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Flash Infrared Kinetics of the Photochemistry of $Tp^*Rh(CO)_2$ and $Bp^*Rh(CO)_2$ in Liquid Xenon Solution

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The photochemistry of $Tp^*Rh(CO)_2$ (**1**; Tp* = hydridotris(3,5-dimethylpyrazolyl)borate) in liquid xenon solution at −50 °C has been examined by flash IR kinetic spectroscopy. IR spectra of the solution taken 2 μs after 308 nm photolysis exhibit two transient bands at 1976−1980 and 1994−1998 cm^{-1}, respectively, both of which decay with the same first-order rate constant ($k = 2 \times 10^4$ s^{-1}). In the presence of excess CO, the rates of decay of both of these bands increase by an order of magnitude and correlate with the rate of recovery of the CO stretch of the parent complex. Photolysis of xenon solutions of $Bp^*Rh(CO)_2$ (**5**; Bp* = dihydridobis(3,5-dimethylpyrazolyl)borate) produces a transient species with a single IR absorption at 1996−2000 cm^{-1}. Upon addition of pyridine to the solution, this transient photoproduct reacts to form the new, stable complex Bp*Rh(CO)(pyridine), with an IR absorption at 1978 cm^{-1}. On the basis of these results, the 1978 and 1996 cm^{-1} bands observed upon photolysis of **1** are attributed to the solvates (η^3-Tp*)Rh(CO)·Xe and (η^2-Tp*)Rh(CO)·Xe (**2·Xe** and **3·Xe**, respectively). Preliminary kinetic data for the reaction of **1** with cyclohexane in xenon solution indicate that both the 1978 and 1996 cm^{-1} transient bands still appear and that their rates of decay correlate with formation of the Rh alkyl hydride product Tp*Rh(CO)(cyclohexyl)(H) (**4**), absorbing at 2032 cm^{-1}.

Introduction

Time-resolved infrared spectroscopy of transition-metal carbonyls in liquid xenon solution has become a useful methodology for characterizing the structures and lifetimes of short-lived, reactive species.[1−5] The medium is less rigidly confining than a matrix and at the same time less reactive than a conventional solvent, although the Xe does appear to stabilize unsaturated metal centers by coordination (bond energies of up to 8 kcal/mol have been measured for such complexes).[6−9] Our group has taken advantage of the inertness of Xe to study metal complexes that react rapidly with the C−H bonds in alkanes.[10−17]

The [hydridotris(3,5-dimethylpyrazolyl)borato]dicarbonylrhodium complex ($Tp^*Rh(CO)_2$; **1**) has been shown to undergo clean and highly photoefficient C−H activation reactions with aliphatic hydrocarbons upon photoextrusion of a CO ligand.[18−24] Bromberg et al. recently published a picosecond flash kinetics study of the reaction of **1** in room-temperature cyclohexane, showing that photoextrusion of CO leads to two successive, spectroscopically characterized intermediates prior to formation of the Rh alkyl hydride product **4** on a nanosecond time scale.[25] These intermediates (**2·C_6H_{12}**,

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(24) For a comprehensive survey of the coordination chemistry of pyrazolylborate ligands, see: Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999.

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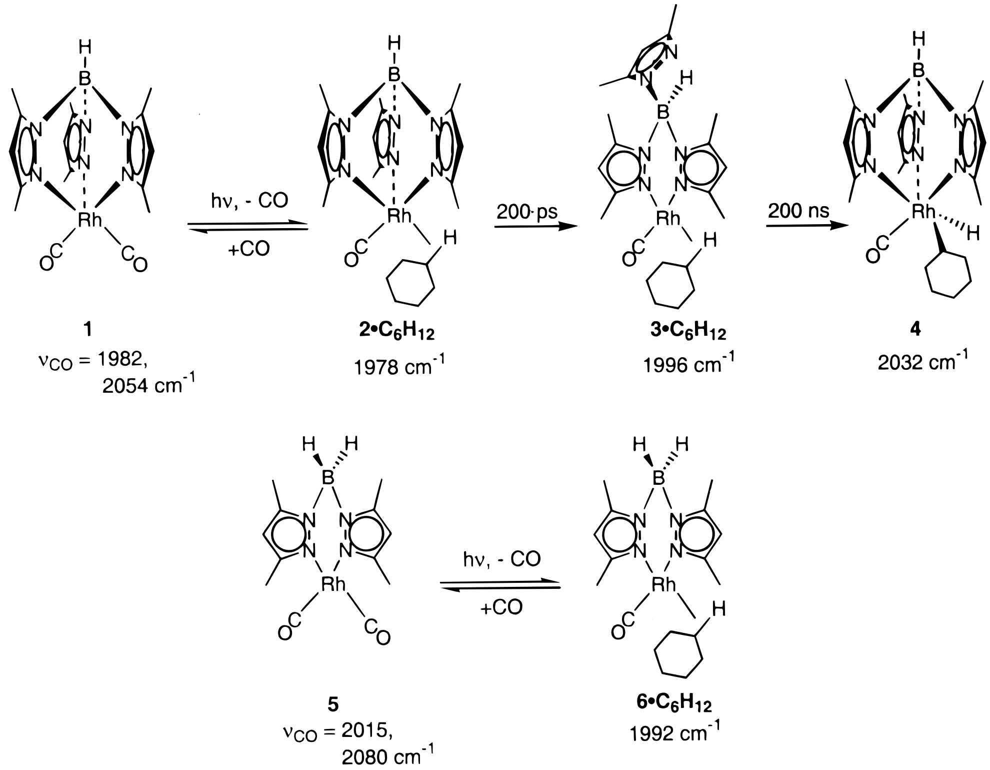
Scheme 1



3·C$_6$H$_{12}$) were proposed to be (η^3-Tp*)- and (η^2-Tp*)Rh(CO) alkane solvates, respectively, differing in the number of pyrazolyl nitrogens coordinated to the metal center (Scheme 1). The structural assignments were based in large part on studies of the related bidentate [dihydrobis(3,5-dimethylpyrazolyl)borato]dicarbonylrhodium complex (Bp*Rh(CO)$_2$; **5**), which was used to model the proposed hapticity change in Tp* coordination to Rh along the C−H activation pathway (Scheme 1). An earlier matrix study by Rest and co-workers also examined the photochemistry of **1** and **5** to probe changes in the coordination geometry of the Tp* ligand after irradiation of **1**.[26] To complement these studies and to garner further evidence for Tp* hapticity changes in solution, we have employed a UV/IR pump−probe scheme to examine the behavior of **1** and **5** upon photolysis in liquid Xe.

Experimental Section

The IR flash kinetics apparatus has been described in detail previously.[13,17] Xenon (99.999%) was obtained from Spectra Gases and used as received. Compounds **1**[27] and **5**[28] were prepared by literature methods and stored under dry N$_2$ prior to use. Reagent concentrations were determined by integration of infrared bands using absorption coefficients from gas-phase studies (for CO, corrected for index of refraction change)[29] or from spectra of standard solutions prepared in hydrocarbon or chlorinated solvents. Exponential fits were refined using a commercially available nonlinear least-squares routine (KaleidaGraph, Version 3.0, Synergy Software, 1996). Errors are given as ±σ.

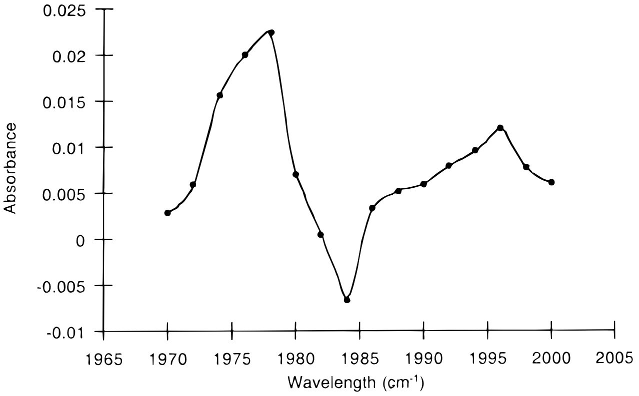


Figure 1. Transient IR difference spectrum 2 μs after 308 nm photolysis of **1** in Xe solution.

Results

Photochemistry of 1 in Liquid Xe. A xenon solution of **1** (0.1 mM) was irradiated at −50 °C with 20 ns 308 nm pulses.[30] Figure 1 shows a transient IR difference spectrum taken 2 μs after the photolysis pulse.[31] The spectrum is characterized by bleaching of the

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[30] Total pulse energies were approximately 100 mJ, but the pulses were unfocused in order to irradiate the sample uniformly. The windows of the sample cell were 1 cm^2 in area, and therefore only the central 1 cm^2 of each 10 cm^2 pulse reached the sample, corresponding to an effective energy per pulse of approximately 10 mJ.

[31] The data presented in Figure 1 do not support a rigorous quantification of the relative intensities of the bands at 1978 and 1996 cm^{-1}. This is due to a steady depletion of substrate during data collection, coupled with power fluctuations and wavelength-dependent signal-to-noise ratios inherent to the probe laser. Consequently, a thorough investigation of the temperature dependence of relative band intensities was not pursued.

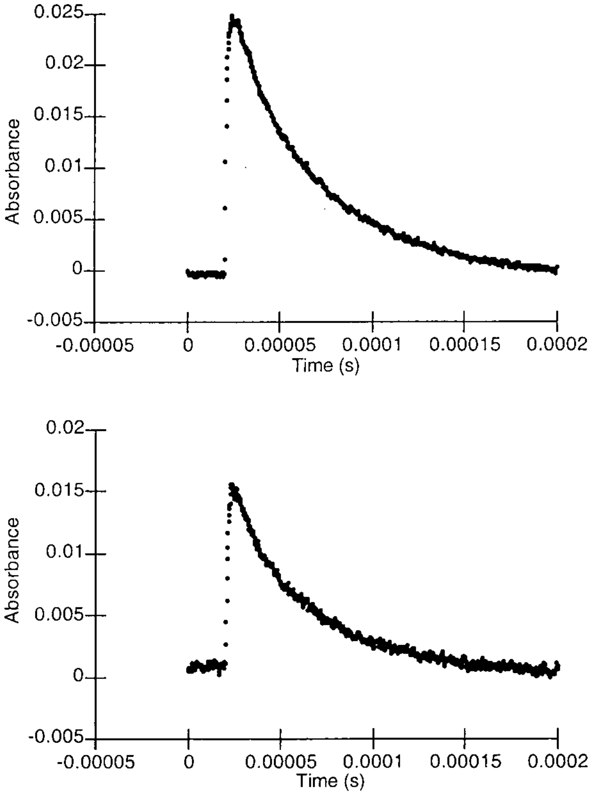

Figure 2. Kinetic traces of the rise and decay of transient absorptions at 1978 cm^{-1} (top) and 1996 cm^{-1} (bottom) after photolysis of **1** in Xe solution.

parent CO stretching band at 1982−1984 cm^{-1} and by the appearance of two new bands at 1976−1980 and 1994−1998 cm^{-1}. These transient bands grow in with an instrument-limited rise time of 300 ns, and they both exhibit single-exponential decays with rate constants of $[2(\pm 0.3)] \times 10^4$ s^{-1}. Representative traces are shown in Figure 2. FTIR spectra taken throughout the experiment indicate that **1** decomposes upon photolysis in Xe to yield unknown products.[32]

In an effort to inhibit this decomposition pathway, transient spectra were taken of **1** in Xe solutions containing excess CO (0.4 mM). The 1978 and 1996 cm^{-1} transient bands still appear with instrument-limited rise times of 300 ns. They both decay with a single-exponential rate constant of $[2.1(\pm 0.2)] \times 10^5$ s^{-1}, while partial recovery of the parent CO band at 1984 cm^{-1} occurs with $k = [2.3(\pm 0.4)] \times 10^5$ s^{-1}.[33]

Photochemistry of 1 in Liquid Xe in the Presence of Alkane. The photoinduced reaction of Tp*Rh-$(CO)_2$ (**1**; 0.1 mM) with a large excess of cyclohexane (0.32 M) in liquid Xe solution has also been examined. Upon irradiation of the solution at −50 °C, transient peaks still grow in at 1978 and 1996 cm^{-1} concurrent with a bleach of the parent CO band at 1984 cm^{-1}. Both transients exhibit single-exponential decays on a microsecond time scale ($k_{1978} = [6.9(\pm 0.6)] \times 10^4$ s^{-1}, $k_{1996} = [7(\pm 1.5)] \times 10^4$ s^{-1}). These decays appear to be kinetically coupled to the growth of a new band at 2032 cm^{-1} ($k = [7.6(\pm 0.7)] \times 10^4$ s^{-1}), which has been assigned to the known[18] CO stretch of the stable C−H activation product Tp*Rh(CO)(cyclohexyl)(H) (**4**). FTIR spectra confirm the conversion of **1** to **4** over the course of the experiment.

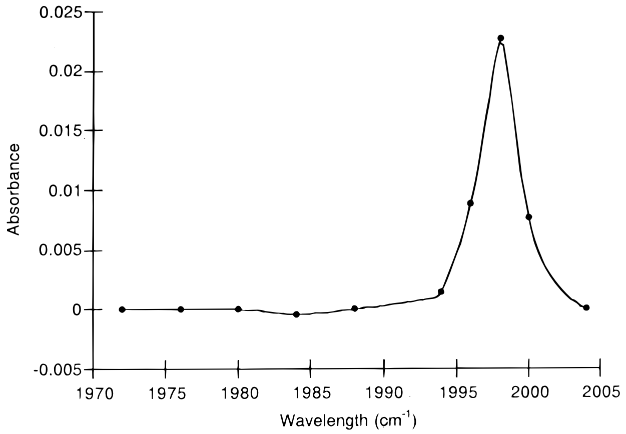

Figure 3. Transient IR difference spectrum 2 μs after 308 nm photolysis of **5** in Xe solution.

Photochemistry of 5 in Liquid Xe. A liquid Xe solution of the related Bp* complex **5** (0.3 mM) was also photolyzed at −50 °C with 308 nm pulses. A transient difference spectrum is shown in Figure 3. The difference spectrum is characterized by a flat baseline in the 1978 cm^{-1} region and a transient band at 1996−2000 cm^{-1}.[34] Like the bands observed upon photolysis of **1**, this band grows in with an instrument-limited rise time of 300 ns. The transient signal decays with a single-exponential rate constant of $[4.2(\pm 0.3)] \times 10^3$ s^{-1}.[35] In the presence of CO (0.7 mM), the decay of the 1996 cm^{-1} band proceeds an order of magnitude more rapidly ($k = [7.7(\pm 0.9)] \times 10^4$ s^{-1}).

Photochemistry of 5 in Liquid Xe in the Presence of a Trap. Several attempts were made to photolyze Xe solutions of **5** in the presence of free dimethylpyrazole, in the hope that the base might bind to the transient photoproduct and thereby mimic a species produced upon photolysis of **1**. However, the solubility of dimethylpyrazole in xenon was insufficient to yield conclusive results.

We therefore switched to pyridine as the trapping agent. In the presence of pyridine (0.03 M), photolysis of **5** in Xe solution does in fact lead to the appearance of a new absorption band at 1978 cm^{-1}, the growth of which is coupled to decay of the transient band at 1998 cm^{-1}. We found that the 1978 cm^{-1} band resulted from absorption by a new isolable product, Bp*Rh(CO)-(pyridine) (**6·py**), which we were able to independently prepare and characterize.[36]

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(32) Due to the relatively low solubility of **1** in Xe, attempts to isolate these photoproducts were unsuccessful. We were also unable to observe bands for the products in FTIR spectra; we observed only the disappearance of the CO bands of **1**. Although **1** is more soluble in aromatic and chlorinated solvents than in Xe, photolysis in these solvents results in oxidative addition of C−H or C−Cl bonds across the Rh center, precluding an independent synthesis of the decomposition products formed in Xe.

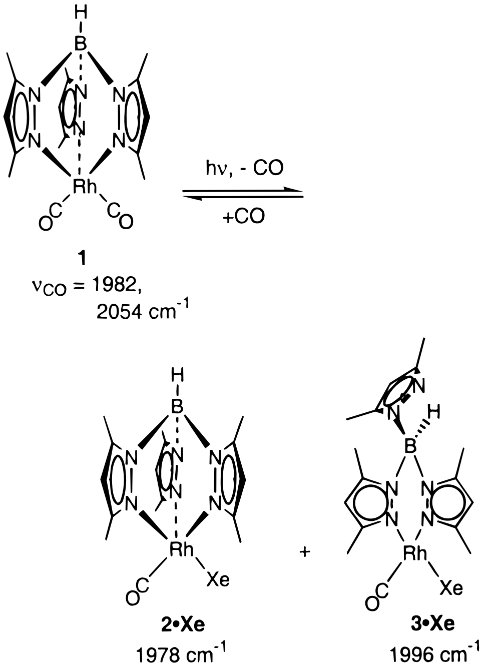
(33) The parent CO band recovered only 60% of its initial intensity in these experiments, suggesting that some decomposition was still occurring. Addition of a larger excess of CO could have increased the recovery percentage, but the rates of the recovery and transient decays would have become too fast to measure using our detection system.

(34) Bleaching of the parent CO band of **5** at 2015 cm^{-1} could not be observed in this experiment because the diode power at that wavelength was relatively low, and consequently the change in the parent band absorption upon photolysis was not above the noise level.

(35) The transient decay at 1996 cm^{-1} appears to be kinetically coupled to formation of a product band at 1984 cm^{-1}, perhaps indicative of dimer formation. This product band is not observed in the presence of buffering CO.

Discussion

Photolysis of Tp* complex **1** at 308 nm in liquid Xe results in two transient IR bands in the CO stretching region, centered at 1978 and 1996 cm^{-1}, respectively. The fact that the transient bands decay an order of magnitude more rapidly in the presence of excess CO than in pure xenon, coupled with the similarity in the decay rates of the transients and the recovery rate of the parent, offers compelling evidence that the complex or complexes responsible for these bands are produced via photodissociation of CO from **1**. We have assigned these bands to (η^3-Tp*)- and (η^2-Tp*)Rh(CO)·Xe solvates (**2·Xe** and **3·Xe**), respectively (eq 1).[37,38] Consistent with these structural assignments, the lower coordination number of **3** reduces electron density at the metal and thereby accounts for the spectroscopic blue shift from 1978 to 1996 cm^{-1} for this complex.



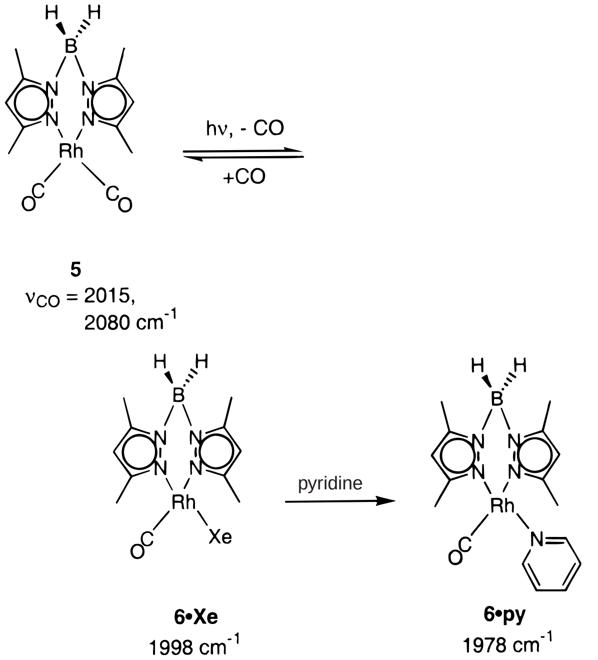
(1)

Table 1. Structural Assignments for Observed CO Bands upon Photolysis of 1 and 5

complex	ν_{CO} (cm^{-1})
Tp*Rh(CO)$_2$ (**1**)	1982, 2054
(η^3-Tp*)Rh(CO)·C_6H_{12} (**2·C_6H_{12}**)	1972[a]
(η^2-Tp*)Rh(CO)·C_6H_{12} (**3·C_6H_{12}**)	1990[a]
Tp*Rh(CO)(C_6H_{11})(H) (**4**)	2032
(η^3-Tp*)Rh(CO)·Xe (**2·Xe**)	1978
(η^2-Tp*)Rh(CO)·Xe (**3·Xe**)	1996
Bp*Rh(CO)$_2$ (**5**)	2015, 2080
Bp*Rh(CO)·C_6H_{12} (**6·C_6H_{12}**)	1992[a]
Bp*Rh(CO)·Xe (**6·Xe**)	1998
Bp*Rh(CO)(pyridine) (**6·py**)	1978

[a] Reference 25: photolysis in cyclohexane.

There is ample literature precedent for variation in the hapticity of the Tp* ligand in Rh complexes.[26,39−42] Moreover, the photochemistry of **5** in liquid Xe lends strong support to the hypothesis. The band at 1998 cm^{-1} produced upon photolysis of **5** is most logically assigned to a Bp*Rh(CO)·Xe solvate (**6·Xe**), which bears significant structural resemblance to the proposed η^2-Tp* solvate **3·Xe** (1996 cm^{-1}). Binding of a pyridine ligand to **6** (eq 2) produces a complex that is structurally analogous to the η^3-Tp* solvate **2**, and both species exhibit CO stretching frequencies of 1978 cm^{-1}. These results (summarized in Table 1) strongly reinforce the structural assignments of **2·Xe** and **3·Xe** to the transient species formed upon photolysis of **1** in liquid xenon.



(2)

There is notable similarity between the CO stretching frequencies of the xenon solvates (**2·Xe**, **3·Xe**) and those of the solvates observed in cyclohexane (**2·C_6H_{12}**, **3·C_6H_{12}**) in the study by Bromberg et al. (Scheme 1).[25] However, the time evolution of these species differs significantly. Whereas in room-temperature cyclohexane the η^3-Tp* complex is converted quantitatively into the η^2-Tp* complex within 200 ps, in Xe at −50 °C the bidentate and tridentate complexes are present at the same time and decay together on a microsecond time

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(36) Bp*Rh(CO)(pyridine) can be prepared cleanly and efficiently by the thermal oxidation of the dicarbonyl **5** with Me_3NO in pyridine solution. The preparation and reaction chemistry of this complex will be described in a forthcoming publication: Yeston, J. S.; Bergman, R. G. *Organometallics,* in press.

(37) The IR data alone are insufficient to determine the number of Xe atoms discretely coordinated to the complexes. For simplicity we have drawn the structures with a single Xe atom bound. An alternative explanation for the two transient bands would be that they both result from a single species, perhaps a dimer formed from reaction of the Rh monocarbonyl photoproduct with the parent complex. Assuming a rise time of 300 ns and a parent concentration of 0.1 mM, the dimerization would require a second-order rate constant of 10^{10} M^{-1} s^{-1} at −50 °C. This rate constant is not unreasonable for a diffusion-controlled reaction in the low-viscosity liquid Xe medium.[38] However, the photochemistry of **5** described in the present study strongly supports the change-in-hapticity hypothesis.

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scale. Since the rise time of the transient bands in the present study is detector-limited to 300 ns, it is reasonable to assume that we observe an equilibrated mixture of **2·Xe** and **3·Xe** in the transient IR spectrum. In Xe, as in cyclohexane, photolysis of **1** may initially produce only the η^3-Tp* solvate, which then equilibrates with the bidentate isomer on a time scale much shorter than 300 ns. In the Bromberg study, the higher temperature and larger steric bulk of cyclohexane (relative to Xe) drive the equilibrium all the way to the η^2-Tp* solvate, while in Xe both Tp* coordination geometries appear to have comparable free energies.

Upon reaction of **1** with cyclohexane in liquid Xe, the bidentate and tridentate solvates both decay with the same observed rate constant to yield the Rh alkyl hydride **4**. This observation is consistent with a Curtin–Hammett kinetic scheme[43] involving rate-limiting C–H bond oxidative addition, which permits fast equilibration of the η^2- and η^3-Tp* solvates prior to the rate-determining step.[44]

Conclusions

Photolysis of Tp*Rh(CO)$_2$ (**1**) at 308 nm in liquid Xe solution gives rise to two transient IR bands centered at 1978 and 1996 cm^{-1}. These bands have been assigned to Tp*Rh(CO)·Xe solvates differing in the coordination geometry of the Tp* ligand. Specifically, the 1978 cm^{-1} absorption is assigned to the CO stretch of the tridentate Tp* complex **2·Xe**, while the blue-shifted absorption is assigned to the bidentate Tp* complex **3·Xe**. These assignments are based in large part on the 1998 cm^{-1} band observed upon photolysis of the bidentate Bp*Rh(CO)$_2$ (**5**) in Xe and the 1978 cm^{-1} band observed when **5** is photolyzed in Xe in the presence of pyridine.

The partitioning between Tp* hapticities in the Xe solvates at −50 °C contrasts markedly with the ligand behavior observed in room-temperature alkane solvent. Bromberg et al. showed that photolysis of **1** in cyclohexane produces only the η^3-Tp*Rh(CO)·C$_6$H$_{12}$ solvate (**2·C$_6$H$_{12}$**), which then undergoes quantitative isomerization to the bidentate isomer **3·C$_6$H$_{12}$** in 200 ps.[25] These differences point to a solvent and temperature dependence in the equilibrium between bidentate and tridentate Tp*Rh(CO) solvates.

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[43] Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

[44] The reaction is complicated by the fact that, in addition to the hapticity equilibrium, there is presumably an equilibrium between Xe and cyclohexane solvates of the Tp*Rh(CO) fragment. Past studies in our group have shown that it is very difficult to spectroscopically distinguish alkane and noble-gas solvates in a liquid noble gas; the CO stretches of the two species tend to differ by less than 1 cm^{-1}.[14] Consequently, it is likely that in Xe/cyclohexane mixtures, the observed transient bands result from both solvates.