

# Quantitative Measurements of CpRh(CO)<sub>2</sub> (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) Photochemistry in Various Hydrocarbon Solutions: Mechanisms for Ligand Photosubstitution and Intermolecular C–H and Si–H Bond Activation Reactions

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The quantitative solution photochemistry of CpRh(CO)<sub>2</sub> (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) involving ligand substitution and intermolecular C–H and Si–H bond activation processes has been investigated in several hydrocarbon solvents at room temperature following excitation in the region 313–458 nm. These photoreactions have been monitored by UV–vis and FTIR spectroscopy, and the absolute quantum efficiencies (φ<sub>cr</sub>), determined to be in the 0.0007–0.31 range, are dependent on the entering ligand concentration, excitation wavelength, and solvent. The observed wavelength dependence is consistent with distinct reaction pathways occurring from two rapidly dissociating ligand-field (LF) excited states. Analysis of the quantitative photochemical results has led to a comprehensive mechanistic description for all of the various competing reaction pathways in the photochemistry of CpRh(CO)<sub>2</sub>. In the absence of an entering ligand, a carbonyl-bridged *trans*-Cp<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub> complex is identified as the major photochemical reaction product; this species is formed with a low quantum efficiency. When excess triethylsilane (Et<sub>3</sub>SiH) is present in the solution, the CpRh(CO)<sub>2</sub> complex is converted cleanly on irradiation to the silyl hydrido CpRh(CO)(SiEt<sub>3</sub>)H photoproduct. Quantum efficiencies recorded for the Si–H activation process are dependent on the Et<sub>3</sub>SiH concentration in the range of 0.001–0.3 M, exhibiting saturation-type kinetics. Kinetic analysis of the φ<sub>cr</sub> data implicates a solvated CpRh(CO) primary photoproduct which is scavenged competitively by Et<sub>3</sub>SiH and CpRh(CO) under these solution conditions. When excess triphenylarsine (AsPh<sub>3</sub>) and triphenylphosphine (PPh<sub>3</sub>) ligands are present in the hydrocarbon solution, the monosubstituted CpRh(CO)AsPh<sub>3</sub> and CpRh(CO)PPh<sub>3</sub> photoproducts are formed cleanly and completely. Quantum efficiencies obtained for these ligand substitution reactions exhibit an increasing linear dependence with [L] in the range 0.05–0.3 M; kinetic analysis implicates a solvated (η<sup>3</sup>-Cp)Rh(CO)<sub>2</sub> primary photoproduct which is competitively scavenged by AsPh<sub>3</sub> and PPh<sub>3</sub>. In contrast, pyridine is determined to be too poor a nucleophile to effectively scavenge this intermediate. Variations in the quantum efficiencies over a range of alkane, aromatic, and chlorinated hydrocarbon solvents are shown to be dependent on nonradiative deactivation pathways from CpRh(CO)<sub>2</sub> and are not affected by the subsequent oxidative-addition step.

## Introduction

The photochemistry of CpML<sub>2</sub> and Cp\*ML<sub>2</sub> (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; M = Rh, Ir; L = CO, olefin, PR<sub>3</sub>) complexes has been vigorously investigated ever since the discovery of their intermolecular C–H bond activation reactivity upon light excitation.<sup>1</sup> Initial synthetic studies provided competitive rates of C–H bond activa-

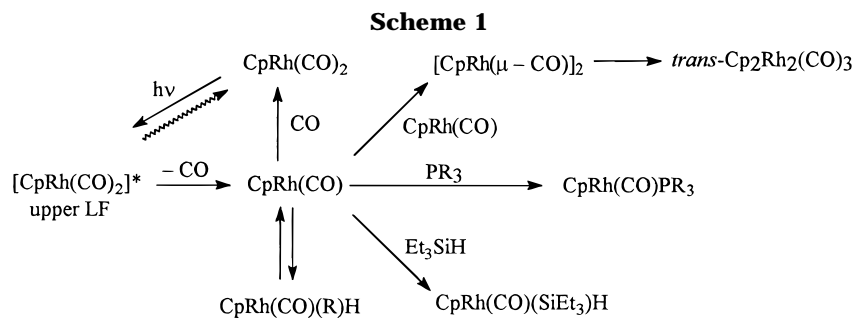
tion for several of these systems.<sup>1,2</sup> Subsequently, a number of photochemical methods have been used to investigate these important reaction mechanisms. These experiments have included low-temperature matrix isolation,<sup>3</sup> laser-flash photolysis (including ultrafast spectroscopy),<sup>4</sup> solvation in liquefied noble gases,<sup>5</sup> and quantum efficiency determination.<sup>6</sup> Measurements on

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(η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)ML<sub>2</sub> and (η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)ML(H)<sub>2</sub> (R = H, Me; M = Rh, Ir; L = CO, olefin, PR<sub>3</sub>) have revealed that the primary photoproduct is a coordinatively-unsaturated 16-electron (η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)ML species which is extremely reactive and rapidly forms a solvent adduct complex, (η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)ML⋯S, in even weakly coordinating solvents (S) before reacting with the hydrocarbon C–H bond. Moreover, the rate of C–H activation of alkane to Cp<sup>\*</sup>Rh(CO)X (X = Kr, Xe) in liquefied rare gas solutions at low temperature<sup>7</sup> and to CpRh(CO) in the vapor phase<sup>8</sup> have now been determined, and these processes are also found to be very fast.

In recent papers, we have reported the first quantum efficiency measurements for the light-induced ligand substitution and C–H/Si–H bond activation reactions of CpRh(CO)<sub>2</sub> and Cp<sup>\*</sup>Rh(CO)<sub>2</sub> in solution.<sup>6</sup> A desirable aspect of this approach is that it generates quantitative data for the photochemical pathways in which the C–H activation process is an integral part of the mechanism. Information of this nature at various excitation wavelengths is essential for the further application of time-resolved methods to such systems. Additionally, the quantitative measurements facilitate a comparison of the photoefficiencies with other intermolecular C–H activation systems.<sup>9</sup> Importantly, the quantum efficiency values, themselves, have also made it possible to elucidate several key features of the ligand substitution and C–H activation mechanisms. A most significant finding in these studies is that the quantum efficiencies determined are dependent on the excitation

wavelength, not only in their magnitude but in the way they are influenced by various scavenging ligands, suggesting that there are two ligand-field (LF) electronically excited states with distinct reactivities involved in the mechanism.<sup>6</sup> Consequently, two different reaction intermediates are implicated in the solution photochemistry of both CpRh(CO)<sub>2</sub> and Cp<sup>\*</sup>Rh(CO)<sub>2</sub>.

It is understood that short-wavelength irradiation at 313 nm of CpRh(CO)<sub>2</sub> in hydrocarbon (R–H) solution leads predominantly to the formation of an upper-energy LF excited state; here, the photochemistry is characterized by facile CO dissociation and high quantum efficiencies ( $\phi_{cr} > 0.1$ ) for ligand substitution and C–H/Si–H bond activation reactions (see Scheme 1).<sup>6b</sup> The photoefficiency data have been shown to be entirely consistent with the primary photoproduct being the hydrocarbon-solvated CpRh(CO) monocarbonyl species.<sup>6,10</sup> It should be noted, though, that the alkyl hydride complex, CpRh(CO)(R)H, is also unstable and has been identified as a reaction intermediate in flash photolysis; this transient species has a lifetime on the order of milliseconds in the absence of a scavenging ligand, and it undergoes reductive elimination to form [CpRh(μ-CO)]<sub>2</sub> and subsequently the *trans*-Cp<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub> product.<sup>4b</sup>

In contrast, it is believed that long-wavelength photolysis at 458 nm predominantly populates a lower energy LF excited state which is characterized by an inefficient ( $\phi_{cr} \approx 10^{-3}$ ) photosubstitution reaction (see Scheme 2).<sup>6b</sup> A ring slippage (η<sup>5</sup> → η<sup>3</sup>) mechanism involving the cyclopentadienyl ligand has been postulated on the basis of  $\phi_{cr}$  results, which are influenced by the nature and concentration of the entering PR<sub>3</sub> ligand.

There are three primary objectives in this current work. The first is to provide a comprehensive kinetic analysis of quantitative photochemical data obtained for all of the scavenging processes of the key solvated CpRh(CO) intermediate described in Scheme 1. As indicated above, the primary photoproduct is extremely reactive (and generally only formed in low concentration), so this important mechanistic information is not readily obtainable using flash photolysis methods alone. Previously, the quantum efficiencies have been rationalized for a limited set of kinetic conditions which did not include the competing dimerization process.<sup>6b</sup> The second objective is to substantiate the postulated ring slippage mechanism (Scheme 2) by determining the photochemical behavior following long-wavelength excitation when other types of ligands are used to scavenge the solvated (η<sup>3</sup>-Cp)Rh(CO)<sub>2</sub> intermediate. The third objective is to explore the effects of different

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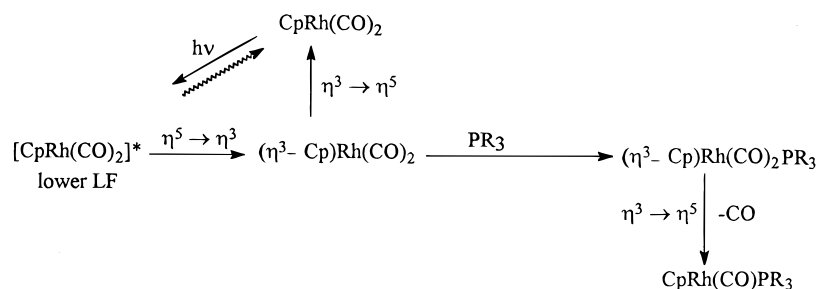
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Scheme 2



hydrocarbon substrates on the photochemical bond activation processes. In this regard, photoefficiency results have been obtained in several different solutions, and these provide valuable insight into the mechanistic events that effectively determine the quantitative C–H/Si–H photochemistry of  $\text{CpRh(CO)}_2$ .

### Experimental Section

**Materials.** Chlorodicyclopentadienylrhodium(I) dimer and cyclopentadienylthallium were obtained in high purity (97–99%) from Pressure Chemical Co. and Aldrich Chemical Co., respectively, and used as received. Solvents used in the photochemical studies were obtained from Aldrich Chemical Co. in high purity (99%). Solvents used in the syntheses were obtained as reagent grade from Fisher Scientific Co. and were dried over anhydrous calcium sulfate (Aldrich Chemical Co.) prior to use. Neutral alumina chromatographic adsorbent (80–200 mesh) was obtained from Fisher Chemical Co. Triphenylarsine ( $\text{AsPh}_3$ ) ligand and triethylsilane ( $\text{Et}_3\text{SiH}$ ) were purchased from Aldrich Chemical Co. in high purity (97–99%); the latter was refluxed over 5 Å molecular sieve (Fisher Scientific Co.) for 4 h and subsequently distilled several times under a nitrogen atmosphere immediately prior to use. The argon gas used for solvent deoxygenation was purchased as high-research grade (>99.99% purity) and was deoxygenated and dried by passage over potassium hydroxide (Fisher Chemical Co.), 5 Å molecular sieves, and a pelletized copper catalyst (BASF R3-11, Chemical Dynamics Co.), according to a previously described procedure.<sup>11</sup> Carbon monoxide was obtained from the Linde Gas division of Union Carbide as CP grade (99.5% purity) and was further purified by passage through a 1-m tube (2-cm diameter) containing the above copper catalyst and then a 25-cm tube (4-cm diameter) containing a mixture of calcium sulfate and 5 Å molecular sieves.

**Syntheses.** The parent  $\text{CpRh(CO)}_2$  complex was prepared via a reflux reaction of chlorodicyclopentadienylrhodium(I) dimer with cyclopentadienylthallium, according to earlier details<sup>6b</sup> and a previously described procedure.<sup>12</sup> The  $\text{CpRh(CO)PPh}_3$  and  $\text{CpRh(CO)(Et}_3\text{Si)H}$  complexes were prepared and characterized as previously reported.<sup>6b,13</sup> The  $\text{CpRh(CO)AsPh}_3$  derivative was prepared by refluxing  $\text{CpRh(CO)}_2$  ( $5 \times 10^{-3}$  M) with  $\text{AsPh}_3$  (0.2 M) in hexanes (50 mL) for 120 h. The product was cooled and concentrated and then column chromatographed on neutral alumina. Following removal of solvent a red-orange solid was obtained in low (ca. 10%) yield. IR,  $\text{CpRh(CO)AsPh}_3$  in hexanes:  $\nu(\text{CO})$   $1946 \text{ cm}^{-1}$ .<sup>6b,13,14</sup>

**Photochemical Procedure.** A Lexel Corp. model 95–4 4 W argon-ion laser was used to perform the visible photolyses at 458 nm; the incident laser light intensity was determined by means of a Ophir Optronics Ltd. Model Nova-Display

external power meter. Typically, laser powers of 90–190 mW were employed, although results were also obtained with reduced laser light powers of between 30 and 75 mW and the determined quantum efficiency values were not changed. The photochemistry was monitored by recording UV–vis and FTIR spectra at regular time intervals throughout the irradiation procedure, generally for almost complete (>90%) photochemical conversions. In the case of the binucleation reaction, the most reproducible results were obtained for relatively small photochemical conversions (<15%) due to the formation of photoproduct precipitate.

Electronic absorption spectra were recorded on a Hewlett-Packard model 8450A diode-array spectrometer and stored on a Hewlett-Packard model 82901M disk drive. Spectra were obtained from solutions held in regular 1-cm quartz cuvettes, and the reported band maxima are considered accurate to  $\pm 2$  nm. Infrared spectra were recorded on a Nicolet model 20SXC Fourier transform infrared (FTIR) spectrometer. Spectra were obtained from solutions using a NaCl cell of 0.5-mm path length, and the reported band maxima are considered accurate to  $\pm 0.5 \text{ cm}^{-1}$ . Infrared carbonyl vibrations observed for the parent and photoproduct complexes during each of the photolysis reactions in solution agree closely with those measured from the isolated complexes.

Throughout photolysis the solutions were rapidly stirred to ensure sample homogeneity and a uniform optical density in the light path. The resultant quantum efficiency values were determined in triplicate and were found to be reproducible to within  $\pm 10\%$  in all cases. The stated uncertainties for the absolute quantum efficiency values incorporate the systematic errors involved in measuring the light intensity. Ligand substitution reactions were also performed in the dark to assess the extent of thermal processes, which were found to be negligible under our experimental conditions. Subsequent plots of quantum efficiency versus entering ligand concentration were fitted by standard least-squares linear regression analyses.

During irradiation, the solution temperatures were controlled to  $\pm 0.1$  K by circulating a thermostated ethylene-glycol–water mixture through a jacketed cell holder mounted on the optical rail. Solutions were stringently filtered through 0.22- $\mu\text{m}$  Millipore filters and deoxygenated by purging with prepurified nitrogen gas for 15 min prior to irradiation. Solutions saturated with CO were obtained by initially bubbling CO through the solution for 30 min and then stirring the solution for a further 30 min under a sealed CO atmosphere. The concentration of CO in the alkane solution at 293 K is approximately  $1.0 \times 10^{-2}$  M.<sup>15</sup>

### Results and Discussion

**Photochemical Reactivity.** The solution photochemistry of  $\text{CpRh(CO)}_2$  has been investigated in deoxygenated decalin following laser excitation at 458 nm. UV–vis spectra recorded during the photolysis at 293 K in the absence of any added scavenging ligand show

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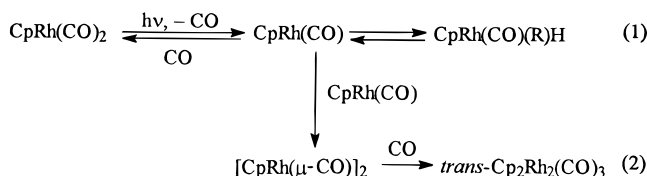
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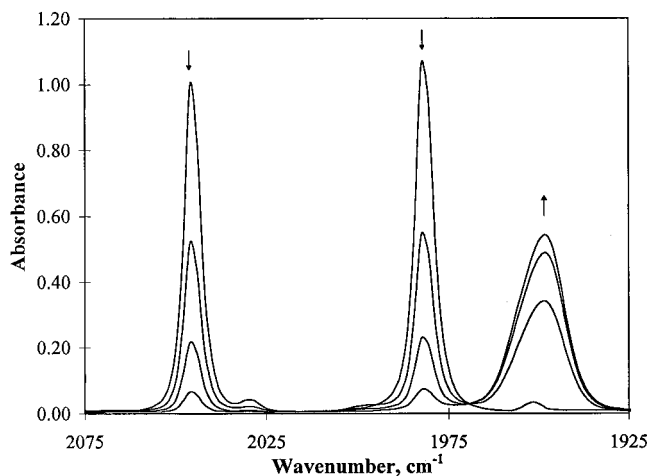
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new absorption bands appearing at approximately 430, 540, and 680 nm (Supporting Information), which are indicative of the red-colored carbonyl-bridged *trans*-Cp<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub> complex.<sup>4b,11</sup> FTIR spectra recorded during this photochemical reaction reveal a gradual decline in the absorbance of the ν(CO) bands at 2046 and 1982 cm<sup>-1</sup> representing the CpRh(CO)<sub>2</sub> complex and the appearance of a new feature centered at 1836 cm<sup>-1</sup>, in agreement with the bridging carbonyl vibration at 1837 cm<sup>-1</sup> reported for *trans*-Cp<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub> in cyclohexane.<sup>4b</sup> Independent flash photolysis measurements have identified the alkyl hydrido complex, CpRh(CO)(R)H, as a reaction intermediate; in the absence of any added ligand, this complex has a transient lifetime on the order of milliseconds and undergoes reductive elimination to form [CpRh(μ-CO)]<sub>2</sub> and then more slowly to *trans*-Cp<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub>.<sup>4b</sup> It has also been established that in this solution environment the primary photoproduct, formally the 16-electron CpRh(CO) species, is rapidly solvated prior to the C–H bond activation step.<sup>4–8</sup> Thus, the photochemical reactivity of CpRh(CO)<sub>2</sub> in decalin (RH) can be represented by a sequence involving initial CO dissociation followed by rapid solvation and then competing C–H activation and binucleation reactions (see eqs 1 and 2).



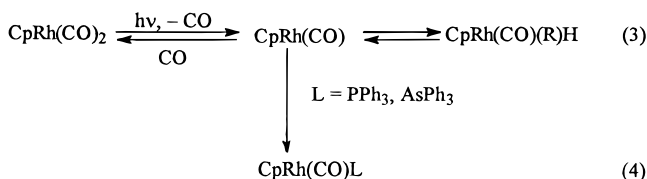
The ligand photosubstitution reaction of CpRh(CO)<sub>2</sub> has been previously investigated following 458 nm irradiation with various concentrations (0.05–0.3 M) of entering PPh<sub>3</sub> ligand, and a comparison is now made for scavenging AsPh<sub>3</sub> ligands. These reactions were carried out at 293 K, where it was determined that there are negligible effects from thermal ligand substitution processes.<sup>16</sup> UV–vis and FTIR spectra obtained throughout these photolyses reveal that the ligand substitution reactions proceed completely and generate the corresponding CpRh(CO)PPh<sub>3</sub> and CpRh(CO)AsPh<sub>3</sub> photoproducts without interference from secondary photoprocesses. Figure 1 illustrates FTIR spectra recorded from the 458-nm photolysis of CpRh(CO)<sub>2</sub> in decalin containing 0.05 M AsPh<sub>3</sub>. The spectra depict a decline of the ν(CO) bands of CpRh(CO)<sub>2</sub> at 2046 and 1982 cm<sup>-1</sup>, and a concurrent increase of a new feature at 1948 cm<sup>-1</sup> representing the ν(CO) band of the CpRh(CO)AsPh<sub>3</sub> photoproduct (accompanying UV–vis changes are included as Supporting Information). Spectral data from the analogous photoreaction with PPh<sub>3</sub> have been previously reported.<sup>6b</sup> It should be noted that the CpRh(CO)PPh<sub>3</sub> and CpRh(CO)AsPh<sub>3</sub> photoproduct complexes are both photochemically and thermally stable under these photolysis conditions.

The CpRh(CO)PPh<sub>3</sub> and CpRh(CO)AsPh<sub>3</sub> complexes have been isolated via thermal syntheses (see Experimental Section), and their spectra are identical to those

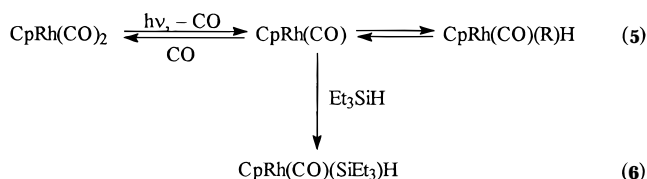


**Figure 1.** FTIR–visible absorption spectral changes accompanying the 458-nm photolysis of  $2.5 \times 10^{-3}$  M CpRh(CO)<sub>2</sub> in deoxygenated decalin solution containing 0.05 M AsPh<sub>3</sub> at 293 K. Spectra are depicted following 4 h irradiation time intervals; initial spectrum recorded prior to photolysis. The weak features at 1952 and 2030 cm<sup>-1</sup> in the initial spectrum are <sup>13</sup>CO isotope bands of the parent complex.

observed during the photolyses, confirming the nature of the products in these solution photoreactions. Consequently, the photochemical reactivity of CpRh(CO)<sub>2</sub> in decalin solutions containing excess ligand is again understood to proceed via the solvated monocarbonyl complex, which is subsequently scavenged by the respective ligand in competition with the C–H activation process (see eqs 3 and 4).



The Si–H bond activation photochemistry of CpRh(CO)<sub>2</sub> has been studied following excitation at 458 nm in 293 K decalin solutions containing various concentrations (0.001–0.3 M) of triethylsilane (Et<sub>3</sub>SiH). The observed UV–vis and FTIR spectral progressions from each of the Et<sub>3</sub>SiH solutions are analogous to those reported previously at higher [Et<sub>3</sub>SiH]<sup>6b</sup> and confirm that these are clean and complete photochemical conversions to the CpRh(CO)(SiEt<sub>3</sub>)H photoproduct. In each case, the spectra of the photoproducts in solution are also identical to that of the isolated complex.<sup>6b</sup> Consequently, the photoreactivity of CpRh(CO)<sub>2</sub> is again interpreted in terms of competing Si–H and C–H activation processes for the solvated CpRh(CO) complex (see eqs 5 and 6). Table 1 summarizes the infrared data



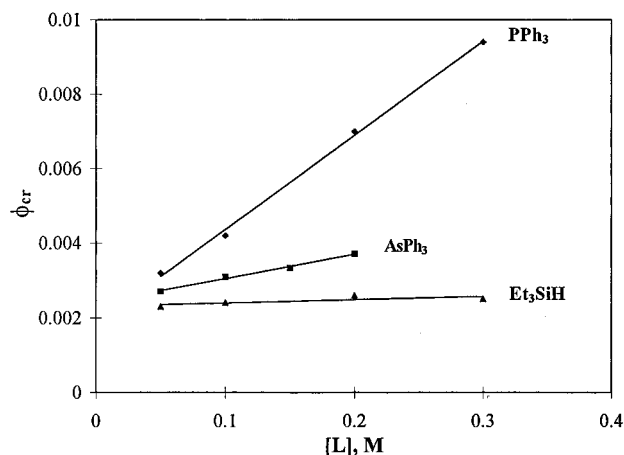
recorded for the various photoproducts generated in room-temperature solution.

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**Table 1. Infrared Carbonyl Stretching Bands for the Parent CpRh(CO)<sub>2</sub> Complex and the Various Photoproducts Generated Following 458-nm Irradiation in Solution at 293 K**

complex	solvent	$\nu(\text{CO}), \text{cm}^{-1}$
CpRh(CO) <sub>2</sub>	decalin	2046, 1982
CpRh(CO)AsPh <sub>3</sub>	decalin <sup>a</sup>	1948
CpRh(CO)PPh <sub>3</sub>	decalin <sup>a</sup>	1954
CpRh(CO)(SiEt <sub>3</sub> )H	decalin <sup>a</sup>	2009
<i>trans</i> -Cp <sub>2</sub> Rh <sub>2</sub> (CO) <sub>3</sub>	decalin	1984, 1836

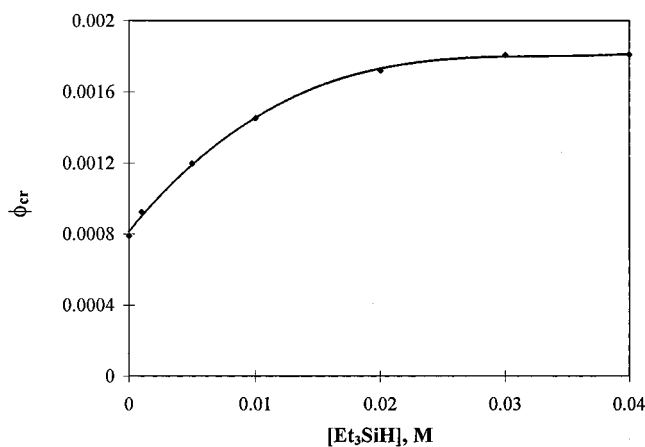
<sup>a</sup> Solutions contain 0.05 M of the respective entering ligand.



**Figure 2.** Plots of photochemical quantum efficiency ( $\phi_{\text{cr}}$ ) versus scavenging ligand [L] concentration for the 458-nm ligand substitution ( $L = \text{PPh}_3$  and  $\text{AsPh}_3$ ) and Si-H bond activation reactions of  $\text{CpRh}(\text{CO})_2$  in deoxygenated decalin at 293 K. Data for  $\text{PPh}_3$  and  $\text{Et}_3\text{SiH}$  are taken from ref 6b.

**Quantum Efficiencies.** Absolute photochemical reaction quantum efficiencies ( $\phi_{\text{cr}}$ ) have been measured for each of the above reactions following 458-nm excitation according to a procedure described in detail previously.<sup>17</sup> This kinetic method takes into account the changing inner filter effects caused by the increasing light absorption of the photoproduct during the reaction. Through this kinetic analysis, it was confirmed that the conversion to the respective monocarbonyl photoproduct proceeds essentially without interference from secondary photoprocesses or side reactions. The measured photochemical reaction quantum efficiencies ( $\phi_{\text{cr}}$ ) for the ligand photosubstitution and Si-H activation reactions of  $\text{CpRh}(\text{CO})_2$  in deoxygenated decalin at 293 K are depicted in Figure 2 for the ligand concentrations between 0.05 and 0.3 M (data for  $\text{PPh}_3$  and  $\text{Et}_3\text{SiH}$  have been obtained previously<sup>6b</sup>). In the case of the  $\text{PPh}_3$  and  $\text{AsPh}_3$  entering ligands, it can be seen that there is an increasing linear dependence of  $\phi_{\text{cr}}$  with  $[\text{PPh}_3]$  and  $[\text{AsPh}_3]$  whereas the  $\phi_{\text{cr}}$  data are essentially unaffected by  $[\text{Et}_3\text{SiH}]$ . Importantly, when photolyses were carried out in a CO-saturated (ca.  $1.0 \times 10^{-2} \text{ M}$ )<sup>15</sup> decalin solution, there was no change observed in either the UV-vis and FTIR spectral progression or the determined quantum efficiencies for any of these photochemical reactions with ligand concentrations in the range 0.05–0.3 M.

Photoreactivity quantum efficiencies at 458 nm have also been obtained for  $\text{CpRh}(\text{CO})_2$  in decalin with lower concentrations (0.001–0.04 M) of added  $\text{Et}_3\text{SiH}$ . These results are shown in Figure 3, including the photochemi-



**Figure 3.** Plots of photochemical quantum efficiency ( $\phi_{\text{cr}}$ ) versus  $\text{Et}_3\text{SiH}$  concentration for the 458-nm Si-H bond activation reaction of  $\text{CpRh}(\text{CO})_2$  in deoxygenated decalin at 293 K.

cal quantum efficiency value representing the binucleation reaction (see eq 2) in the absence of  $\text{Et}_3\text{SiH}$  (the intercept point). Significantly, when the binucleation reaction was measured under the CO-saturated conditions, it was found that no photochemical change took place at all. It is concluded, therefore, that the photo-produced solvated  $\text{CpRh}(\text{CO})$  complex is, under these kinetic conditions, effectively scavenged by CO and returns to the parent complex instead of forming  $[\text{CpRh}(\mu\text{-CO})_2]$  and subsequently *trans*- $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ . However, at  $\text{Et}_3\text{SiH}$  concentrations above 0.04 M, it was determined that there was no influence of added CO on the  $\phi_{\text{cr}}$  values.

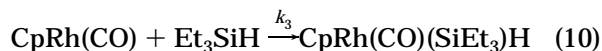
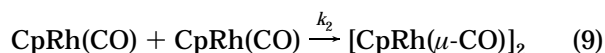
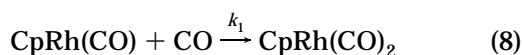
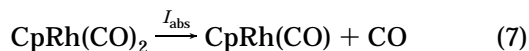
**Photochemical Pathways.** From the above quantum efficiency results it is clear that there are two different reaction routes occurring upon 458-nm excitation. In accordance with the above discussion, the key reaction intermediates in both mechanisms are understood to be produced rapidly following light absorption and ligand dissociation from ligand-field (LF) excited states.<sup>6</sup> All of the reaction pathways observed to take place have been rationalized by invoking the initial formation of the 16-electron  $\text{CpRh}(\text{CO})$  intermediate. As noted above, this species is extremely reactive, and it undergoes rapid solvation and subsequently effective C-H bond activation at the high concentrations of decalin (RH) in solution.<sup>4–8</sup> However, this species has not been observed in any of our solution photochemical experiments, as anticipated since flash photolysis measurements have shown that the alkyl hydrido  $\text{CpRh}(\text{CO})(\text{R})\text{H}$  photoproduct has a transient lifetime on the order of milliseconds.<sup>4b</sup> In the absence of an added scavenging ligand, the solvated  $\text{CpRh}(\text{CO})$  intermediate eventually reacts either with another  $\text{CpRh}(\text{CO})$  molecule or CO (both of which are present at low concentration) to form  $[\text{CpRh}(\mu\text{-CO})_2]$  (and subsequently *trans*- $\text{Cp}_2\text{Rh}_2(\text{CO})_3$  or  $\text{CpRh}(\text{CO})_2$ , respectively). The latter process does not affect the overall photochemistry, whereas the former route does yield the identified carbonyl-bridged complex. Overall, the binuclear reaction takes place with a low quantum efficiency (see the intercept point of Figure 3) and is completely suppressed in a CO-saturated solution. However, in the presence of excess  $\text{AsPh}_3$ ,  $\text{PPh}_3$ , and  $\text{Et}_3\text{SiH}$  ligands, the solvated  $\text{CpRh}(\text{CO})$  complex is clearly able to react completely

(17) Lees, A. J. *Anal. Chem.* **1996**, *68*, 226.

to form the corresponding CpRh(CO)AsPh<sub>3</sub>, CpRh(CO)-PPh<sub>3</sub>, and CpRh(CO)(SiEt<sub>3</sub>)H photoproducts.

The linear dependence of the  $\phi_{cr}$  results for AsPh<sub>3</sub> and PPh<sub>3</sub> at high [L] (see Figure 2) is unusual though, and it is necessary to invoke a second process to rationalize this. Previously, an initial ring slippage step has been postulated (see Scheme 2) to account for the low quantum efficiency at 458 nm. The implication is that the back ring-slip reaction ( $\eta^3 \rightarrow \eta^5$ ) dominates at low concentrations of entering ligand, which effectively returns the intermediate to starting complex. This route is inconsequential with respect to the overall photochemistry and makes no contribution to the quantum efficiency. When higher concentrations of the entering AsPh<sub>3</sub> or PPh<sub>3</sub> ligands are present, however, then the ligand substitution reaction becomes competitive with the back ring-slip process and the route to the CpRh(CO)L photoproducts is more efficient. Hence, incorporating this kinetic feature does explain why the quantum efficiencies increase at higher [L] values. The results for AsPh<sub>3</sub> support this postulated competitive scavenging mechanism because it is clear from a comparison of the line slopes in Figure 2 that PPh<sub>3</sub> is able to scavenge much more effectively than AsPh<sub>3</sub>, presumably because it is a better nucleophile with less steric constraint.

**Kinetic Analyses.** As noted above, different photochemical pathways appear to occur from the two excited states, so it is necessary to treat their kinetics separately. The following equations represent a kinetic analysis for the CpRh(CO)<sub>2</sub> molecules undergoing rapid CO dissociation from the higher energy LF state, eqs 7-13. It considers the competing pathways for the solvated primary photoproduct and derives a quantum efficiency ( $\phi$ ) expression for the case when Et<sub>3</sub>SiH is present as a scavenging ligand.



thus,

$$\frac{d[\text{CpRh(CO)}]}{dt} = I_{\text{abs}} - k_1[\text{CpRh(CO)}][\text{CO}] - k_2[\text{CpRh(CO)}][\text{CpRh(CO)}] - k_3[\text{CpRh(CO)}][\text{Et}_3\text{SiH}] = 0 \quad (11)$$

on rearrangement,

$$\phi = \frac{k_3[\text{Et}_3\text{SiH}]}{k_1[\text{CO}] + k_2[\text{CpRh(CO)}] + k_3[\text{Et}_3\text{SiH}]} \quad (12)$$

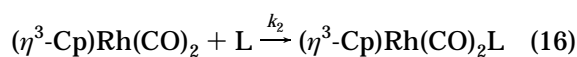
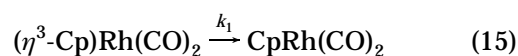
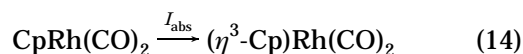
where,

$$\phi = 1; \text{ when } \{k_1[\text{CO}] + k_2[\text{CpRh(CO)}]\} \ll k_3[\text{Et}_3\text{SiH}] \quad (13)$$

It should be recognized that the reaction of CpRh(CO) with RH is not incorporated in the above analysis, as CpRh(CO)(R)H is unstable and does not influence the overall photochemistry or the reaction quantum efficiency. In eq 7, it is assumed that the hydrocarbon-solvated CpRh(CO) intermediate is produced with unity efficiency on light absorption and so the analysis does not account for nonradiative deactivation mechanisms from the excited state. In fact, the actual quantum yield for photoproduct formation ( $\phi_{cr}$ ) will be represented by the above expression for  $\phi$  (eqs 12 and 13) multiplied by the branching ratio  $k_{CO}/(k_{CO} + k_{nr})$ , where  $k_{CO}$  is the rate constant for the CO dissociation reaction from the excited state to produce the CpRh(CO) intermediate and  $k_{nr}$  is the summation of the nonradiative relaxation rate constants from this excited state. However, this kinetic analysis, which is based on an immediate CO dissociation process from the upper energy LF excited state, does predict that  $\phi_{cr}$  will be independent of ligand concentration at low concentrations of CpRh(CO)<sub>2</sub> and CO, as actually revealed by the experimental data for Et<sub>3</sub>SiH (see Figure 2). Similar analyses can be performed for the ligand substitution reactions with AsPh<sub>3</sub> and PPh<sub>3</sub> (here L simply replaces Et<sub>3</sub>SiH in the above eqs 10-13), accounting for the small values of  $\phi_{cr}$  at low L concentration. Significantly, prior saturation of the hydrocarbon solution with CO gas (ca.  $1 \times 10^{-2}$  M) was not observed to influence the measured  $\phi_{cr}$  values for ligand substitution when [L] > 0.04 M; this is consistent with the kinetic conditions of eq 13 and a negligible extent of back reaction with CO.

The above kinetic scheme also rationalizes the behavior of the  $\phi_{cr}$  data observed at low Et<sub>3</sub>SiH concentration (see Figure 3). Here, the quantum efficiencies exhibit saturation-type kinetics, the conditions for eq 13 only existing at the plateau (for [Et<sub>3</sub>SiH] > 0.04 M), when there is complete conversion to the CpRh(CO)-(SiEt<sub>3</sub>)H photoproduct (via eq 10). At lower [Et<sub>3</sub>SiH] values though, scavenging of the solvated CpRh(CO) intermediate by CO and CpRh(CO) (eqs 8 and 9) becomes significant and the quantum efficiencies for the Si-H activation reaction are reduced following the addition of CO. Indeed, no photochemistry whatsoever was observed in CO-saturated decalin solutions without Et<sub>3</sub>SiH present.

Turning to the other mechanism, the following kinetic analysis illustrates the competing processes following an initial ring slippage ( $\eta^5 \rightarrow \eta^3$ ) process of the Cp ligand from the lower energy LF excited state of CpRh(CO)<sub>2</sub>, eqs 14-19. Here, a quantum efficiency ( $\phi$ ) is derived for the situation when scavenging PPh<sub>3</sub> and AsPh<sub>3</sub> ligands (L) are present.



thus,

$$\frac{d[(\eta^3\text{-Cp})\text{Rh}(\text{CO})_2]}{dt} = I_{\text{abs}} - k_1[(\eta^3\text{-Cp})\text{Rh}(\text{CO})_2] - k_2[(\eta^3\text{-Cp})\text{Rh}(\text{CO})_2][\text{L}] \quad (17)$$

on rearrangement,

$$\phi = \frac{k_2[\text{L}]}{k_1 + k_2[\text{L}]} \quad (18)$$

where,

$$\phi = \frac{k_2[\text{L}]}{k_1} \text{ when } k_2[\text{L}] \ll k_1 \quad (19)$$

Once again, this kinetic analysis does not account for quantum inefficiencies, and it assumes that the hydrocarbon-solvated  $(\eta^3\text{-Cp})\text{Rh}(\text{CO})_2$  intermediate is formed in unity efficiency on excitation. Thus, the actual quantum efficiency for photoproduct formation ( $\phi_{\text{cr}}$ ) will be represented by the above expression for  $\phi$  (eqs 18 and 19) multiplied by the branching ratio  $k_{\text{slip}}/(k_{\text{slip}} + k_{\text{nr}})$ , where  $k_{\text{slip}}$  is the rate constant for the cyclopentadienyl ring slippage ( $\eta^5 \rightarrow \eta^3$ ) process (itself a dissociative step) and  $k_{\text{nr}}$  is the summation of the rate constants for non-radiative decay from the excited state. Importantly, this kinetic analysis is based on ligand scavenging of the photoproduct intermediate that is competitive with the back ring slip ( $\eta^3 \rightarrow \eta^5$ ) process. The mechanism does, however, predict the linear dependence of  $\phi_{\text{cr}}$  on  $[\text{L}]$ , which is experimentally observed at high concentrations of scavenging ligand for both  $\text{PPh}_3$  and  $\text{AsPh}_3$  (see Figure 2).

Strictly speaking, the quantum efficiencies ought to go to zero in the absence of entering ligand (as all  $\eta^3\text{-Cp}$  species revert to the  $\eta^5\text{-Cp}$  complex). However, the low-lying absorption band of  $\text{CpRh}(\text{CO})_2$  is broad, and the excitation at 458 nm takes place into a long-wavelength shoulder. Obviously, the lowest energy LF excited state is not populated exclusively at 458 nm. One should note that similar kinetic expressions could be reached even if a more extensive  $\eta^5 \rightarrow \eta^1$  hapticity change occurred (or indeed if the Cp ligand is completely dissociated but able to recombine competitively with the ligand scavenging, *vide infra*). Another relevant point is that for the linear dependence of  $\phi_{\text{cr}}$  with  $[\text{L}]$  to occur, then the reactions quantum efficiencies must be low (as a condition of eq 19); this is indeed the case for the excitations at 458 nm. Clearly, such kinetic behavior rationalizes why the quantum efficiencies are influenced by the different scavenging abilities of the various  $\text{AsPh}_3$  and  $\text{PPh}_3$  ligands, as reflected in the slopes of these lines of Figure 2. In a similar vein, the photochemistry of  $\text{CpRh}(\text{CO})_2$  was also studied at 458 nm in decalin solution containing 0.05 M pyridine; however, under these experimental conditions, the only reaction observed was the residual dimerization of  $\text{CpRh}(\text{CO})_2$  occurring from the higher energy LF excited state (eq 9). Apparently, the pyridine ligand is too poor a nucleophile to effectively scavenge the solvated  $(\eta^3\text{-Cp})\text{Rh}(\text{CO})_2$  intermediate.

It should be noted that one could reach a similar kinetic conclusion if the above electronically excited state,  $[\text{CpRh}(\text{CO})_2]^*$ , is considered to react directly with the entering ligand to form a 20-electron species via an associative process. This pathway is unrealistic, though,

because ultrafast spectroscopic measurements have confirmed that the CO dissociation and solvation steps are much too rapid<sup>4</sup> for diffusion-controlled ligand scavenging processes to be competitive. Consequently, the wavelength-dependent behavior of  $\phi_{\text{cr}}$  has made it necessary to invoke two different *reaction intermediates* in the mechanism. Additionally, it should be recognized that nonradiative relaxation rates may begin to be affected at the higher  $[\text{L}]$  values. Such solvation effects would, however, not account for the observed plots as they would tend to increase  $k_{\text{nr}}$  processes and, hence, result in lower  $\phi_{\text{cr}}$  values.<sup>9c</sup>

#### Relationship to Other Photochemical Studies.

A significant feature of this study is that it has been able to comprehensively rationalize the solution photochemistry of the C–H activating  $\text{CpRh}(\text{CO})_2$  system. As noted earlier, the quantum efficiencies implicate two different LF excited states which are populated in varying proportion depending upon the wavelength of excitation.<sup>6b</sup> The present work illustrates that there are two short-lived reaction intermediates formed upon 458-nm irradiation and via quantitative measurements portrays their different reactivities toward hydrocarbon, silane, and other scavenging ligands. Importantly, the interpretation of the photophysical and quantitative photochemical properties is entirely consistent with the previous observations concerning  $\text{CpRh}(\text{CO})_2$  and related molecules.<sup>3–9</sup>

Recent ultrafast spectroscopy with  $(\text{acac})\text{Rh}(\text{CO})_2$  ( $\text{acac}$  = acetylacetonate) has shown that on excitation the unsolvated  $(\text{acac})\text{Rh}(\text{CO})_2$  species is formed promptly and that the solvated complex,  $(\text{acac})\text{Rh}(\text{CO})\cdots\text{S}$ , is reached within just a few picoseconds.<sup>4d</sup> Indeed, our observed solution photochemistry agrees with the infrared spectra obtained on photolysis of  $\text{LM}(\text{CO})_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{L} = \text{RCOCHCOR}'$ ;  $\text{R}, \text{R}' = \text{CH}_3, \text{CF}_3$ ) complexes at high dilution in  $\text{CH}_4$ , Ar, CO, and  $\text{N}_2$  matrices at 12 K which has provided evidence for  $\text{LM}(\text{CO})$ ,  $\text{L}'\text{M}(\text{CO})_2$  ( $\text{L}' =$  unidentate form of L), and  $\text{LM}(\text{CO})(\text{N}_2)$  species.<sup>18</sup> Moreover, in liquefied rare gas (Kr, Xe) solvents, the  $\text{Cp}^*\text{Rh}(\text{CO})\text{Kr}$  and  $\text{Cp}^*\text{Rh}(\text{CO})\text{Xe}$  complexes have been generated and it has been shown that they react rapidly with hydrocarbons, incurring activation energies of only a few kcal mol<sup>-1</sup>.<sup>5c,d,7</sup> In the gas phase, the unsolvated  $\text{CpRh}(\text{CO})_2$  complex has been detected spectroscopically and the rates of reaction with alkanes have been measured; it has been found that the activation of C–H bonds essentially occurs immediately upon collision for an alkane of moderate size.<sup>8</sup> It should also be noted that while matrix isolation work on  $\text{CpRh}(\text{CO})_2$  has identified only small amounts of the monocarbonyl complex, presumably because of an effective back reaction with “caged” CO, it has again been shown that the reaction of the photoproduct intermediate with RH is rapid, even in the matrix at 12 K.<sup>3</sup> Consequently, the present interpretation of the quantitative solution reactivity, which implicates extremely fast decay from a LF excited state to rapidly yield a monocarbonyl primary photoproduct, is fully concordant with all of the previously obtained photochemical data on  $\text{CpRh}(\text{CO})_2$ . Importantly, the current rationale is also consistent with the extensive information available for other metal carbonyl systems, which has concluded that following

(18) Brouwers, A. M. F.; Oskam, A.; Narayanaswamy, R.; Rest, A. *J. Chem. Soc., Dalton Trans.* **1982**, 1777.

UV light absorption the CO dissociation reaction takes place promptly (within picoseconds) to yield highly reactive photofragments.<sup>19,20</sup>

The present results imply that there is an additional primary photoproduct formed immediately after light absorption, supporting our earlier suggestion of a reaction pathway involving a ring slipped η<sup>3</sup>-Cp intermediate.<sup>6b</sup> The lifetime of this solvated intermediate, (η<sup>3</sup>-Cp)Rh(CO)<sub>2</sub>···S, can be estimated from the scavenging data. Recognizing that the φ<sub>cr</sub> results are already above the value for the CO dissociation reaction when either [AsPh<sub>3</sub>] or [PPh<sub>3</sub>] = 0.05 M (see Figure 2) and making an assumption that the scavenging process is diffusion controlled (with k<sub>diff</sub> between 10<sup>9</sup> and 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>),<sup>19,20</sup> then the lifetime of this transient should lie between 2 and 20 ns. However, it is perhaps not surprising that the previous time-resolved studies have not discovered the presence of this second reaction intermediate, considering that all of these investigations were carried out at shorter excitation wavelengths than the present work at 458 nm and, hence, have been concerned with the CpRh(CO) primary photoproduct. Furthermore, a solvated ring slipped species, (η<sup>3</sup>-Cp)-Rh(CO)<sub>2</sub>···S, will be substantially more difficult to identify spectroscopically (either in transient UV-vis or IR spectra) than the monocarbonyl complex if it is initially produced in a very low concentration because of inadequate light absorbance into the long-wavelength LF tail. Importantly, though, there is other convincing spectroscopic evidence for a η<sup>3</sup>-Cp species. In the photolysis of CpCo(CO)<sub>2</sub> at high dilution in a CO matrix at 12 K, the CpCo(CO)<sub>3</sub> complex is produced.<sup>21</sup> Moreover, in recent matrix isolation work it has been determined that (η<sup>3</sup>-Cp)Rh(CO)<sub>3</sub> is formed upon prolonged long-wavelength (>400 nm) irradiation of CpRh(CO)<sub>2</sub> in CO matrices<sup>22</sup> and, as noted above, a η<sup>3</sup>-Cp intermediate is well-established in the thermal chemistry of CpRh(CO)<sub>2</sub>.<sup>13,16</sup>

It is striking that the two key reaction intermediates in Schemes 1 and 2 exhibit such divergent kinetic reactivities. The quantum efficiency data and analysis of the reaction pathways illustrate that the CpRh(CO)···S species is highly reactive toward C–H and Si–H bonds, whereas the (η<sup>3</sup>-Cp)Rh(CO)<sub>2</sub>···S complex is unable to activate the alkane or silane molecules. The key to this observation may lie in the fact that the electron densities at the metal centers are so different.

**Table 2. Photochemical Quantum Efficiencies (φ<sub>cr</sub>) as a Function of Excitation Wavelength for the Intermolecular Si–H Bond Activation Reaction of CpRh(CO)<sub>2</sub> in Various Solvents at 293 K<sup>a</sup>**

solvent <sup>b</sup>	λ <sub>ex</sub> , nm		
	313	366	458
<i>n</i> -hexane	0.29	0.078	0.0032
<i>n</i> -heptane	0.29	0.060	0.0023
<i>n</i> -octane	0.22	0.081	0.0026
isooctane	0.31	0.089	0.0026
decalin	0.15	0.060	0.0024
benzene	0.035	0.017	0.00074
benzene- <i>d</i> <sub>6</sub>	0.054	0.024	0.00071
toluene	0.036	0.0074	0.00082
<i>p</i> -xylene	0.061	0.033	0.0014

<sup>a</sup> Values were determined in triplicate and were reproducible to within ±10%. <sup>b</sup> Solutions contain 0.05 M Et<sub>3</sub>SiH.

The CpRh(CO)···S complex obviously has only one CO ligand, and this may provide sufficient electron density at the metal center for it to undergo oxidative addition. In comparison, the (η<sup>3</sup>-Cp)Rh(CO)<sub>2</sub>···S species has two CO ligands which will clearly be more effective at withdrawing electron density from the metal, perhaps leaving the complex with insufficient electron density to activate C–H bonds. Further work in our laboratory is continuing on a series of (Cp-X)Rh(CO)<sub>2</sub> (X = substituent) complexes to explore the relationship between the electronic characteristics of the photoproduct intermediate and its C–H activation efficiency.

**Solvent Dependence.** Photochemical excitations have been performed on CpRh(CO)<sub>2</sub> in various deoxygenated hydrocarbon solutions following excitation at wavelengths between 313 and 458 nm. In each case, excess Et<sub>3</sub>SiH (0.05 M) was added to the solution, which facilitates scavenging of the unstable CpRh(CO)(R)H species and results in conversion to the CpRh(CO)-(SiEt<sub>3</sub>)H photoproduct (according to eqs 5 and 6). Under these conditions, the solution photochemistry was observed to be clean and complete without significant interference from secondary photoprocesses or side reactions at any of the excitation wavelengths used. Furthermore, these solutions were monitored in the dark, and it was determined that at 293 K there is a negligible thermal reaction taking place during the course of these photolysis experiments. The smooth transformations have enabled quantitative photochemical measurements to be made using the procedure described above; absolute quantum efficiencies obtained for the range of hydrocarbon solvents and excitation wavelengths studies are shown in Table 2.

It is again clear from the quantum efficiency values in all of the solvents that the photoreactivity is strongly dependent on the exciting wavelength. These results further support the above rationale that in CpRh(CO)<sub>2</sub> there are two LF excited states with quite different reactivities. However, the photoefficiency data also reveal a general trend, with φ<sub>cr</sub> for a common excitation wavelength apparently ordered for the hydrocarbons: chain alkane > decalin > aromatic. Moreover, within the aromatic solvents, the φ<sub>cr</sub> data at a particular excitation wavelength are generally higher if there are more CH<sub>3</sub> groups in the molecule. It is also noticeable that the φ<sub>cr</sub> value obtained for benzene-*d*<sub>6</sub> is not dissimilar to the other aromatic solvents. Importantly, the photochemical reactions were further investigated with solutions that had been prior saturated with CO gas

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([CO] =  $1 \times 10^{-2}$  M),<sup>15</sup> and this addition did not affect the observed spectral results or the quantum efficiencies determined.

To interpret the quantum efficiency data, one must again consider the initial kinetic events taking place in the photochemistry. Following light absorption the photoproducted monocarbonyl complex is known to be solvated rapidly in the hydrocarbon solution, and the lack of a CO concentration dependence on  $\phi_{cr}$  is confirmation that the back reaction with CO (eq 8) is not competitive with either the solvation step or the subsequent reaction of the solvated complex with Et<sub>3</sub>SiH (eq 10). Therefore, the solvent variations in  $\phi_{cr}$  cannot be attributed to differing kinetic reactivities of the substrates. Although there may well be different rates of oxidative addition among these hydrocarbons and also for the subsequent transformation of CpRh(CO)(R)H to CpRh(CO)(SiEt<sub>3</sub>)H, these steps will not influence the quantum efficiency here as there is always a complete conversion to the photoproduct, without an effective back reaction. Consequently, the quantum efficiencies in CpRh(CO)<sub>2</sub> must be predominantly determined by the photophysical events that occur prior to the CO dissociation. The observed lack of any significant isotope effect for benzene-*d*<sub>6</sub> is also consistent with an interpretation where the oxidative addition step does not influence the  $\phi_{cr}$  value. It should be also noted that these conclusions are substantiated by recent ultrafast spectroscopic observations on Cp\*M(CO)<sub>2</sub> (M = Rh, Ir) in solution, which have eliminated the possibility of both geminate and diffusional CO recombination processes influencing the molecular dynamics following light absorption.<sup>4e</sup>

Hence, the major factor affecting the photoefficiencies is understood to be the extent of nonradiative relaxation from the higher energy LF excited state responsible for the dissociative pathway. In effect, it is the branching ratio between the photophysical deactivation and ligand dissociation processes of [CpRh(CO)<sub>2</sub>]\* which determines the amount of primary photoproduct formed, prior to all of these medium becoming solvated and eventually converted to the CpRh(CO)(SiEt<sub>3</sub>)H product. Consequently, the key to understanding the varying nonradiative relaxation rates in this system may lie in the vibrational coupling taking place between the excited state of CpRh(CO)<sub>2</sub> and the solvent medium. Each hydrocarbon has several vibrational modes that could couple with the [CpRh(CO)<sub>2</sub>]\* complex, although it is perhaps relevant that the aromatic molecules (which have lower  $\phi_{cr}$  values) exhibit similar modes to those of the Cp ring and that benzene and toluene possess overtone bands in the carbonyl-stretching region. In this respect, earlier studies of intermolecular C–H activation in (HBPz<sub>3</sub>)Rh(CO)<sub>2</sub> (Pz = 3,5-dimethylpyrazolyl)<sup>9c</sup> and luminescence from W(CO)<sub>5</sub>L (L = a

substituted pyridine)<sup>23</sup> have concluded that the rates of nonradiative decay from the excited state are increased in aromatic solvents compared to the alkanes.

**Radical Mechanism.** As noted in the kinetic analysis above, a ring slippage intermediate is implicated in the photochemistry from the lower energy LF excited state, although the  $\phi_{cr}$  results do not preclude a mechanism involving complete Cp ligand dissociation and then recombination of the radicals formed. Indeed, spin trapping ESR experiments on Cp\*Rh(CO)<sub>2</sub> have provided evidence of such radicals following long-wavelength photolysis in hexane solution.<sup>24</sup> In order to investigate this possibility further, absolute quantum efficiencies for photoreaction of CpRh(CO)<sub>2</sub> in the radical scavenging solvents CHCl<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Br have been measured at 458 nm to see if the photoefficiencies are increased. The quantum efficiency results in CHCl<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Br are  $3.1 \times 10^{-3}$  and  $3.1 \times 10^{-3}$ , respectively, quite similar, in fact, to the values obtained in the alkanes. This observation cannot account for the low quantum efficiencies at long wavelength and does, therefore, not support a dissociative mechanism involving complete dissociation of the Cp ligand as the main reaction pathway.

## Conclusions

Quantitative measurements of the solution photochemistry of CpRh(CO)<sub>2</sub> in various hydrocarbon solvents have illustrated that different reactivities occur from two low-lying LF excited states. Kinetic analysis of the quantum efficiency data has enabled us to comprehensively account for all of the photochemical pathways, including dimerization, CO recombinations, ligand substitution, and both C–H and Si–H bond activation processes. Variations in the quantum efficiencies for the different hydrocarbon solutions are shown to be brought about by photophysical events taking place prior to CO dissociation.

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**Supporting Information Available:** Figures of UV–vis absorption spectral changes accompanying the 458-nm photolysis of CpRh(CO)<sub>2</sub> in decalin solution with and without added AsPh<sub>3</sub> ligand (3 pages). Ordering information is given on any current masthead page.

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