 10 ps and a small 60 ps decay component. A small solvent background signal centered around $t = 0$ has been subtracted from all the figures presented here.[18]

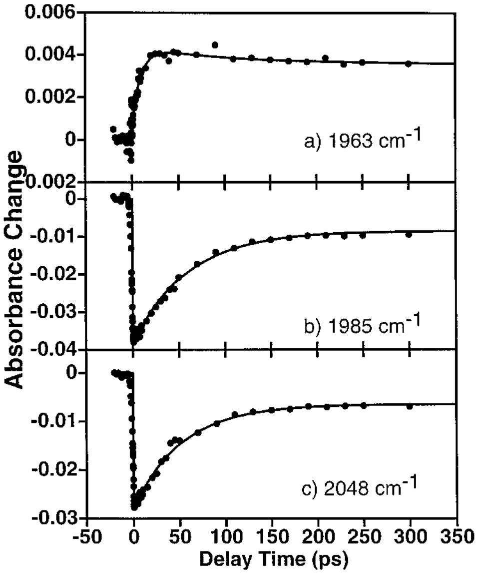

Figure 3. Kinetics of $CpRh(CO)_2$ in cyclohexane measured at 1963 (Panel a), 1985 (panel b), and 2048 cm^{-1} (panel c).

As shown in Figures 2 and 3, about 75% of the bleached absorptions at 1985 and 2048 cm^{-1} have recovered within 200 ps. The corresponding 25% loss of the parent molecules can be attributed to the CO loss channel, since no long-lived nondissociative excited states were present. For $CpRh(CO)_2$ in decalin solution, the quantum yield for photosubstitution by phosphine[16,22] was determined earlier to be around 20% with 313 nm photolysis. This yield is consistent with our estimate of a 25% CO loss channel in our experiments. The measured 55 ps recovery time of the bleaches is due to the return of excited parent molecules to the lowest vibrational level of their ground electronic state; this time constant contains the contributions of both electronic relaxation (radiationless decay) as well as vibrational relaxation. Metal carbonyls with excess vibrational energy have been shown earlier to exhibit broad and featureless IR bands which are red shifted compared to the CO stretching bands of the corresponding vibrationally cold molecules. These broad features can be attributed to the anharmonic coupling of CO stretch-

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[17] The small feature at 1940 cm^{-1} has been carefully examined in a separate experiment that focused on that region. We found that it was not a reproducible peak within the current signal-to-noise level of our experiment. Similarly, within the signal-to-noise of the data, there are no other new peaks besides the one at 1963 cm^{-1}.

[18] Under the same experimental conditions, a small signal in neat cyclohexane, which has a peak absorbance change of ca. 5 mOD at $t = 0$ and decays to negligible values at 5 ps, was observed. This pump-induced solvent signal, whose origin is so far not clear, appears to be independent of wavelength in this spectral region. An identical feature can also be observed in $CpRh(CO)_2$ samples and is subtracted from all the figures presented here.

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ing modes with highly populated low-frequency modes in the molecules. As the metal carbonyls dissipate their excess vibrational energy to the surrounding solvent molecules, the broad features narrow and shift to higher energy and the bleach recovers.[19] This type of feature is also present in our transient spectra at 1 and 10 ps as shown in Figure 2. The vibrational relaxation times in metal carbonyls of similar size are typically about 10−20 ps for low-frequency modes and over 30 ps for CO stretching modes.[20,21] We conclude that irradiation of $CpRh(CO)_2$ leads to excited states with a dissociative channel and a short-lived nondissociative channel. The lifetime of the latter channel, which undergoes radiationless decay back to the electronic ground state, is estimated to be less than 10 ps based on the lack of distinct vibrational peaks associated with this channel at 10 ps.

The reactive channel leads to a transient that exhibits only one new metal carbonyl IR stretching band, suggesting that this species is a monocarbonyl intermediate. In a previous study of the photolysis of $CpRh(CO)_2$ in an Ar matrix,[5] a CO stretching band at 1968 cm^{-1} was assigned to η^5-CpRh(CO). The well-known stable 18-electron η^5-CpRh(CO)(PR_3) complexes typically absorb near 1952 cm^{-1}.[16,22] We therefore believe that the transient species detected in our experiments is the solvated complex η^5-CpRh(CO)(C_6H_{12}), shown in Figure 1a. This assignment is consistent with the observation that there is no further change of its frequency up to 1 ns. The "naked" 16-electron complex is not directly observed here (nor was it observed in the previous Tp* study) because the complex formation between CpRh(CO) and a surrounding solvent molecule is expected to be a process with a negligible barrier and should occur in the hundreds of femtosecond to a few picosecond time scale at room-temperature solution in which solute−solvent collision occurs on the 100 fs time scale. For example, solvate formation between nascent $Cr(CO)_5$ and alkanes and alcohols[23] was observed to occur in the 1−2 ps time scale. The formation time of the CpRh(CO)(C_6H_{12}) band at 1963 cm^{-1} is well fit by a 10 ps exponential rise as shown in Figure 3. This formation time contains contributions from both the formation of vibrationally hot CpRh(CO)(C_6H_{12}) and the cooling of the hot monocarbonyl. Identifying the spectral features of the short-lived naked species and separating the time scale for solvent addition and vibrational cooling is difficult because of the very broad nature of the IR spectra for these vibrationally hot nascent species. A 10 ps rise time is typical of the vibrational relaxation time for low-frequency modes.[19] The small 60 ps decay component measured at 1963 cm^{-1}, which is identical to the bleach recovery time, can be attributed to the cooling of hot $CpRh(CO)_2$ molecules, whose broadened and red-shifted CO stretching bands have a small absorption in the 1920−1980 cm^{-1} and 2000−2050 cm^{-1} region, as shown in Figure 2.

The final C−H bond-activated product, CpRh(CO)(R)(H), has a CO stretching mode at around 2024 cm^{-1}.[5] None of this material is formed on the nanosecond-or-shorter time scale. We expect that the C−H bond cleavage should occur on the 10−100 ns time scale, based on the results of the Tp*$Rh(CO)_2$ study[6] and the estimated activation barrier measured in the Cp*Rh($CO)_2$/liquefied noble gas experiments[8] discussed above. Our ongoing research will investigate the bond activation step by measuring the kinetics in the nanosecond to millisecond time scale using step-scan FTIR. The activation of Si−H bonds, which was reported to occur in the picosecond time scale for $CpMn(CO)_3$,[24] will also be investigated for the $CpRh(CO)_2$ system.

Our experiment is the first direct observation of the reactive monocarbonyl−alkane complex, η^5-CpRh(CO)(C_6H_{12}), in room-temperature alkane solution. Our results are consistent with the idea that this alkane complex solvate is formed on the pathway to the final C−H oxidative addition product, as suggested for the Cp* and Tp* systems. Because we see only one intermediate here, there is a clear difference between the behavior of this system and that of Tp*$Rh(CO)_2$, where a second (presumably pyrazolyl-detached) species was detected. It seems reasonable that ligand detachment would be more favorable in that system, since bis(pyrazolyl)borate complexes have been identified as stable species in closely related complexes.

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