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Time Resolved Studies of Bond Activation by Organometallic Complexes

Matthew J. Wilkens

Chemical Sciences Division

May 1998

M.S. Thesis

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Time Resolved Studies of Bond Activation by Organometallic Complexes

by

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M.S. Thesis

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May, 1998

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Matthew J. Wilkens

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Chapter 1

Introduction

1.1 History and Motivation

The ability to selectively break chemical bonds with increasing ease and precision has been a driving force behind a great deal of the research conducted in modern chemistry. Synthetic chemistry is built upon this ability, and the success or failure of a given synthetic project can in large part be traced to the extent to which it is able to achieve selectivity and specificity under reasonable conditions. Physical chemists share a concern for the nature of the chemical bond, since it is the bond and its properties which determine many of the physical phenomena in kinetics, reaction dynamics, and thermodynamics, to name only a few areas of interest. A more complete understanding of the bonds between common organic elements is especially desirable because of the obvious applicability of such knowledge not only to problems of inter-

est to physical chemists, but also to important and ongoing research in synthetic and industrial settings.

The bond between carbon and hydrogen is among the most interesting of this group. Hydrocarbons are (nearly) by definition the basic constituents of organic chemistry and thus represent a class of molecules which are of great interest to the synthetic organic chemists, whose work is necessarily concerned with breaking and forming such bonds. As a practical matter, the petroleum and petrochemicals industries have an enormous stake in the advancement of our understanding in the field. Finally, physical chemists can find in this area the opportunity to move beyond the simplest of systems into those which have not yet been well characterized by either experiment or theory. It is with these motivations in mind that we have undertaken the study of bond activation in alkanes.

The carbon-hydrogen (C-H) bond in typical linear and cyclic alkanes is quite strong, on the order of ~ 100 kcal/mol [1, page 266]. This means that such bonds are extremely stable, normally requiring high temperatures and/or pressures if they are to be broken. It also means that alkanes and other molecules which contain plentiful C-H bonds are rich reservoirs of chemical potential energy. These characteristics are exploited in the use of alkanes and alkane derivatives as combustion fuels. The unfortunate disadvantage of this situation, from the perspective of the synthetic chemist, is that alkane functionalization and substitution reactions can be quite difficult to carry out under ambient or near-ambient experimental conditions. In 1971, Jetz and

Graham discovered that the silicon-hydrogen (Si-H) bond in silanes could be broken under mild photochemical conditions in the presence of certain transition metal carbonyls according to the general reaction scheme:

where $M = Cr, Mn, Co, \text{ or } Fe$ and $R = C_6H_5 \text{ or } Cl$ [2]. Such reactions fall within the class of *oxidative addition*. A decade later, similar reactivity was discovered in alkanes by Janowicz and Bergman [3,4] and Hoyano and Graham [5]. In these cases, a C-H bond in non-functionalized alkanes was broken through the oxidative addition of $Cp^*Ir(H)_2L$ ($Cp^* = (CH_3)_5C_5$, $L = PPh_3$, $Ph = C_6H_5$)¹ to form $Cp^*ML(R)(H)$ or of $Cp^*Ir(CO)_2$ to form $Cp^*Ir(CO)(R)(H)$.

These discoveries opened an entirely new field of research, one which naturally included mechanistic studies aimed at elucidating the various paths involved in these and related reactions. It was quickly evident, however, that many of the intermediate steps occur too quickly under standard conditions to be characterized using conventional methods, including Fourier transform IR (FTIR), UV/Vis, and fluorescence spectroscopies. For this reason, experiments were conducted under non-standard conditions, including those in the gas phase [6], in low temperature/high pressure liquid noble gases [7,8], and in low temperature matrices [9-11]. In each of these cases,

¹Note that Cp^* is the permethylated form of the well-known cyclopentadienyl (Cp) ligand. Here and throughout, the * notation indicates such a form. Both Cp and Cp^* are π -bound η^5 five-membered rings.

the timescale of the intermediate steps was slowed sufficiently so as to allow characterization using techniques with time resolution of tens of nanoseconds (ns) or slower. Much was learned from these experiments, as will be discussed below, but they shared the disadvantage of studying under highly non-standard conditions a system which is of interest largely because of its characteristics under standard conditions.

Ultrafast time-resolved IR spectroscopy provides an ideal solution to this problem: because it allows the resolution of chemical events taking place on the femto-through picosecond time scales, it is possible to study this important class of reactions under the ambient conditions which are most of interest to the practicing synthetic chemist. Certain of the molecules in question, moreover, are particularly well-suited to study using the ultrafast IR spectrophotometer described in the experimental section below because they contain one or more carbonyl ligands. Carbonyl stretches in the $1850\text{--}2050\text{ cm}^{-1}$ range have large absorption cross sections and display significant shifts ($>10\text{ cm}^{-1}$) with changing chemical environment, including changes in hapticity, electronic structure, and ligand identity, making them useful spectroscopic probes of chemical reactivity at the metal center. By following changes in these spectroscopic features through time, it is possible not only to identify reaction intermediates but to correlate the various intermediates to one another. This information can then be used to determine reaction mechanisms, branching ratios, energy barriers, and intermediate structures for each reaction.

1.2 Previous Work

The work to be reported in Chapters 3 and 4 represents an extension of that which has been carried out in this and in other groups. The previous work has provided both a point of reference and a framework for problems to be addressed. For this reason, a selection of major results from previous work is presented here.

1.2.1 Conventional Methods

These experiments offer limited temporal resolution and are conducted under non-ambient conditions. They have established, however, the basic series of events involved in certain bond activation and related reactions. They also provide relative dynamic and spectral information which is useful for comparison to novel findings.

Gas Phase Spectroscopy

Studying $\text{CpRh}(\text{CO})_2$, Wasserman *et al.* proposed the oxidative addition reaction scheme [6]:

In these experiments, $\text{CpRh}(\text{CO})_2$ was introduced at its room-temperature vapor pressure (~ 400 mtorr) into 12 to 30 torr of an Ar buffer gas which contained alkanes in

concentrations on the order of zero to several hundred millitorr. Immediately following photoexcitation at 308 nm, they found two bleaches in the IR region of the spectrum, centered at 2003 and 2060 cm^{-1} , which they attributed to depletion of the parent dicarbonyl. They also observed the growth of a single new peak at 1985 cm^{-1} which was attributed to formation of the monocarbonyl intermediate $\text{CpRh}(\text{CO})$. In the absence of alkanes, this intermediate decayed rather slowly ($t_{1/2} \approx 1\mu\text{s}$), presumably to the dimer $\text{Cp}_2\text{Rh}_2(\text{CO})_3$, shown in Figure 1.1.

Figure 1.1: Structure of the $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ dimer.

When 300 mtorr of cyclohexane was added to the reaction mixture, $t_{1/2}$ decreased to 250 ns and a new peak at 2037 cm^{-1} was observed to form on an identical time scale within the uncertainty of the experiment. The 2037 cm^{-1} peak was identified as the final alkyl-hydride product and was observed to be stable on the millisecond time scale. The researchers were unable to determine activation energies for most of the steps involved in the reaction because the parent dicarbonyl was excited to an energy far in excess of any reaction barrier, leaving the reaction rate under simple gas-kinetic control.

Liquid Noble Gases

Bengali *et al.* studied the closely related $\text{Cp}^*\text{Rh}(\text{CO})_2$ in liquid Kr and Xe at ~ 300 psi between 163 and 193 K [7]. Although peak and bleach positions were slightly shifted relative to those discussed above due to the methyl substitution of the Cp^* ligand, this study observed similar reactivity. In a sample of liquid Kr free of alkanes, photolysis of $\text{Cp}^*\text{Rh}(\text{CO})_2$ at 308 nm results in instantaneous ($1\ \mu\text{s}$, instrument limited) formation of a single product peak at $1946\ \text{cm}^{-1}$ which decays quite slowly ($t_{1/2} \approx 1\ \text{ms}$). This peak was identified as a monocarbonyl-solvent complex based on an analysis of previous work [12–17] and the fact that the peak decayed two orders of magnitude more quickly in Kr solvent than in Xe. Since it is known that Xe binds metal centers much more strongly than Kr [18], it is reasonable to expect that the displacement of the solvent molecule necessary for dimer formation (the only available decay channel in the absence of dissolved alkanes) would occur less frequently in Xe than in Kr and that the rate of decay would therefore be greater in Kr, as was observed. The possibility that the observed disparity in rates of decay could have arisen from different excited state spin multiplicities was dismissed after experiments in which small amounts of triplet liquid oxygen were added to the reaction mixture failed to yield substantially different results from those conducted in pure Kr and Xe.

In the presence of dilute neopentane $(\text{CH}_3)_4\text{C}$, the solvent complex was observed to decay much more quickly and concomitantly with the formation of a long-lived new

species indicated by a peak at 2008 cm^{-1} . The observed rates of reaction k_{obs} for the decay and formation processes were observed to be $3.76 \times 10^4\text{ s}^{-1}$ and $4.08 \times 10^4\text{ s}^{-1}$, respectively, in liquid Kr at 193 K in the presence of 3.8 mM neopentane, compared to $\sim 700\text{ s}^{-1}$ in neat Kr.² The 2008 cm^{-1} peak was attributed to the final activation product, $\text{Cp}^*\text{Rh}(\text{CO})(\text{H})(\text{C}_5\text{H}_{11})$. Unfortunately, the identity of the solvent complex was no longer clear as the solvent in question might have been either a Kr atom or a neopentyl molecule, both of which result in solvent complexes with IR absorptions at 1946 cm^{-1} . For this reason, perdeuteroneopentane $(\text{CD}_3)_4\text{C}$ was substituted for neopentane, resulting in the observation of a new transient peak at 1947 cm^{-1} . In this case the kinetics of the reaction were somewhat more complex, but can be summarized as follows.³ The 1946 cm^{-1} peak, $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$, exhibited a biexponential decay with fast component $k_1 = 1.17 \times 10^4\text{ s}^{-1}$ and slow component $k_2 = 1.90 \times 10^3\text{ s}^{-1}$. Using these rate constants, the kinetics of the 1947 cm^{-1} peak were deconvolved from those of the 1946 cm^{-1} peak. It was found that the 1947 cm^{-1} peak corresponding to the deuterioalkyl solvent complex $\text{Cp}^*\text{Rh}(\text{CO})\cdot(\text{CD}_3)_4\text{C}$ grew in with a rate constant $k_3 = 1.15 \times 10^4\text{ s}^{-1}$ and decayed with a slow rate constant $k_4 = 1.60 \times 10^3\text{ s}^{-1}$. Finally, the oxidative addition product $\text{Cp}^*\text{Rh}(\text{CO})(\text{D})(\text{C}_5\text{D}_{11})$ at 2008 cm^{-1} was

²Rates of reaction k , half-lives $t_{1/2}$, and rate constants τ are related as follows:

$$[A]_t = [A]_0 \exp(kt) = [A]_0 \exp(t/\tau), \text{ and thus } t_{1/2} = \tau \ln 2 = \frac{\ln 2}{k} \quad (1.3)$$

³These reaction rates are not directly comparable to those measured for neopentane (above), due to the fact that the deuterated experiment was carried out at 165 K so as to minimize the width of the transient peaks ($2\text{--}3\text{ cm}^{-1}$), thereby enhancing their resolution.

observed to form with $k_{\text{product}} = 2.00 \times 10^3 \text{ s}^{-1}$. Reported uncertainties averaged 15%. These results suggest that the Kr solvate is formed immediately upon photoinitiation, followed by the rapid replacement of the Kr atom by an alkyl molecule. The alkyl solvate then reacts slowly to form the alkyl deuteride product. An analysis of the temperature dependence of these oxidative addition reactions suggested that the alkyl solvate complexes were 2-3 kcal/mol more stable than the Kr solvates and that the activation energy of the bond cleavage step was 6-7 kcal/mol. Again, however, these experiments lacked time resolution sufficient to distinguish early events in the reaction, namely the formation of the Kr solvate, nor did they provide a detailed reaction mechanism. More seriously, it is not clear that results involving a Kr- or Xe-solvated intermediate at cryogenic temperatures are applicable to the real problem of interest, namely bond activation in neat alkanes at room temperature.

Matrix Isolation

Introduction of $\text{Tp}^*\text{Rh}(\text{CO})_2$ Although the various Cp and Cp^* transition-metal containing compounds discussed above have proven both useful and interesting, it may be possible to improve upon certain of their properties for practical use. In 1987, Ghosh and Graham discovered that the related species $\text{Tp}^*\text{Rh}(\text{CO})_2$ ($\text{Tp}^* = \text{HBPz}_3^*$, $\text{Pz}^* = 3,5\text{-dimethylpyrazolyl}$), shown in Figure 1.2 on the next page, activated C-H bonds in aromatic and saturated hydrocarbons with several marked advantages relative to the Cp and Cp^* compounds. It was observed that $\text{Tp}^*\text{Rh}(\text{CO})_2$ success-

Figure 1.2: Structures of $\text{Tp}^*\text{Rh}(\text{CO})_2$ and the activated product $\text{Tp}^*\text{Rh}(\text{CO})(\text{R})(\text{H})$.

fully activated benzene, cyclohexane, and methane C-H bonds in room temperature solutions with product yields of 95% or greater, compared to the ~60% activation yield reported by Hoyano and Graham for the same reactants by $\text{Cp}^*\text{Ir}(\text{CO})_2$ [5]. Moreover, the photoexcitation sources necessary to produce activated products of the type shown in Figure 1.2 were much less powerful than the UV Hg arc lamps previously required. In fact $\text{Tp}^*\text{Rh}(\text{CO})_2$ was found to produce activated products in the presence of ambient natural and laboratory light. It was inferred from this fact that the quantum yield of this reaction was substantially higher than that of $\text{Cp}^*\text{Ir}(\text{CO})_2$ and the related Cp and Cp^* compounds. Conversion to the product form was generally complete within minutes, and no measurable decomposition of parent or product molecules was observed with continued irradiation.

As the focus of this work lay primarily on synthesis and characterization, no kinetic studies were performed and no reaction mechanism was proposed. The authors did note, however, that the Tp^* ligand can undergo a facile transition from the η^3 to the η^2 form,⁴ thereby reducing electron density at the metal center. This process, which

⁴ η^x denotes the number of atoms x through which a multidentate ligand is bound to the metal

mirrors the loss of a carbonyl ligand in producing a 16-electron Rh center, might be expected to facilitate C-H bond cleavage by increasing the electron affinity of the metal center.

Experimental Results in Matrices Seeking to expand upon the work of Ghosh and Graham, Bloyce *et al.* undertook a series of experiments concerning $\text{Tp}^*\text{Rh}(\text{CO})_2$ and related compounds in low temperature matrices [10]. These non-time-resolved experiments involved static irradiation of the transition metal compounds in a variety of matrices (Ar, CH_4 , CO, N_2) and mulls (perfluorokerosine, Nujol), and in paraffin wax, all between 12 and 77 K. In close agreement with previous work, the parent molecule $\text{Tp}^*\text{Rh}(\text{CO})_2$ exhibited CO absorptions near 1980 and 2055 cm^{-1} prior to irradiation in all media. Following irradiation at various wavelengths in the visible and near-UV, two photoproducts were observed. The minor product was a monocarbonyl species at $\sim 1965 \text{ cm}^{-1}$ analogous to that which had been proposed as the reactive intermediate in previous studies of the Cp and Cp^* compounds. In this case, however, the monocarbonyl species was stable over the course of minutes to hours as required by the nature of the experiment, in high contrast to the expected behavior of a highly reactive intermediate species. This was found to be true even in the CH_4 matrix in which, quite surprisingly, no C-H activation was observed. The major photoproduct, a dicarbonyl displaying absorptions near 2019 and 2085 cm^{-1} , was assigned to $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})_2$. This assignment was based on the observation that the carbonyl peaks had shifted to

center.

markedly higher energy, indicating decreased electron density on the metal center, and the fact that the closely related η^2 16-electron species $\text{Bp}^*\text{Rh}(\text{CO})_2$ ($\text{Bp}^* = \text{H}_2\text{BPz}_2^*$; note that one of the pyrazole rings has been replaced by a hydrogen atom) absorbs at 2018 and 2084 cm^{-1} . The 30 to 40 cm^{-1} increase in carbonyl stretching frequency, moreover, is consistent with other metal-carbonyl species produced through the loss of a nitrogen-donor ligand in low-temperature matrices [19,20]. Similar results were obtained in identical experiments on $\text{Bp}^*\text{Rh}(\text{CO})_2$, including the observation of an η^2 - $\text{Bp}^*\text{Rh}(\text{CO})$ monocarbonyl and a dechelated η^1 - $\text{Bp}^*\text{Rh}(\text{CO})_2$ dicarbonyl, both of which are 14-electron species. No C-H bond activation was observed in either case.

The lack of C-H bond activation by species which had been previously shown to do so was clearly the most striking feature of this work. The authors proposed that this anomaly was best explained by the postulation of a thermally-activated step following photolabilization of the first CO ligand. This theory is supported by the fact that C-H activation products *were* observed at higher temperatures (≥ 77 K) in those media (mulls and wax) which can withstand them.⁵ The authors also suggested that steric hindrances involving the tridentate-bidentate interconversion might have an effect on activation reactivity. To complicate matters further, C-H activation by $\text{CpIr}(\text{CO})_2$ and $\text{Cp}^*\text{Ir}(\text{CO})_2$ *was* observed in mulls and matrices at 12 K. Unfortunately, the lack of time resolution in these experiments precluded the possibility of realistic speculation regarding the validity or the specific origin of the

⁵Matrices such as those used by Bloyce *et al.* generally evaporate at ~ 50 K.

proposed thermal barrier, the structure of relevant intermediates, or the activation barriers associated with any particular intermediate.

1.2.2 Ultrafast Methods and Early Dynamics

It is clear from the preceding discussion that ultrafast methods in the visible and infrared regions of the spectrum are necessary if questions concerning the early dynamics of bond activation are to be answered satisfactorily. As both a practical and a theoretical matter, our group first undertook experiments designed to explain the striking aforementioned difference in efficiency of bond activation between $\text{Cp}^*\text{M}(\text{CO})_2$ ($\text{M} = \text{Ir}, \text{Rh}$) and $\text{Tp}^*\text{Rh}(\text{CO})_2$. The practical importance of this issue arises from the relatively small signals inherent in ultrafast work as compared to static or low time resolution spectroscopy. With a reported quantum yield of C-H bond activation of only $\sim 1\%$ ⁶ $\text{Cp}^*\text{Ir}(\text{CO})_2$ [21, 22], it is extremely unlikely that acceptable signal to noise ratios could be obtained using the femtosecond infrared spectrophotometer described in Section 2.1. More importantly, an understanding of the photochemically relevant differences between the Cp^* and Tp^* systems is an important step toward a more robust understanding of bond activation in general.

It is known that the coordinatively unsaturated $\text{Cp}^*\text{M}(\text{CO})$ monocarbonyl tran-

⁶Note that this figure is not inconsistent with the 60% reaction yield cited above for static measurements. Quantum yield refers to the fraction or percentage of molecules which, for a given *single* excitation, go on to form the indicated product. Reaction yield, of course, refers to the overall fraction or percentage of the indicated product which is produced as a result of *all* excitations, relative to the quantity which would result from unit conversion of the starting materials.

sient is extremely reactive in alkane solvents at room temperature. This suggests that the low quantum yield of C-H bond activation in this system arises from the presence of a non-dissociative pathway through which the excited $\text{Cp}^*\text{M}(\text{CO})_2$ may decay to the ground state without the loss of a carbonyl ligand. Ultrafast visible absorption experiments on $\text{Cp}^*\text{Ir}(\text{CO})_2$ and $\text{Cp}^*\text{Rh}(\text{CO})_2$ at ~ 1 mM in neat room temperature cyclohexane and *n*-pentane revealed a broad transient absorption throughout the visible between 440 and 740 nm following UV excitation at 295 nm by a 1 ps 10 μJ laser pulse [23]. At all wavelengths studied, the transient absorption was observed to form on an instrument-limited timescale (≤ 1.5 ps) and to decay in a biexponential manner according to the equation:

$$A = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2) \quad (1.4)$$

where A represents the magnitude of the transient absorption. For all wavelengths studied, it was found that the fast decay component was best fit to $\tau_1 \approx 3\text{-}5$ ps and that the slow component τ_2 was reasonably constant at between 25 and 40 ps. The variations in τ_1 and τ_2 fell within the uncertainty of the measurements and no trend in either τ_1 or τ_2 was observed with varying probe wavelength. It was observed, however, that the pre-exponential term C_1 of the fast decay increased from 0.61 to 0.77 with increasing wavelength in $\text{Cp}^*\text{Ir}(\text{CO})_2$ and from 0.60 to 0.84 in $\text{Cp}^*\text{Rh}(\text{CO})_2$. The transient absorptions were observed to decay essentially to the baseline within

several hundred picoseconds following excitation, in accordance with the reported 1% quantum yield.

It is impossible, of course, to rule out *a priori* a CO-dissociative decay mechanism, despite its implausibility. If the observed intermediate were a monocarbonyl, however, it would have three decay channels available: (a) geminate recombination with the dissociated CO ligand, (b) non-geminate (diffusional) recombination, and (c) reaction with the solvent. Geminate recombination has been shown to occur on the sub-picosecond time scale [24, 25], while diffusional recombination at millimolar concentrations occurs on the microsecond time scale. Neither of these processes match the observed kinetics. Channel (c), which would result in C-H activation, was eliminated on the basis of comparison to data obtained by Dougherty *et al.* which showed no observable evidence of C-H activated products following photoexcitation of $\text{Cp}^*\text{M}(\text{CO})_2$ ($\text{M} = \text{Ir}, \text{Rh}$) at 289 nm. It was therefore concluded that nearly all excited state $\text{Cp}^*\text{M}(\text{CO})_2$ molecules return to the ground state via a non-dissociative mechanism which does not activate alkane C-H bonds. The markedly higher quantum yield of C-H bond activation of $\text{Tp}^*\text{Rh}(\text{CO})_2$ is thus presumably attributable to a relatively more accessible CO-dissociative pathway.

It was suggested that the non-dissociative pathway might involve a fast decay from the initially generated excited state to another, longer lived electronic excited state which in turn undergoes decay to the ground state with $\tau \approx 30$ ps. This possibility is supported by the observation of a moderate wavelength dependence of the relative

pre-exponential factors C_1 and C_2 . The signal to noise ratio of the experiment, however, was not sufficiently large so as to rule out the possibility of direct decay to a vibrationally excited level or levels of the ground electronic state, a mechanism which would not be expected to show wavelength dependence of the relative amplitudes.

1.3 Remaining Questions

From the studies discussed above, certain conclusions can be drawn. The most important are as follows:

1. C-H bond activation in saturated and aromatic hydrocarbons proceeds via an oxidative addition mechanism following UV photoexcitation in the presence of several transition metal-containing compounds.
2. Dissociation of a carbonyl ligand is necessary if bond activation is to take place.
3. The coordinatively unsaturated monocarbonyl species which can arise from photolysis rapidly forms a weakly bound solvent complex.
4. The nascent solvent complex then undergoes oxidative addition across the C-H bond to form the final product on a time scale significantly slower than that required for initial solvation.
5. The oxidative addition step is likely under thermal control, making it highly sensitive to reaction conditions. It may involve an $\eta^3 \rightarrow \eta^2$ dechelation of the Tp^*

ligand in $\text{Tp}^*\text{Rh}(\text{CO})_2$.

6. Absent carbonyl dissociation, photoexcited $\text{Cp}^*\text{Rh}(\text{CO})_2$ and $\text{Cp}^*\text{Ir}(\text{CO})_2$ complexes decay to the ground state within several hundred picoseconds in room temperature solutions without undergoing oxidative addition/bond activation.

Important questions remain to be answered, however. The following will be addressed in Chapters 4 and 5:

1. The validity of conclusions drawn from various non-solution phase media to the reactions as they occur in the solution phase and at room temperature.
2. The identity and structure of both early and late intermediate species.
3. Activation energies of the various steps involved in the bond activation reactions.
4. The effect of solvents on reaction rates and free energy barriers.
5. The feasibility of direct observation of metal-hydride vibrational modes.

Taken together, the answers to these questions will allow for the nearly complete elucidation of the C-H bond activation reaction involving $\text{Tp}^*\text{Rh}(\text{CO})_2$.

Chapter 2

Experimental

As one may gather from the discussion in Chapter 1, infrared absorptions by carbonyl ligands attached to the metal center of a reactive species have proven to be extraordinarily useful as probes of chemical reactivity at the metal center itself [26]. M-H, M-R, and R-H infrared absorptions are relatively weak by comparison and the analysis thereof is often complicated by the sheer multitude of absorptions which occur at similar frequencies. Carbonyl absorptions, by contrast, tend to occur as discreet, well-separated peaks in the IR spectrum, making them easier to identify and assign to particular reactive species. Discrete absorptions also assist in kinetic analyses by eliminating the need for computational deconvolution of overlapping spectral features. For these reasons, the present work was conducted using time resolved IR spectroscopy almost exclusively.

2.1 Femtosecond Infrared Spectrophotometer

The femtosecond IR spectrophotometer [27] used in the present work is shown in Figure 2.1 on the following page. Technical specifications are summarized in Table A.1 of Appendix A (page 68). A Ti:Sapphire oscillator is pumped using the unfiltered output of a continuous wave (CW) Coherent Innova 310 Ar⁺ laser operating at 5.0 W. The oscillator itself is of the standard Z-shaped cavity type, constructed according to the plans of Murnane *et al.* [28, 29]. The output of the oscillator is amplified using a two-stage LDS 798 dye amplifier pumped by a 30 Hz Quanta-Ray Nd:YAG laser and is then compressed through a prism pair to produce 50 fs pulses at 820 nm with pulse energies of 10 μ J. This amplified beam is then split into three parts, each of which is amplified separately using dye amplifiers pumped by the Quanta-Ray YAG. The first of the newly-split beams is simply reamplified at 820 nm to produce 20 μ J, 70 fs pulses. The other two beams are first focused onto separate sapphire windows to produce white light continua from which are selected the desired wavelengths for subsequent amplification. This configuration allows for the generation of independently tunable femtosecond pulses in the spectral region from 560 to 1000 nm. In a typical configuration, 10 nm full width at half maximum (FWHM) band pass filters are used to select pulses centered at 700 and 590 nm. The 700 nm pulses are then amplified to 100 μ J using LDS 698 dye, while the 590 nm pulses are amplified to 400 μ J using Rodamine 610.

The 590 nm pulse train is compressed to 200 fs using a pair of prisms, then sent

Figure 2.1: Schematic diagram of the femtosecond IR spectrophotometer.

across a variable-delay translation stage, and subsequently frequency-doubled in a BBO crystal of 300 μm thickness to produce UV pulses at 295 nm. These are the pump pulses. Pump power is attenuated so as to eliminate multiphoton photoionization of the neat solvent in the sample. The 700 and 820 nm beams are focused onto a 2mm LiIO_3 difference frequency crystal, generating IR pulses centered near 2000 cm^{-1} (5000 nm) of 70 fs FWHM duration. Assuming a Gaussian pulse shape, the time-energy uncertainty product yields a spectral bandwidth of approximately 150 cm^{-1} .¹ IR pulses centered from 1800 to 2300 cm^{-1} can be generated without changing band-pass filters in the pre-amplification stage by adjusting the phase-matching angle of the LiIO_3 crystal. Changing filters and dyes allows for the possibility of IR probe pulses anywhere in the 3300 to 1600 cm^{-1} ($\sim$ 3000–6000 nm) range.

After the UV and IR pulses have been generated and the beams recollimated, the UV beam is reflected from a wavelength-selective mirror which passes the remaining 590 nm light to a beam block. The 295 nm UV is then focused to a diameter of 200 μm in the sample cell. The UV beam path is noncolinear to the IR beam path to prevent entry of any UV light into the monochromator or detection apparatus. The IR beam is split into two beams following its generation in the LiIO_3 crystal, using a 50% germanium beam splitter. The first beam is used as a reference and passed

¹Calculated as:

$$\Delta E = 2 \frac{\hbar}{\Delta t} = 3.01 \times 10^{-21} \text{ J} = 152 \text{ cm}^{-1} \quad (2.1)$$

directly through the monochromator to the detection apparatus. The second beam is focused to a diameter of 200 μm and overlapped with the UV beam in the sample cell. This IR beam is then recollimated and passed through the monochromator to the detection apparatus. The beams travel parallel to one another through the monochromator (CVI, Digikrom 240), but are vertically displaced by 1 cm. The size of the slits in the monochromator can be varied from 10 μm to 2 mm, but in practice is generally set to 400 μm , the minimum size found not to interfere with the 300 μm IR beams. Following the monochromator, the beams are separated and each is focused onto a separate HgCdTe liquid nitrogen cooled detector. The output from each detector is sent to a boxcar integrator and then to a digitizer for collection by a PC. The counts from the signal and reference channels are normalized so as to remove the effect of shot-to-shot fluctuations in the laser power, which typically average 20-30%. Anomalous measurements are excluded by ignoring those counts which, after normalization, deviate from the average by more than 40%. The primary source of error is the presence of dark counts from the detectors, which average 1% of the total counts for any given shot. $\sqrt{N}$ dependence in the magnitude of random error with signal averaging leads to about 0.1% noise in a reasonably large signal after averaging 100 shots (a typical number).

Two types of experiments are typically performed using this apparatus. In the first, a full IR spectrum is collected at a fixed time after photoinitiation of the reaction. To do so, the translation stage is held at a fixed position while the monochromator

is scanned over the appropriate range of wavelengths. The translation stage is then moved to another position corresponding to a different time delay relative to photoinitiation and the process is repeated. Spectra are usually collected between 1900 and 2080 cm^{-1} and at time delays of -10, 10, 66, 200, and 660 ps. The results of a typical experiment of this type are shown in Figure 3.1 on page 31. Spectral resolution is about 4 cm^{-1} . These experiments are useful in the identification of relevant spectral features and estimation of their time scales.

In experiments of the second type, the monochromator is fixed at a wavelength corresponding to a spectral feature of interest while the translation stage is scanned through an appropriate range of time delays. The stage can be moved in increments of as little as 1 μm , corresponding to a change in delay time of 6.7 fs (since the beam path is changed by twice the length of the stage step). In practice such small steps are rarely used, because the time resolution of the experiment as determined by autocorrelation of the pump and probe pulses is approximately 240 fs. These experiments provide detailed information about the rates of formation and decay of the relevant spectral features. Lastly, the instrument response function has been measured by substituting for the sample cell a thin silicon wafer, which provides a very large and very short rise in IR absorption following photoexcitation at 295 nm. The rise time of this absorption is limited by the instrument response function. It corresponds closely to a Gaussian function with 240 fs FWHM.

2.2 Step-Scan FTIR Spectrophotometer

The nano- to millisecond step-scan FTIR spectrophotometer [30] used in the present work is shown in Figure 2.2 on the facing page. The system is in many respects similar to a conventional Fourier-transform IR spectrophotometer. Where a conventional system contains an interferometer mirror which moves smoothly through its range of motion, however, the step-scan mirror moves sequentially through a series of fixed mirror positions. The IR signal as a function of time following photoinitiation is recorded at each mirror position so that after a complete run, a set of several hundred time slices, each consisting of intensity *vs.* time data, are obtained. The data are then rearranged such that intensity *vs.* mirror position is represented at a range of fixed time delays. The data in this form represent a series of time-dependent interferograms, each of which is similar to a conventional FTIR interferogram. Each interferogram is then Fourier transformed into a wavelength-dependent spectrum at a given time delay after photoinitiation. The process as a whole is depicted in Figure 2.3 on page 26.

Among the challenges of this type of spectroscopy is the miniscule size of the changes to the interferogram stack due to the transients of interest, relative to the overall size of the static interferogram. If transient and static dc-coupled interferograms are compared to one another, it is impossible to detect such small changes because the entire dynamic range of the digitizer is used in representing the largest features of the interferograms. If, however, the ac-coupled output of the detector is

Figure 2.2: Schematic diagram of the time-resolved step-scan FTIR spectrophotometer.

Figure 2.3: Functional processes of the step-scan FTIR spectrophotometer. Interferograms are extracted from the time slices, then Fourier-transformed to give time-resolved spectra.

used, then only the *difference* between the static and transient signals is observed. This difference signal, reflecting only the small laser-induced change in intensity, can then be amplified so as to utilize the entire ± 1 V dynamic range of the digitizer. The InSb detector used in the present work is capable of producing both dc- and ac-coupled signals simultaneously. In early experiments, a dc-coupled interferogram stack was collected in the absence of laser excitation and subsequently used for phase correction of the ac-coupled spectrum collected immediately thereafter. In later experiments, a software upgrade enabled the simultaneous collection of ac- and dc-coupled data, thereby eliminating the need for a separate dc-coupled run.

The instrument itself consists of a Bruker IFS88 FTIR spectrophotometer with a 40 MHz 12 bit digitizer, coupled to auxiliary electronics (CAL-AV Laboratories

7930 500 MHz and LeCroy 6103 150 MHz amplifiers; LeCroy 9360 600 MHz digital oscilloscope) for signal modulation and a PC for data acquisition. Either the third or the fourth harmonic (355 and 266 nm, respectively) of a Quanta-Ray DCR-2A Nd:YAG laser operating at 10 Hz is used as the excitation source. Typical pulse energies average 4-5 mJ. Beam diameter at the sample is ~ 1 cm. A specular reflection from a quartz plate in the UV beam path is diverted to a photodiode which in turn is used to trigger the digitizer. Beyond the use of the step-scan technique and the laser excitation source, the apparatus can be understood as a conventional FTIR spectrophotometer. It features interchangeable detectors, of which a Kolmar InSb model with 42 ns resolution was predominately employed. Resolution was determined by measuring the FWHM output signal of the detector upon illumination by a 9 ns FWHM 1064 nm laser pulse. A 1.5 mm thick germanium plate was used to exclude scattered laser light from the detector and from interferometer optics. The instrument was isolated from environmental vibrations using a Newport RS4000 air-suspended laser table. Stability of the mirror position was measured to be ± 1.4 nm. Samples were circulated continuously to prevent interference from photoproduct build-up using a gravity feed drip pumped by an isolated peristaltic pump.

2.3 Sample Preparation and Experimental Details

$\text{Tp}^*\text{Rh}(\text{CO})_2$ was used exclusively as the bond activating reagent in the present studies. It was prepared by Dr. Bruce McNamara and Mr. Jake Yeston in the

laboratory of Professor R. G. Bergman according to the standard published method [31,32] and characterized fully using conventional methods. Samples were prepared in a drybox and remained sealed throughout the course of all experiments. Care was taken to minimize exposure of any prepared $\text{Tp}^*\text{Rh}(\text{CO})_2$ solution to environmental light. Solutions were prepared to ~ 1 mM and adjusted to an optical density (OD) between 0.6 and 1.0 at the pump wavelength. Similar UV/Vis spectra were observed in all solvents used in this work. Samples were sparged with dry N_2 and/or Ar gases prior to use. Spectral grade solvents were purchased from Aldrich Chemical and dried over molecular sieves and degassed prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

In both the femtosecond and nanosecond experiments, samples were circulated continuously through a Harrick infrared sample cell with CaF_2 windows using a MasterFlex peristaltic pump. A broad wavelength-independent transient signal arising from the CaF_2 windows was subtracted from the femtosecond data. The Viton tubing used in these experiments was found to be completely unreactive in the presence of all relevant solvents. Static UV/Vis and FTIR measurements were collected during the course of each experiment to monitor sample decomposition. Representative static UV/Vis and FTIR spectra are shown in Figure 2.4 on the facing page. The temperature of the sample solutions was not controlled, but the sample volume was large enough to easily dissipate any heat accumulated from laser irradiation. All experiments were conducted at room temperature and ambient pressure.

(a) UV/Vis Spectrum

(b) FTIR Spectrum

Figure 2.4: Static UV/Visible and FTIR absorption spectra of ~ 1 mM $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane.

Chapter 3

Results

3.1 Ultrafast Regime

3.1.1 Spectra

Figure 3.1 on the next page shows the time-evolution of transient difference infrared spectra of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane. Note that here and throughout, the ordinal axis runs from lower to higher energy, the opposite of some conventions in static IR spectroscopy. The last panel shows the static difference spectrum of the same solution recorded after photolysis at 308 nm. This represents the final reaction products. Transient difference spectra are obtained by subtracting a transient IR spectrum collected at a fixed time relative to photolysis from a transient IR spectrum collected prior to photolysis. Thus depletions of any absorbing species which is initially present in the sample manifest themselves as negative peaks in the difference

Figure 3.1: Ultrafast time-resolved spectra of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane. A static FTIR difference spectrum is included in the last panel for reference.

spectrum (bleaches), while newly formed absorbing species are present as positive peaks. A negative time delay indicates that the probe pulse arrives at the sample prior to the pump pulse; since no photolysis has taken place, difference spectra collected at negative times should always show zero change in absorbance ΔA at all wavelengths. In the static difference spectrum shown in the last panel of Figure 3.1, three peaks are observed. The bleaches at 1981 and 2054 cm^{-1} correspond to the parent dicarbonyl peaks shown in Figure 2.4(b) on page 29. The lone positive peak at 2032 cm^{-1} has been observed in other studies [33–36] and identified unambiguously as the final monocarbonyl alkyl hydride product, $\text{Tp}^*\text{Rh}(\text{CO})(\text{c-C}_6\text{H}_{11})(\text{H})$.

Several salient features are evident in the transient spectra. At the earliest time delay after photolysis, strong bleaches are observed at 1981 and 2054 cm^{-1} . The bleaches are subsequently observed to recover more than half of their intensity, an amount in rough agreement with the previously noted 30% quantum yield and quantified below. There is also observed a series of peaks at 1945, 1958, and 1972 cm^{-1} , of which only the 1972 cm^{-1} peak (labeled **A1**) persists beyond 10 ps. It is most likely that the two peaks at lower energy arise from vibrationally excited states of the carbonyl stretching mode of the intermediate species, while the 1972 cm^{-1} peak arises from the ground vibrational state. Such vibrationally excited states have been observed to form quickly and to relax to the ground vibrational state with time constants of 20–30 ps in other transition metal carbonyls [27, 37, 38]. In the 200 ps spectrum, peak **A1** begins to decay and a new peak **A2** is observed at 1990 cm^{-1} .

By 660 ps, **A1** has decayed almost completely, leaving **A2** as the lone well-resolved positive spectral feature. There is no evidence of the peak at 2032 cm^{-1} attributed to the activated product. Also noteworthy is the absence of a peak at 1990 cm^{-1} in the static FTIR spectrum. There clearly exist important dynamic processes which occur on a time scale too slow to be resolved using our ultrafast apparatus. Observations of these processes are detailed in Section 3.2. Qualitatively identical results with somewhat lower signal-to-noise were obtained using neat *n*-pentane as the solvent.

Figure 3.2 on the next page shows the time-evolution of transient difference infrared spectra of the 16-electron species $\text{Bp}^*\text{Rh}(\text{CO})_2$ ($\text{Bp}^* = \text{H}_2\text{BPz}_2^*$) in cyclohexane. Recall that this molecule is similar to $\text{Tp}^*\text{Rh}(\text{CO})_2$, but possesses only two pyrazolyl groups on the ligand, thereby limiting the ground state chelation number to two. The positions of the bleaches are shifted relative to those of $\text{Tp}^*\text{Rh}(\text{CO})_2$, but the relative peak positions are quite similar. Of note is the presence of a single positive peak at 1992 cm^{-1} which does not appear to decay on the time scale shown. In fact no decay is observed through $1\text{ }\mu\text{s}$, as shown in Figure 3.3 on page 35. Note that this peak is not identical to the 1990 cm^{-1} feature observed above, but is instead analogous to the 1972 cm^{-1} peak in $\text{Tp}^*\text{Rh}(\text{CO})_2$. There is not, however, any evidence of an alkyl hydride product peak corresponding to that observed at 1990 cm^{-1} (i.e., shifted to higher energy relative to the parent bleach) in $\text{Tp}^*\text{Rh}(\text{CO})_2$. The implications of this observation will be discussed in Chapter 4.

Figure 3.2: Time-resolved spectra of $\text{Bp}^*\text{Rh}(\text{CO})_2$ in cyclohexane.

Figure 3.3: Transient spectrum of $\text{Bp}^*\text{Rh}(\text{CO})_2$ in cyclohexane $1\ \mu\text{s}$ after photolysis. The $1992\ \text{cm}^{-1}$ feature is not observed in static spectra.

3.1.2 Kinetics

Figure 3.4 on the next page shows the kinetic evolution of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in *n*-pentane over the first 800 ps following photoinitiation at several relevant wavelengths. At $1972\ \text{cm}^{-1}$ (Figure 3.4(a)), there is observed a rapid growth ($\tau = 23\ \text{ps}$) followed by a 200 ps decay. The 23 ps growth corresponds to the vibrational cooling time of the excited states of the transient molecule, observed at 1945 and $1958\ \text{cm}^{-1}$. The decay of this peak is kinetically correlated with an identical 200 ps rise at $1990\ \text{cm}^{-1}$ (Figure 3.4(b)). No decay of the $1990\ \text{cm}^{-1}$ peak is observed on the sub-nanosecond time scale. Identical results within experimental uncertainty were observed in cyclohexane, but with somewhat lower signal-to-noise.

The parent bleach at $2054\ \text{cm}^{-1}$ (Figure 3.4(c)) grows in with an instrument-limited rise time and is observed to recover 50% of the initial depletion with a time

Figure 3.4: Ultrafast kinetics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in *n*-pentane at (a) 1972 cm^{-1} . *Inset*: Schematic diagram of vibrational relaxation in the initially formed transient species. (b) 1990 cm^{-1} , and (c) 2054 cm^{-1} . Time constants indicated are for exponential fits to the data.

constant of 70 ps. The fact that the bleach does not recover to 70% of the initial value (corresponding to 30% quantum yield) is indicative of ultrafast geminate recombination of dissociated CO with the nascent monocarbonyl species to reform the ground state parent dicarbonyl on a time scale less than 1 ps. In this case, the initial magnitude of the bleach does not reflect the total number of dissociative events, since some ground state molecules are regenerated through recombination prior to IR probing. The 70 ps time constant does not correspond to the time scale on which geminate recombination occurs (on the order of hundreds of femtoseconds), but is instead indicative of the rate of decay to the ground state via non-dissociative channels.

3.2 Nanosecond to Millisecond Regime

Figure 3.5 on the following page shows the nanosecond time evolution of the transient difference infrared spectrum of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane. Four features are readily apparent: two parent bleaches at 1981 and 2054 cm^{-1} and two new peaks, one at 1990 cm^{-1} (labeled **A2**), another at 2032 cm^{-1} (labeled **A4**). Kinetic traces of these two peaks are shown in Figure 3.6 on page 39. **A2** is observed to form at an instrument-limited rate ($\tau \ll 50$ ns) and to subsequently decay with a time constant of 280 ns. The final product **A4** forms with a single exponential time constant of 230 ns. It is likely that **A2** and **A4** are kinetically coupled despite the observed discrepancy in their respective time constants of formation and depletion. The kinetics of peaks which occur close to strong bleaches can be obscured by time dependent changes

in the refractive index of the solvent which arise from variations in temperature following absorption of laser pulses [39]. In the present case, A2 lies within 9 cm^{-1} of the parent bleach at 1981 cm^{-1} , while A4 is separated from the parent bleach at 2054 cm^{-1} by 22 cm^{-1} .

Figure 3.5: Nanosecond time-resolved spectrum of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane.

Similar nanosecond spectral and kinetic studies were performed on $\text{Tp}^*\text{Rh}(\text{CO})_2$ in other cyclic and linear alkanes. The nanosecond time resolved spectral evolution of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclopentane, which is quite similar to that observed in cyclohexane, is shown in Figure 3.7 on page 40. As noted above, there were observed no substantive differences in the behavior of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane *vs.* *n*-pentane solvent in

Figure 3.6: Nanosecond kinetics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane at 1990 and 2032 cm^{-1} . Time constants indicated are for exponential fits to the data.

the femto- to picosecond regime. As indicated in Figures 3.8 and 3.9, however, bond activation was observed to be complete in the linear alkane solvents *n*-pentane and *n*-hexane within 100 ns after photolysis, a time scale which is nearly instrument limited. This is substantially faster than the 230 ns time constant (corresponding to ~ 700 ns complete reaction time) for formation of the final product in cyclohexane. Thus it appears that the rate limiting step of the reaction occurs substantially more quickly in linear than in cyclic alkanes. Possible explanations for this behavior will be discussed in Chapter 4.

3.3 Non-Carbonyl Features

As discussed in Chapter 1 and evinced by the data shown above, spectral features arising from carbonyl stretching modes are valuable probes of chemical reactivity.

Figure 3.7: Nanosecond time-resolved spectrum of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclopentane.

Figure 3.8: Early nanosecond time-resolved spectra of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in linear alkanes. Note that the intermediate species at 1990 cm^{-1} has disappeared and that the product peak at 2032 cm^{-1} has grown in completely by the 100 ns time slice.

Figure 3.9: Nanosecond kinetics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in *n*-pentane and cyclopentane.

It is sometimes desirable, however, to make direct measurements of an intermediate or product feature. To this end, experiments were undertaken with the aim of first observing, and then measuring the kinetics of, the Rh-H stretch in the final product. Figure 3.10 on page 43 shows two FTIR spectra of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane. The first of these spectra was collected 100 ms after photolysis using the rapid scanning FTIR mode of the Bruker IFS88. This mode is identical to conventional FTIR spectroscopy, but optimized for minimal scan time. Several spectra are collected in immediate succession, allowing time resolution in the millisecond regime. The second spectrum is a static FTIR spectrum collected several seconds after photolysis. Of note is the peak at 2080 cm^{-1} , which has not been previously observed in either fast transient studies or in static experiments. The absence of previous observations is addressed below and in Chapter 4. The position of this peak, along with its relatively small size, suggest that it may correspond to the Rh-H stretching mode of the

activated product. The location of the new peak is in reasonable agreement with the previous observation at $\sim 2140\text{ cm}^{-1}$ of a peak attributed to the Ir-H stretch in $\text{CpIr(CO)(H)(C}_6\text{H}_{11})$ [5,40]. If this assignment is correct, the 2080 cm^{-1} peak ought to form on a time scale identical to that of the final alkyl hydride product carbonyl stretch at 2032 cm^{-1} . This behavior was confirmed in both linear and cyclic alkanes, as shown in Figure 3.11 on page 44.

To more fully establish this newly observed peak as that of the Rh-H stretch, isotopic substitution studies were undertaken. Based solely on a calculation of the reduced mass of the $\text{D-Rh(Tp}^*)(\text{CO})(\text{R})$ oscillator relative to the $\text{H-Rh(Tp}^*)(\text{CO})(\text{R})$, it is expected that the Rh-D stretch ought to appear at $\frac{1}{\sqrt{2}} \times 2080 \approx 1470\text{ cm}^{-1}$. To test this hypothesis, nanosecond time resolved spectra and kinetics traces of $\text{Tp}^*\text{Rh(CO)}_2$ in perdeuterocyclohexane and perdeuterobenzene were collected.

The millisecond transient FTIR spectrum of $\text{Tp}^*\text{Rh(CO)}_2$ in perdeuterobenzene is shown in Figure 3.12 on page 45. Perdeuterobenzene must be used in place of perdeuterocyclohexane when measuring IR absorptions in certain sectors of the carbonyl stretch region due to strong interfering absorptions from the C-D stretches in perdeuterocyclohexane. Notable is the absence of any peak at or near 2080 cm^{-1} . This observation is in agreement with the prediction that the Rh-D stretch be shifted to substantially lower frequency. Lastly, nanosecond time resolved spectra of $\text{Tp}^*\text{Rh(CO)}_2$ in perdeuterocyclohexane were collected in the spectral region surrounding the expected Rh-D stretching mode ($1350\text{--}1650\text{ cm}^{-1}$). As shown in Fig-

Figure 3.10: Millisecond and static FTIR spectra of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane. Note the peak at 2080 cm^{-1} which is present in the 100 ms spectrum.

Figure 3.11: $\text{Tp}^*\text{Rh}(\text{CO})_2$ nanosecond kinetics at 2032 and 2080 cm^{-1} in (a) cyclopentane and (b) *n*-pentane.

ure 3.14 on page 46, this region of the spectrum is quite complex relative to the carbonyl region. It is possible, however, to isolate certain features and to measure the kinetics thereof. Best fits to the kinetic data obtained in this experiment are shown in Table 3.1 on the next page.

The signal to noise ratio obtained in these experiments is necessarily lower than that which is possible for carbonyl features; on calculating the integrated absorption intensity, it was found that the absorption cross section of the Rh-H stretch in activated cyclohexane was $\sim 2\%$ that of the carbonyl stretch. The failure of other studies to observe these features is likely attributable to the unprecedentedly large signal to noise ratio achieved in the work presented here.

Figure 3.12: Millisecond transient FTIR spectrum of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in perdeuterobenzene. Note the absence of any peak at 2080 cm^{-1} .

Figure 3.13: Nanosecond kinetic traces of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in perdeuterobenzene. Time constants are for exponential fits to the data.

$\bar{\nu}$ (cm^{-1})	τ (ns)	$\pm$ (ns)
2032 ^a	230	3
2032	510	20
1483	300	100
1540	380	100
1551	490	100

^aIn cyclohexane; see Figure 3.6 on page 39

Table 3.1: Time constants for growth and decay of some Rh-H and Rh-D related features of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in perdeuterocyclohexane.

Figure 3.14: Rh-D stretch region nanosecond time resolved spectra and kinetic traces of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in perdeuterocyclohexane.

Chapter 4

Discussion

4.1 The Mechanism of C–H Bond Activation

4.1.1 Photolysis and Vibrational Cooling

As discussed in Chapter 1, the reactive intermediate formed immediately following UV photolysis is a monocarbonyl. This species is formed in a vibrationally excited state as evinced by the presence of several small peaks near the primary transient absorption **A1** at 1972 cm^{-1} (Figure 3.1 on page 31). These ancillary peaks, often referred to as “hot bands,” are assigned to the $v = 1 \rightarrow 2$, $2 \rightarrow 3$, ... transitions in the ground vibrational state of the transient species. The spacing of the peaks, $\sim 13\text{ cm}^{-1}$, is consistent with the anharmonicity observed in other transition metal carbonyls [41–43]. The shift arises from the anharmonicity of the vibrational potential energy surface; if the vibrational modes in question behaved as perfect harmonic

oscillators, each of the vibrational transitions in question would lie at a frequency identical to the other vibrational transitions within the same electronic state.

The first two vibrational transitions in question are represented schematically in the inset of Figure 3.4(a) on page 36. The absorption at 1972 cm^{-1} arises from the $v = 0 \rightarrow 1$ transition. As expected, this is the most energetic vibrational transition available to the molecule under the experimental conditions. As the higher vibrational energy levels become more closely spaced, the photon energy required to promote a molecule to the next highest energy level is reduced. This explains both the shifted positions of the peaks relative to one another and their spectral evolution through time. Recall that the 1972 cm^{-1} peak was observed to form with a time constant $\tau = 23\text{ ps}$. If, as is argued here, the hot bands represent absorptions attributable to population of vibrationally excited states, the absorption arising from population in the ground vibrational state ought to grow on a time scale appropriate to vibrational cooling in transition metal carbonyls. This is indeed the case; previous studies conducted in the Harris group [16, 24, 27, 38] and by others [37, 42, 44] have shown vibrational relaxation to occur on similar time scales.

Lastly, the shift from the parent absorption at 1981 cm^{-1} to the transient at 1972 cm^{-1} is characteristic of a species containing an electron-rich metal center. The loss of an electron-withdrawing carbonyl ligand from the parent molecule increases the electron density at the rhodium center. This in turn results in increased back bonding between the occupied d_π orbital of the Rh atom and the unoccupied antibonding

Figure 4.1: Schematic diagram of $d_{\pi} \rightarrow \pi^*$ back bonding in transition metal carbonyls. Shaded orbitals are occupied; +/- signs designate symmetry. (Adapted from [45])

π^* molecular orbital of the remaining carbonyl ligand, as illustrated in Figure 4.1 [45, pp. 13–17]. As the antibonding character of the carbonyl is increased, the oscillator strength of the $C \equiv O$ bond is decreased, thereby decreasing the vibrational frequency and shifting the position of the IR absorption to lower energy. This supports our assignment of the 1972 cm^{-1} peak to a monocarbonyl species and explains the observation of this peak slightly red-shifted relative to the parent bleach.¹

It has been shown that carbonyl loss is complete within less than 100 fs after photoexcitation [49, 50]. The vibrationally hot monocarbonyl which is formed is a co-ordinatively unsaturated 16 electron species with the central Rh atom in formal oxidation state I. It complexes a solvent molecule in a barrierless reaction which ought to occur on a time scale similar to that of geminate recombination, i.e. determined by the time scale of molecular motion within the solvent cage. Solvation is therefore

¹For detailed discussion of the molecular orbital interactions in transition metal carbonyl systems and their interaction with alkane species, see [46–48].

expected to be complete in less than 1 ps, in agreement with the data presented here. On the basis of the above evidence, it is concluded that the initial event in the C-H bond activation process by $\text{Tp}^*\text{Rh}(\text{CO})_2$ following CO loss is the formation of a vibrationally excited monocarbonyl-solvent species which relaxes rapidly ($\tau = 23$ ps) to its ground state. All processes which occur subsequently are purely thermal, that is to say they do not depend on the influx of additional photons and proceed independently of the fact that the intermediate absorbing at 1972 cm^{-1} was produced via photolysis.

4.1.2 Pyrazolyl Dechelation

As shown in Figure 3.4 on page 36, the transient species **A1** decays with a time constant $\tau = 200$ ps, following vibrational cooling to the ground state. There is also observed the concomitant formation of a new peak at 1990 cm^{-1} , labeled **A2** in Figure 3.1 on page 31. The species which gives rise to this new peak has not been specifically addressed in previous studies. The $\sim 20\text{ cm}^{-1}$ shift in the observed peak position relative to **A1** suggests that electron density at the Rh atom has once again been altered, in this case to a density lower than that of either **A1** or the parent bleach at 1981 cm^{-1} . In the absence of a second carbonyl stretching mode absorption or any trace of the product absorption at 2032 cm^{-1} , it is reasonable to exclude both an altered state of the parent dicarbonyl and the activated product from consideration as possible identities of **A2**.

Purwoko and Lees have shown that in the dicarbonyl ground state, there exists an equilibrium between the fully chelated η^3 -Tp*Rh(CO)₂ and the η^2 form in which one arm of the Tp* ligand is dechelated [34]. Although the equilibrium constant $K_{eq} = 100$ favors the η^3 form, the interconversion of the two forms clearly does not face an insurmountable energetic barrier at room temperature. A related system studied by Wick and Goldberg, η^2 -Tp*Pt(Me)₂, was shown to activate C-H bonds, forming η^3 -Tp*Pt(Me)(R)(H) following initial reaction with B(C₆F₅)₃ [51]. Wick proposed that B(C₆F₅)₃ abstracts a methyl group from the parent molecule to give the coordinatively unsaturated intermediate species η^2 -Tp*Pt(Me), which then undergoes C-H activation via a mechanism in which the third pyrazolyl arm of the Tp* ligand is chelated, forming the coordinatively saturated product. These studies suggest a plausible identification of A2: an η^2 -Tp*Rh(CO)·RH complex, illustrated in Figure 4.2.

Figure 4.2: Structure of the intermediate species A2, η^2 -Tp*Rh(CO)·RH.

Although such a species is highly unsaturated and might therefore be predicted

to be highly unstable, Zaric and Hall have performed *ab initio* density functional calculations which show that in the gas phase, $\text{Tp}^*\text{Rh}(\text{CO})(\text{Me})$ is ~ 9 kcal/mol more stable in the η^2 form than in the η^3 form [52]. These calculations also indicated that the CO stretching frequency of the η^2 form is expected to be higher than that of the η^3 form. The exact mechanism by which dechelation occurs is open to question, but is most likely explained by the strong overlap of the Rh d_π with the unpopulated σ^* antibonding orbital of each of the metal-ligand Rh-N bonds. Recalling that the loss of the first CO ligand increases the electron density in the d_π orbital of the Rh atom, dechelation is facilitated by electron transfer to the aforementioned σ^* antibonding orbital. Dechelation in turn decreases the electron density at the metal center by eliminating ligand-to-metal electron donation from the pyrazolyl ring. It is this decrease in electron density at the metal center which explains the observed shift of the monocarbonyl absorption peak to higher frequency.

Additional support for this mechanistic step is provided by observation of the behavior of $\eta^2\text{-Bp}^*\text{Rh}(\text{CO})_2$ in alkane solvents. Having only two pyrazolyl rings, this molecule is incapable of forming an η^3 complex. It is therefore expected that upon UV photolysis in alkane solvent, a complex analogous to **A1** would be formed, but that the reaction ought not to proceed any further. An $\eta^2 \rightarrow \eta^1$ transition is very unlikely because of the unfavorable energetics inherent in the resultant 12 electron metal center. As shown in Figures 3.2 on page 34 and 3.3 on page 35 and discussed on pages 33 *ff.*, $\text{Bp}^*\text{Rh}(\text{CO})_2$ does in fact exhibit a long-lived transient absorption at

1992 cm^{-1} which is directly analogous to the **A1** feature at 1972 cm^{-1} in $\text{Tp}^*\text{Rh}(\text{CO})_2$. Moreover, no blue-shifted peak is observed and no activated product is formed.² On the strength of this evidence, species **A2** is identified as $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})\cdot\text{RH}$, having the structure shown previously in Figure 4.2. The lack of an activated product in this system suggests that rechelation may actually be required to stabilize the final activated product.

4.1.3 Alkane C–H Bond Cleavage and Pyrazolyl Rechelation

The dechelated intermediate appears to decay concomitantly with the formation of the final product on a time scale roughly three orders of magnitude slower than the formation of the intermediate. Time constants of $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})\cdot\text{RH}$ decay and product formation are 280 and 230 ns, respectively. The latter value is believed to be the more accurate of the two; the origin of the discrepancy in these rates was discussed in Section 3.2. There exist two steps which must yet occur subsequent to the formation of the intermediate dechelated monocarbonyl-solvent complex **A2**. These are actual oxidative addition across the R–H bond of the solvent alkane, and rechelation of the detached pyrazolyl group. It is reasonable to assume that of these two steps, bond cleavage is that which limits the rate of formation of the product. $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})\cdot\text{RH}$ (**A2**) is a moderately stable co-ordinatively unsaturated 14 electron species. Bond

²The 1992 cm^{-1} peak in $\text{Bp}^*\text{Rh}(\text{CO})_2$ does decay to an unknown product or products on a time scale $\gg 1$ ms. Likely decay mechanisms include recombination with free CO and dimerization of the observed intermediate species.

cleavage produces the highly unstable $\eta^2\text{-Tp}^*\text{Rh}(\text{CO})(\text{R})(\text{H})$ (**A3**), in which the Rh atom is in oxidation state III. The increase in the oxidation state reduces electron density at the Rh atom, which in turn facilitates rapid rechelation of the detached pyrazolyl arm to form the stable 18 electron final product, $\eta^3\text{-Tp}^*\text{Rh}(\text{CO})(\text{R})(\text{H})$ (**A4**).

4.1.4 Activation Energies

It is possible to calculate energy barriers for each of the mechanistic steps following vibrational cooling of the first monocarbonyl intermediate (**A1**) using simple transition state theory. The relevant equation is:

$$k \approx \frac{1}{\tau} = \frac{k_b T}{h} \exp \left(- \frac{\Delta G^\ddagger}{RT} \right) \quad (4.1)$$

where k is the rate constant, k_b is Boltzmann's constant, h is Planck's constant, R is the universal gas constant, T is the temperature, and $\Delta G^\ddagger$ is the transition state energy. The application of this equation to the rates of reaction derived from the time constants measured in the present work yields $\Delta G_{\text{A1} \rightarrow \text{A2}}^\ddagger = 4.2$ kcal/mol (using $\tau = 200$ ps) and $\Delta G_{\text{A2} \rightarrow \text{A3}}^\ddagger = 8.3$ kcal/mol (using $\tau = 230$ ns). The latter value is comparable to the 7.2 kcal/mol reported by Schultz *et al.* for the free energy barrier to oxidative addition across C-H bonds of cyclohexane by $\text{Cp}^*\text{Rh}(\text{CO})_2$ in liquid Kr at 183 K, extrapolated to 298 K [53]. The fast rechelation step **A3**→**A4** cannot be

resolved with the current apparatus, but must proceed on a time scale $\ll 230$ ns, i.e. $\Delta G_{A3 \rightarrow A4}^\ddagger \ll 8.3$ kcal/mol. The entire mechanism as discussed in the preceding sections is shown, along with free energy barriers, in Figure 4.3 on the next page

4.2 Solvent Effects

As noted previously, the ultrafast dynamics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclic and linear alkanes solvents are indistinguishable, indicating that the early steps of the reaction as described above are solvent independent. In the nanosecond regime, however, this is not the case. Linear alkanes show product formation much more quickly than do cyclic alkanes (see Figure 3.9 on page 41). Time constants of product formation in *n*-pentane and *n*-hexane range from 5 to 10 ns, values which are substantially instrument limited. Cyclopentane and cyclohexane, however, form activated products with time constants of 180 and 230 ns, respectively. Nanosecond kinetics experiments in methylcyclohexane show behavior identical to that observed in linear alkanes, lending further credence to the suggestion that there exists an important difference between hydrogen atoms attached to primary carbons and those attached to secondary carbons.

It is unlikely that this difference is attributable to a substantial difference in C-H bond energies between linear and cyclic alkanes. In fact, the C-H bond of a secondary carbon is typically ~ 5 kcal/mol *weaker* than that of a primary carbon atom. Instead, this phenomenon is most likely attributable to the increased steric hindrance faced by

Figure 4.3: Proposed mechanism and energy diagram of C-H bond activation by $\text{Tp}^*\text{Rh}(\text{CO})_2$. Note that the values of ΔG shown are relative.

cyclic alkanes as they move from the loosely bound solvent configuration to the fully bound oxidative addition product $\cdots \text{H-Rh-C} \cdots$. This is a reasonable assumption in light of the large pyrazolyl substituents of the Tp^* ligand. *Ab initio* quantum calculations performed by Zaric and Hall suggest that Rh-H and Rh-C distances are shortened by $\sim 1 \text{ \AA}$ as the solvent complex is bound [52, 54]. The observed solvent dependence of the oxidative addition reaction is thus attributed to the aforementioned steric factors.

4.3 Rh-H and Rh-D Observations

As discussed in Chapter 3, direct observation of the metal hydride stretching mode is a worthwhile yet elusive goal. The long-lived transient at 2080 cm^{-1} in cyclohexane, however, may prove to be such an observation, the first in transient studies. Several factors weigh in favor of this assignment. First, our observation is in reasonable agreement with the identification by Bergman *et al.* [55], of the Ir-H stretch in $\text{CpIr(CO)(H)(C}_6\text{H}_{11})$ at 2150 cm^{-1} . The peak at 2080 cm^{-1} , moreover, is observed to form at a rate identical to that of the product at 2032 cm^{-1} , suggesting that the two are strongly kinetically linked. This is true in both *n*-pentane and cyclopentane, despite the fact that the rates of formation of the final product in these two solvents are markedly different. This is significant because it confirms that the kinetics of the species absorbing at 2080 cm^{-1} do indeed mirror those of the activation product. The 2080 cm^{-1} peak does not appear in studies involving

deuterated solvents, but features with kinetics similar to those of the 2080 cm^{-1} peak are observed in the region of the spectrum from 1450 to 1600 cm^{-1} as expected in accordance with the increased mass of deuterium.

The kinetics of the species in this region bear additional explanation. Although the comparatively low signal to noise ratio relative to features in the carbonyl region makes analysis more difficult, it is clear from Figure 3.14 on page 46 and the data presented in Table 3.1 on page 45 that spectral evolution of several features is taking place on time scales related to that of overall product formation. In perdeuterocyclohexane, growth of the product peak occurs with a time constant of 510 ps , compared to 230 ps in cyclohexane. A shift in the time scale of bond activation is expected under these conditions as a result of the kinetic isotope effect. This effect arises from the lower zero-point energy of the C-D vibrational mode relative to the C-H vibrational mode. In the case of C-H and C-D bond cleavage, the reaction coordinate is the distance along the bond axis, with a fixed separation corresponding to bond breaking. At the point of cleavage, the two atoms are well separated, yielding a low oscillator strength and therefore a minimal change in the energy of the transition state with isotopic substitution. The lower zero-point energy of the C-D stretch thus demands a larger quantity of energy to reach the transition state and results in a correspondingly slower rate of reaction at a given temperature. The kinetic isotope effect typically results in rates of reaction which are two to ten times slower in the deuterated species than in the non-deuterated species. The observed time constants

are consistent with these values.

The peak observed at 1483 in perdeuterocyclohexane grows with a time constant of 300 ± 100 ns. Recalling that the difference in reduced mass between the deuterated product $\text{Tp}^*\text{Rh}(\text{CO})(\text{C}_6\text{D}_{11})(\text{D})$ and the non-deuterated product results in a shift of the Rh-D stretch to roughly 1470 cm^{-1} from 2080 cm^{-1} for Rh-H, it is likely that this peak corresponds to the Rh-D stretching mode of the final product. The peaks observed at 1540 and 1551 cm^{-1} also show long-time ($\tau > 100$ ns) kinetic behavior similar to that of the product, but are also observed to initially grow (1540 cm^{-1} peak) and bleach (1551 cm^{-1} peak) on an instrument-limited time scale. These peaks lie outside the expected regions of Rh-D and C-D stretching modes. They are also too high in energy to be associated with bending modes of the pyrazolyl methyl groups, and too low in energy to arise from C-H stretches in those same groups. The fact that they show evidence of kinetic coupling to the product suggests that they can perhaps be attributed to ring stretching modes of the pyrazolyl ligands, which are known to occur near 1550 cm^{-1} . It is reasonable to expect that the changing hapticity of the Tp^* ligand will influence the vibrational modes of the pyrazole rings of which it is composed.

Two problems remain, however. The first is that it is not presently possible to compare these results to the kinetics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in non-deuterated alkanes in the $1450\text{--}1600\text{ cm}^{-1}$ region of the spectrum due to the presence of strongly interfering alkane absorptions. Thus it is not yet possible to rule out the possibility that the

observed kinetics in that region arise from other, as yet unidentified species. The second difficulty is the absence of the 2080 cm^{-1} peak in static spectra following photolysis. It is possible that the nascent alkyl hydride undergoes one or more reactions subsequent to its formation. This possibility is supported by the work of Ghosh and Graham [33], in which the $\text{Tp}^*\text{Rh}(\text{CO})(\text{H})(\text{R})$ product was stabilized by conversion to the chloride derivative. If this is the case, however, it seems likely that there would be observed at least a small shift in the position of the peak 2032 cm^{-1} . No such shift is observed. Studies aimed at resolving these difficulties are currently under way in the Harris group.

Chapter 5

Conclusions

Returning to the questions posed at the end of Chapter 1, it is now possible to draw several conclusions. Firm evidence exists in support of the reaction mechanism detailed in the previous chapter. For the first time, this mechanism has been observed from initiation to completion under ambient conditions in neat solvents. These investigations have spanned fifteen orders of magnitude in time and demonstrated unprecedented signal to noise ratios in the nanosecond step-scan regime. Possible future work in this area may include attempts to resolve the earliest time dynamics of carbonyl loss and initial solvation on the sub-picosecond time scale. Fruitful work also remains to be done concerning direct observation of rechelation following bond cleavage. To do so would require the *in situ* preparation of η^2 -Tp^{*}Rh(CO)(R)(H) for analysis in the femtosecond apparatus; at the moment the method by which this may be accomplished is not yet clear. There remain issues concerning the direct

observation of metal-hydride and metal-deuteride species, as discussed in Section 4.3. Lastly there exist numerous opportunities for the extension of the present work to related solvents and novel transition-metal complexes.

Concerning the validity of previous studies conducted under non-standard conditions, it is concluded that those intermediates which have been observed in prior studies have been correctly identified. The current work, however, presents the first conclusive argument in favor of the dechelation and rechelation mechanistic steps. It is hoped that this work will provide a basis for both continued exploration of the chemical dynamics of bond activation and the simultaneous development of practical techniques deriving from this knowledge.

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Appendix A

Technical Specifications

Table A.1: Technical specifications of the femtosecond IR spectrophotometer.

Component	Attribute	Value	Units
Ti:Sapph. Oscillator	Input power ¹	5.0	W
	Output power	400	mW
	Repetition rate	150	MHz
	Output frequency ²	817	nm
	Pulse width	40	fs
Nd:YAG Laser	Output power	15.0	W
	Repetition rate	30	Hz
	Pulse energy	500	mJ
	Output frequency ³	532	nm
	Pulse width	6	ns
820 nm Pulse Chain	Pulse energy	20	μ J
	Pulse width	70	fs

continued ...

¹Coherent Innova 300 CW Ar⁺ laser, all lines green.

²Peak frequency; output is uncertainty broadened by ~ 20 nm FWHM

³Frequency doubled using second harmonic generation(SHG).

Component	Attribute	Value	Units
700 nm Pulse Chain	Pulse energy	100	μJ
	Pulse width	70	fs
590 nm Pulse Chain	Pulse energy	400	μJ
	Pulse width	200	fs
IR Pulses	Pulse energy	2	μJ
	Pulse width	80	fs
UV Pulses	Pulse energy	16	μJ
	Pulse width	200	fs
<i>Overall Time Resolution</i>		240	fs