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Organometallic CO Substitution Kinetics in Liquid Xe by Fast Time-Resolved IR Spectroscopy

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Abstract: The reaction of $Cp^*Rh(CO)Xe$ ($Cp^* = C_5Me_5$) with CO was studied using time-resolved IR spectroscopy of liquid rare gas solutions. IR spectra for $Cp^*Rh(CO)Xe$ were obtained using pulsed UV laser photolysis of $Cp^*Rh(CO)_2$ in liquid Xe and a rapid-scan FTIR spectrometer with 0.09-s time resolution. Assignment to the Xe complex was confirmed from the similarity of the spectra and lifetime of the complex when a mixture of Xe in liquid Kr was used. The reaction of $Cp^*Rh(CO)Xe$ with added CO is very fast, and the rate constant was measured by fast time-resolved IR spectroscopy to be $(5.7 \pm 0.6) \times 10^5$ to $(1.9 \pm 0.2) \times 10^6$ $M^{-1}\ s^{-1}$ over the temperature range 202–242 K. The kinetics are consistent with an associative substitution mechanism with activation parameters for the bimolecular rate constant of $\log(A) = 8.8 \pm 0.3$ ($\Delta S^{\ddagger} = -20 \pm 1$ cal/(mol K)) and $E_a = 2.8 \pm 0.3$ kcal/mol ($\Delta H^{\ddagger} = 2.4 \pm 0.3$ kcal/mol).

Introduction

Rare gas atoms form surprisingly strong bonds with coordinatively unsaturated metal carbonyl complexes. Although this phenomenon was discovered some time ago,[1] it was not until recently that the bond energies were measured. From the temperature dependence of the gas-phase unimolecular decay constants of $M(CO)_5Xe$ (M = Cr, Mo, and W), the bond energies were determined to be 9.0 ± 0.9, 8.0 ± 1.0, and 8.2 ± 1.0 kcal/mol, respectively.[2] The value for $W(CO)_5Xe$ was independently determined to be 8.4 ± 0.2 kcal/mol from low-temperature kinetic studies of the reaction of $W(CO)_5Xe$ with CO using pulsed laser photolysis and rapid-scan FTIR spectroscopy of liquid Xe solutions.[3] The mechanism of this reaction is dissociative, and the observed rate constant is a function of the equilibrium constant for dissociation of Xe from $W(CO)_5Xe$. Therefore the temperature dependence of the rate constant gives the bond enthalpy directly.

Turner and co-workers have previously used CO substitution kinetics in liquid rare gases to determine the bond energy of a weak ligand.[4] In a pioneering study of the reaction of CO with $Ni(CO)_3(N_2)$ in liquid Kr using conventional lamp photolysis and IR spectroscopy, they found the existence of parallel associative and dissociative substitution pathways. Even though the kinetic analysis is complicated, they were able to extract a value for the N_2–$Ni(CO)_3$ bond energy of ~10 kcal/mol. The results for $W(CO)_5Xe$ are encouraging, and there is interest in using that approach with other rare gas organometallic complexes to determine how the bond energy varies with metal center.

The cyclopentadienyl compounds of the group IX metals ($CpM(CO)_2$ and $Cp^*M(CO)_2$ where M = Rh, Ir; $Cp = C_5H_5$; $Cp^* = C_5(CH_3)_5$) are of particular interest due to their ability to insert into the C–H bonds of alkanes.[5] The first direct rate measurement of an intermolecular C–H insertion reaction and real-time detection of the intermediate were carried out using a novel combination of techniques: fast time-resolved IR spectroscopy and low-temperature rare gas solutions.[6] Solutions of $Cp^*Rh(CO)_2$ and cyclohexane in liquid Kr were photolyzed with a pulsed UV laser, and the reaction was followed by IR absorption of a CO laser. Liquid Kr provided a low-temperature, inert medium that served to dilute the alkane concentration and slow the reaction rate to the 10^{-6}-s time regime at ~180 K. However, in liquid Xe, the reaction rate was much slower ($\tau \sim 10^{-3}$ s) even though the temperature was significantly higher (242 K). The proposed intermediate in both cases was $Cp^*Rh(CO)Q$ (Q = Kr, Xe). The much longer lifetime of $Cp^*Rh(CO)Xe$ indicated a significantly stronger bond with Xe than with Kr.

In an effort to obtain information about the energy of the bond between Xe and $Cp^*Rh(CO)$, we have measured the kinetics of the reaction of $Cp^*Rh(CO)Xe$ with CO in liquid Xe using time-resolved IR spectroscopy. A pulsed UV laser was used to photolyze $Cp^*Rh(CO)_2$ dissolved in liquid Xe, and a rapid-scan FTIR spectrometer was used to obtain IR spectra of $Cp^*Rh(CO)Xe$ on the 10^{-1}-s time scale. A single CO stretching vibration was observed at 1946 cm^{-1} for the intermediate in liquid Xe consistent with photodissociation of the parent to form $Cp^*Rh(CO)Xe$. With added CO, the reaction of $Cp^*Rh(CO)Xe$ with CO is very fast and a CO laser was used for fast time-resolved IR spectroscopy on the microsecond time scale. Unlike the case for $W(CO)_5Xe$, the CO substitution mechanism for $Cp^*Rh(CO)Xe$ is apparently associative and the very low activation energy (2.8 ± 0.3 kcal/mol) for this process gives only a lower bound to the Xe–Rh bond energy. The relevance of these results to previous ligand substitution studies and to recent C–H activation work is discussed.

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Experimental Section

The FTIR experiments were conducted at The Aerospace Corp. and are described elsewhere.[7,8] An excimer laser (Questek) was synchronized to the moving mirror of the FTIR spectrometer (Nicolet 800). The spectrometer was operated in the rapid scan mode with 8-cm^{-1} resolution and 0.09 s between spectra. Photolysis was carried out at 248 nm using a single laser pulse of ~40 mJ. The kinetics measurements were carried out at the University of California, and some of the experimental details have been described previously.[6,9,10] The liquid rare gas cells used in the kinetics and FTIR experiments are very similar, with all of the relevant dimensions being the same. The temperature precision of the Berkeley and Aerospace cells is ±1 and ±0.1 °C, respectively. The infrared detector used for the CO laser detection was a large-area (3 × 5 mm) Cu:Ge element cooled to 4 K and had a rise time of ~100 ns. The large-area detector was used in favor of a smaller area InSb detector to order to mitigate thermal lens deflections of the IR laser beam. The majority of the noise in the kinetic traces (i.e. Figure 2) is largely due to this artifact, which is a significant problem in these experiments. It is minimized through careful alignment of the photolysis and probe beams and of the probe beam on the detector surface. An excimer laser (Lambda Physik) was used for photolysis (308 nm, ~10 mJ), and typically 32 shots were averaged. An FTIR spectrometer (Perkin-Elmer) was aligned perpendicular to the CO laser beam and was used to measure the IR spectra of $Cp^*Rh(CO)_2$ and to quantify the concentration of CO. As discussed previously,[11] the absorption intensity of a molecule in dilute solution (A_{sol}) is related to the gas-phase absorption intensity (A_{gas}) by the refractive index of the solvent (n): $A_{sol} = ((n^2 + 2)/9n)A_{gas}$. For most solvents this correction is about 10–15% and is typically within the uncertainty limits of gas-phase absorption intensities. When this correction is taken into account, the integrated band strengths for several small molecules dissolved in liquid oxygen are in good agreement with the gas-phase values.[11] For liquid Xe, this correction is significant ($A_{sol} = 1.22A_{gas}$), and we use it along with the gas-phase CO band strength[12] to determine the CO concentration from the integrated CO absorption intensity. $Cp^*Rh(CO)_2$ was either synthesized according to literature procedures[13] or purchased (Strem) and used without further purification. $Cp^*Rh(CO)_2$ was transferred to the high-pressure cell by using an aliquot of a cyclohexane solution and subsequently evaporating the solvent. For the experiment using a mixture of Xe in liquid Kr, the percent of Xe in Kr refers to the amounts of gases used and is only an approximation of the true value in solution. Rare gases (research grade) were obtained from Spectra Gases, and CO (research grade) was obtained from Matheson. Data analyses were carried out using the program Igor (WaveMetrics), and all errors presented are one standard deviation.

Results and Discussion

Figure 1 shows the FTIR spectrum resulting from photolysis of $Cp^*Rh(CO)_2$ in liquid Xe at 162.0 K. The spectrum presented is the difference between spectra taken before and after photolysis. A single laser pulse was used and 20 scans were averaged. The positive band at 1940 cm^{-1} is the only new carbonyl band observed and is consistent with loss of CO from the parent to form a monocarbonyl species. There is no evidence for bridging CO bands. Figure 1 also shows the FTIR spectrum observed when $Cp^*Rh(CO)_2$ was photolyzed in a mixture of ~6% Xe in Kr under similar conditions. The carbonyl band observed at 1946 cm^{-1} is shifted slightly to a higher frequency relative to that in liquid Xe, as are the two bands for the starting material. In addition, the lifetime of this species is similar to that observed in pure liquid Xe ($\tau \sim 0.5$ s). Although the frequency observed for Cp*Rh(CO)Kr in liquid Kr (1947 cm^{-1}, see below) is similar,[14] we rule it out on the basis of lifetime. Cp*Rh(CO)Kr has a lifetime of less than 1 ms at 163 K in pure Kr. The shifts in frequency we observe for Cp*Rh(CO)Xe in liquid Kr relative to liquid Xe are very similar to those observed for $W(CO)_5Xe$.[3] In both cases, the starting material and Xe complex bands are shifted by the same amount and we attribute this to the difference in solvent. The frequencies observed for Cp*Rh(CO)Q (Q = Xe, Kr) are similar to those assigned to Cp*Rh(CO) in matrix isolation experiments.[15] In light of these observations, we assign the positive bands in Figure 1 to Cp*Rh(CO)Xe.

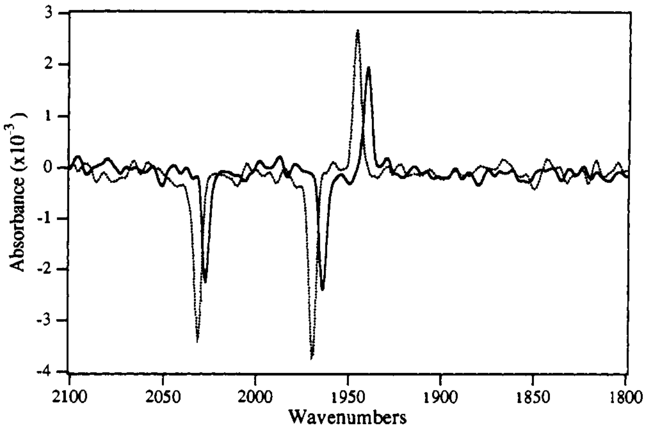

Figure 1. Rapid-scan FTIR spectra of Cp*Rh(CO)Xe in liquid Xe and Kr. Both are difference spectra resulting from photolysis of $Cp^*Rh(CO)_2$ at 248 nm at 162.0 K. The solid line is for liquid Xe solvent and the broken line is for a mixture of ~6% Xe in Kr. The negative bands (2031, 1969 cm^{-1} in Xe; 2027, 1963 cm^{-1} in Kr) are due to photolysis of $Cp^*Rh(CO)_2$ and the positive bands (1946, 1940 cm^{-1}) are assigned to Cp*Rh(CO)Xe. Each spectrum is an average of 20 laser shots.

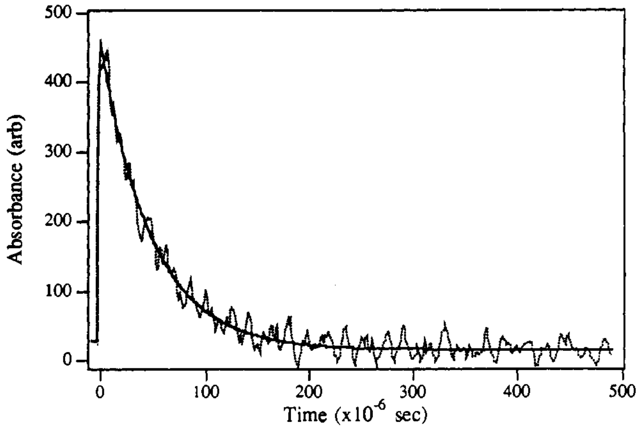

Figure 2. Kinetic trace of Cp*Rh(CO)Xe in liquid Xe. The CO concentration is 0.0124 M and the temperature is 242 K. The solid line is the best fit to an exponential decay with decay constant $k_{obs} = (2.11 \pm 0.04) \times 10^5$ s^{-1}. The trace is an average of 32 laser shots.

Using the CO laser apparatus, we have measured the kinetics of the reaction of Cp*Rh(CO)Xe with added CO. We observe a transient absorption at the CO laser line, 1943.5 cm^{-1}, as shown in Figure 2 for 242 K and a CO concentration of 0.0124 M. This frequency is somewhat higher than in the FTIR spectrum discussed above due to the higher temperature and the fact that CO laser lines are available at only ~4-cm^{-1} intervals. The decay in Figure 2 is well-fit by a simple exponential with a decay constant $k_{obs} = (2.11 \pm 0.04) \times 10^4$ s^{-1} as shown. Figure 3 shows that a plot

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[14] The frequencies observed are influenced by the solvent and temperature as well as the identity of the coordinated rare gas atom. Given the limited resolution of these spectra, the coincidence of Cp*Rh(CO)Kr and Cp*Rh(CO)Xe in liquid Kr is reasonable.

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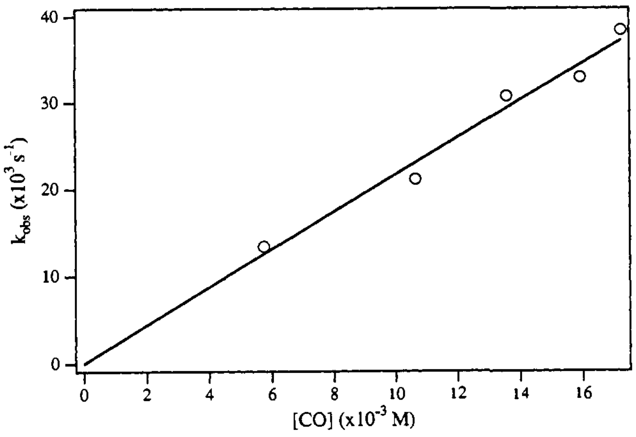


Figure 3. CO concentration dependence of k_{obs}. The temperature is 242 K and the solid line is the linear least-squares fit with slope, $k_{CO} = (2.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1}.

Table I. Rate Constants for Cp*Rh(CO)Xe + CO

temp (K)	$10^{-5}k_{CO}$ (M^{-1} s^{-1})	temp (K)	$10^{-5}k_{CO}$ (M^{-1} s^{-1})
242	18.6 ± 1.9	212	8.6 ± 0.9
232	14.3 ± 1.4	202	5.7 ± 0.6
222	10.7 ± 1.1		

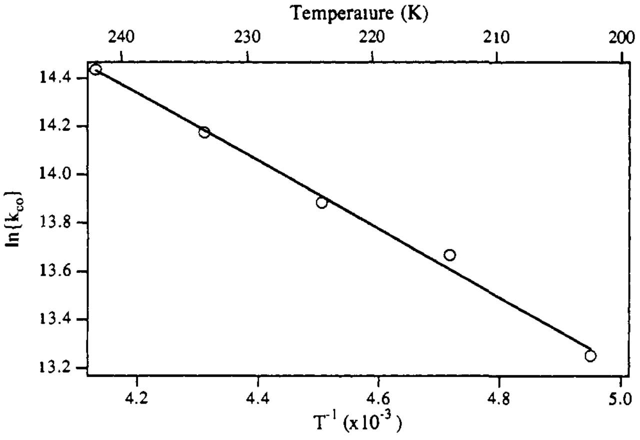
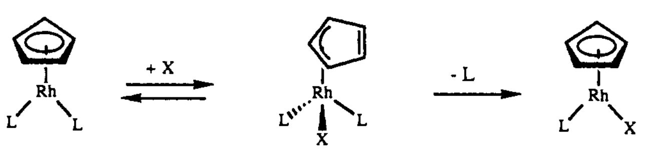


Figure 4. Arrhenius plot of ln(k_{CO}) vs T^{-1}. The derived activated parameters are log(A) = 8.8 ± 0.3 ($\Delta S^{‡} = -20 \pm 1$ cal/(mol K)) and $E_a = 2.8 \pm 0.3$ kcal/mol ($\Delta H^{‡} = 2.4 \pm 0.3$ kcal/mol).

of k_{obs} as a function of CO concentration displays good linearity ($r = 0.99$) with a slope of $k_{CO} = (2.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1} and an intercept of 180 s^{-1} that is not statistically significant. The temperature-dependent values for k_{CO} are shown in Table I. Figure 4 shows that a plot of ln(k_{CO}) versus $1/T$ from 202 to 242 K is linear ($r = 0.997$). The derived activation parameters are E_a = 2.8 ± 0.3 kcal/mol ($\Delta H^{‡}$ = 2.4 ± 0.3 kcal/mol) and log(A) = 8.8 ± 0.3 ($\Delta S^{‡} = -20 \pm 1$ cal/(mol K)).[16,17] The errors presented are the statistical results ($\pm\sigma$) propagated from the 10% error in k_{CO}.

We have also measured the rates of reaction of CO with Cp*Rh(CO)Kr similarly generated in liquid Kr. In liquid Kr over the temperature range 163–193 K, we find maximum absorption for the transient at 1947 cm^{-1}, 4 cm^{-1} higher in frequency than in liquid Xe. This is consistent with previous observations for W(CO)$_5$Q (Q = Xe, Kr).[2] Over this temperature range, we find that $k_{CO} = (1.1 \pm 0.5) \times 10^8$ M^{-1} s^{-1} with *no significant temperature dependence*.

Scheme I



In order to interpret these results, we need to identify the mechanism for the CO substitution reaction. The ligand substitution kinetics of CpRh(CO)$_2$ and related compounds have been shown to proceed by associative mechanisms.[18] This observation is one piece of evidence for the intermediacy of "ring-slipped" cyclopentadienyl species in the replacement of CO by ligands such as ^{13}CO and phosphines (Scheme I).[19]

As outlined previously,[4,20] the possibilities for the mechanism of our reaction are associative (A), dissociative (D), or interchange (I). In this case, the leaving ligand (Xe) is very weakly bound and an outer sphere intermediate with a strong ligand like CO, Cp*Rh(CO)Xe·CO, would not have a significant lifetime. Therefore the interchange mechanism seems unlikely. If the displacement of Xe by CO proceeds by an associative mechanism

$$\mathrm{Cp^*Rh(CO)Xe + CO \xrightarrow{k_a} Cp^*Rh(CO)_2 + Xe} \qquad (1)$$

the observed rate constant would be a simple function of [CO], $k_{obs} = k_a$[CO], consistent with the data in Figure 3.

Alternatively the reaction could proceed by a dissociative mechanism:

$$\mathrm{Cp^*Rh(CO)Xe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cp^*Rh(CO) + Xe} \qquad (2)$$

$$\mathrm{Cp^*Rh(CO) + CO \xrightarrow{k_2} Cp^*Rh(CO)_2} \qquad (3)$$

This pathway has been found to be operative for at least one related compound containing weakly bound ligands, CpCo(PPh$_3$)$_2$.[21] However, under the conditions of this experiment, it is not distinguishable kinetically from the associative mechanism. The expression for k_{obs} for the dissociative mechanism is:

$$k_{obs} = \frac{k_1 k_2[\mathrm{CO}]}{k_{-1}[\mathrm{Xe}] + k_2[\mathrm{CO}]} \sim \frac{K_1 k_2[\mathrm{CO}]}{[\mathrm{Xe}]} \qquad (4)$$

Here we have reduced the expression as shown because ligand recombination rate constants are typically very fast and [Xe] ≫ [CO]. For example, the reaction of CpRh(CO) with CO has been measured in the gas phase to be (1.5 ± 0.3) × 10^{-10} cm^{-3} s^{-1} molecule^{-1}, or about half the gas kinetic value (collision rate).[10] It is likely that the reaction of Cp*Rh(CO) with Xe (k_{-1}) or CO (k_2) is similarly fast and is probably diffusion controlled in solution. Given the fact that [Xe] > 100[CO] under the conditions of this experiment, it is reasonable to make the approximation that k_{-1}[Xe] ≫ k_2[CO]. Therefore the expression for k_{obs} simplifies as we have shown and predicts a linear dependence on [CO] consistent with the data in Figure 3.[22] It should be noted that we see no evidence for a nonzero intercept in Figure 3 as might be expected for parallel A and D pathways.[4]

The experimentally derived A factor (or $\Delta S^{‡}$) can be used to gain insight into the reaction mechanism. For the associative

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(16) We use the relations $A = (ekT/h)\exp(\Delta S^{‡}/R)$ and $E_a = \Delta H^{‡} + RT$ (ref 17) and a standard state of 1 M.

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(22) The dependence of k_{obs} on [Xe] could be examined if one could vary the concentration of Xe in a solution with Kr in a controlled fashion. However we have not discovered a reliable method for measuring the concentration of Xe in Kr solution.

mechanism, the slope in Figure 3 gives the elementary bimolecular rate constant k_a directly and the *A* factor derived from Figure 4 should be appropriate for a bimolecular reaction. For related bimolecular organometallic reactions, the value is generally in the range 10^8 to 10^{10} M^{-1} s^{-1} ($\Delta S^{\ddagger} = -24$ to -14 cal/(mol K)).[23] The closest system for which temperature-dependent kinetics data are available is the reaction of $CpRh(CO)_2$ with phosphine ligands; for L = $PPhEt_2$ and $POBu_3$, $\Delta S^{\ddagger} = -20$ and -16 cal/(mol K), respectively.[18a] These values are very similar to our result for $Cp^*Rh(CO)Xe + CO$ ($\Delta S^{\ddagger} = -20 \pm 1$ cal/(mol K)) and are strong evidence in favor of a bimolecular substitution mechanism.

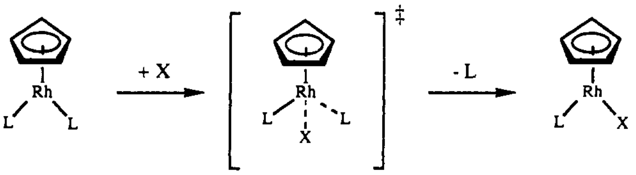
In the case of the dissociative mechanism, the recombination reactions (k_{-1} and k_2) are typically very fast, barrierless reactions and both are probably diffusion controlled in solution, as discussed above. In this case, k_{-1} and k_2 would approximately cancel each other in the expression for k_{obs} (eq 4) to give $k_{obs} \sim k_1[CO]/[Xe]$ or $[Xe]k_{CO} \sim k_1$. Therefore if the dissociative mechanism is operative, a plot of $\ln([Xe]k_{CO})$ versus $1/T$ should give an *A* factor appropriate for a unimolecular rate constant, 10^{13} to 10^{14} s^{-1} ($\Delta S^{\ddagger} = -1$ to $+2$ cal/(mol K)).[24] When this is done using the temperature-dependent values for the Xe density,[25] a linear plot results with $E_a = 2.4 \pm 0.1$ kcal/mol and $\log(A) = 9.7 \pm 0.1$ ($\Delta S^{\ddagger} = -15.5 \pm 0.5$ cal/(mol K)). Clearly this value is well outside the expected range for a unimolecular reaction while the *A* factor from Figure 4 is within the expected range for a bimolecular rate constant.

The value of k_{CO} in liquid Kr is consistent with this interpretation. The lack of a temperature dependence for k_{CO} over the range 163–193 K coupled with the estimated error in k_{CO} (±50%)[26] allows us to place an upper bound on the activation energy for the reaction with CO in liquid Kr: $E_a \leq 0.7$ kcal/mol. This is in good agreement with the value we calculate using the measured value for k_{CO}, the *A* factor determined for $Cp^*Rh(CO)Xe$ ($\log(A) = 8.8 \pm 0.3$), and the mean temperature (178 K): $E_a = 0.6$ kcal/mol.

These results contrast strongly with observations made on the replacement of Xe by CO in $W(CO)_5Xe$ (liquid Xe solvent), which was recently shown to be a dissociative process.[3] In the tungsten system, a plot of $\ln([Xe]k_{CO})$ vs T^{-1} gave $\log(A) = 13.3 \pm 0.2$ ($\Delta S^{\ddagger} = 1 \pm 1$ cal/(mol K), consistent with a unimolecular reaction), in contrast to the lower value observed for $Cp^*Rh(CO)Xe$. In addition, the activation energy for the $W(CO)_5Xe$ substitution (and the derived W–Xe bond energy) is 8.4 ± 0.2 kcal/mol, substantially higher than the barrier observed for $Cp^*Rh(CO)Xe$ (2.8 kcal/mol). The contrasting activation parameters for the two systems indicate that they undergo substitution by different mechanisms, which in turn supports our conclusion that the $Cp^*Rh(CO)Xe$ substitution is associative. In addition, if the Rh–Xe bond energy is similar to that measured for several other systems (i.e., in the 8–10 kcal/mol range),[2,3] the 2.8-kcal barrier observed here for $Cp^*Rh(CO)Xe$ is much smaller than would be required to generate free $Cp^*Rh(CO)$.[27]

It is interesting to compare our results to the substitution mechanisms observed for related CpRhLX complexes. Complexes in which L and X are small and strongly bound (e.g., CO) undergo replacement by associative mechanisms.[18] Because the starting materials are closed-shell, 18-electron complexes, the mechanism postulated for this process involves the reversible formation of an η^3-Cp intermediate which loses CO in a second step (Scheme I).

Scheme II



Simple substitution kinetics cannot, of course, distinguish between this process and a direct displacement mechanism (Scheme II). Furthermore, an η^3-Cp complex has never been directly detected as an intermediate in substitution reactions. However, much circumstantial evidence supports the η^3-Cp picture. Perhaps the most persuasive is the fact that complexes having electron-withdrawing substituents on the Cp ring and (η^5-indenyl)MLX complexes (in which η^3–η^5 isomerization should be very facile) undergo substitution many orders of magnitude more rapidly than simple CpMLX systems.[18] Complexes with more weakly-bound but sterically bulky ligands (i.e., $CpCo(PPh_3)_2$) undergo dissociative substitution presumably because the large ligands retard attack at the crowded metal center.[20] $Cp^*Rh(CO)Xe$, then, is unique in that its leaving ligand is quite weakly bound to the metal center but is not hindered enough to prevent attack of the incoming ligand.

The very low activation energy for the reaction of $Cp^*Rh(CO)Xe$ with CO is more consistent with a direct displacement (Scheme II) although we cannot rigorously rule out a stepwise η^5–η^3 mechanism (Scheme I). If one considers the stepwise alternative, it seems unlikely that the barrier associated with the first step (attack by CO/ring slip) would depend very strongly on the nature of the leaving ligand since the bond between the metal and ligand is not broken in this step. Therefore, if this mechanism is operative for complexes with either weak (Xe and Kr) or strong (CO) ligands, the activation energy for the overall reaction should reach a limiting value as the metal–ligand bond energy decreases (i.e., the E_a value associated with conversion of the starting material plus ligand to the η^3-Cp^*ML_3 intermediate). However, rather than leveling off at a finite value, we find a very small value (2.8 kcal/mol) for the $Cp^*Rh(CO)Xe$ plus CO reaction, and a negligible value for $Cp^*Rh(CO)Kr$ plus CO. In the latter case, the barrier for elimination of Kr is so small that an η^3-Cp* intermediate probably has an insignificant lifetime and the stepwise mechanism would merge into the direct process.

The relationship of the activation energy derived for $Cp^*Rh(CO)Xe$ to the Rh–Xe bond energy is of the most interest to us. As discussed above, the most likely mechanism for our reaction is the direct displacement as presented in Scheme II. Because the transition state for this reaction has partially formed Rh–Xe and Rh–CO bonds, we cannot use this barrier to determine the Rh–Xe bond energy. However, the activation enthalpy does allow us to place a lower bound on the bond energy of 2.4 kcal/mol.

Our results also make an interesting contrast with recent work on the photochemistry of $CpM(CO)_2$ complexes. In studies of the C–H activation reaction of benzene with $CpIr(CO)_2$ in hexafluorobenzene (proposed initially to be an inert solvent), the quantum yield for loss of starting material was found to be dependent upon the concentration of benzene.[28] However, it was later acknowledged that hexafluorobenzene was in fact not inert, but forms a strong complex with the CpIr(CO) fragment as shown by Perutz et al.[29] In subsequent studies of the photochemical substitution reactions of $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ with phosphines in hydrocarbon solvents, two regimes were identified.[30] With strong entering ligands such as phosphines, the quantum yield was once again shown to be dependent upon the concentration

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(26) The error for this measurement is much larger due to the very fast rate of this reaction.

(27) In this context, it is worth noting that the desorption energy for Xe from W(111) and Pt(111) surfaces is very similar at ~9 kcal/mol: Dresser, M. J.; Madey, T. E.; Yates, J. T. *Surf. Sci.* **1974**, *42*, 533–551. Rettner, C. T.; Bethune, D. S.; Scheizer, E. K. *J. Chem. Phys.* **1990**, *92*, 1442–1457.

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of entering ligand. These results were rationalized (like the bimolecular thermal reactions discussed above) by postulating direct attack by phosphine on the excited state prior to loss of CO to give an η^3-intermediate. In contrast, reactions of CpRh(CO)$_2$ or Cp*Rh(CO)$_2$ with silanes showed *no* dependence of quantum yield on the concentration of silane, indicating that, in this case, the rate of reaction with the excited state is not competitive with dissociation of CO. It should be noted that these studies were carried out in a hydrocarbon solvent (decalin) that is not inert to C–H bond insertion reactions. Indeed the rate of C–H bond insertion in hydrocarbon solvents at room temperature is extremely fast,[31] but this competitive reaction was not included in the analysis of the data.

Lees' silane results are consistent with our spectroscopic data that show prompt loss of CO and rapid generation of a Cp*Rh(CO)–solvent complex before reaction with CO or alkane. However, his phosphine results are perplexing, since we believe that our entering ligand (CO) is more similar in character to phosphine than to a silane. The results presented here as well as earlier[6] are more consistent with the picture developed on the basis of several ultrafast kinetic studies of metal carbonyl photochemistry:[32] that CO is lost within picoseconds of absorption of a photon, leading to a vibrationally hot, solvated photofragment that undergoes cooling by collision with solvent molecules somewhat less rapidly. The vibrationally cooled solvate then undergoes thermal substitution, the rate of which can approach diffusion control ($<10^{10}$ s^{-1}) but is still much slower than dissociation of CO from the initial excited state ($\sim 10^{13}$ s^{-1}). It is possible that some fraction of the excited-state species initially formed from Cp*Rh(CO)$_2$ might be susceptible to direct attack by a ligand, especially if the latter were present at the high concentrations used in Lees' studies. Resolution of the incomplete consistency between the quantum yield studies of Lees' and the flash kinetics experiments reported here, previously,[6] and from other laboratories will have to await a careful study in which both quantum yield and flash kinetics experiments are performed on substitution reactions using exactly the same system and reaction conditions.

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