Quantitative Photochemistry and Mechanisms for a Series of Rhodium Dicarbonyl Derivatives

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A comparison of the electronic properties and photochemical reactivity efficiencies for a series of rhodium dicarbonyl complexes with the general formula $XRh(CO)_2$, where X = Cp (η^5-C_5H_5), Cp′ (η^5-C_5H_4Me), Cp″ (η^5-C_5HMe_4), Cp* (η^5-C_5Me_5), and ind (η^5-C_9H_7), and acac ($C_5H_7O_2$), has been achieved. The photochemical reactions of these molecules have been studied under a variety of experimental conditions, where binucleation, intermolecular Si−H and C−H bond activation, and ligand substitution processes occur. Modifications of the unique ligand in this system enable the photoefficiency of the CO dissociation reaction to be substantially changed. The absolute reaction quantum efficiencies (ϕ_{cr}) are markedly different and strongly wavelength dependent for each of the molecules studied. The values of ϕ_{cr} decrease in the order $CpRh(CO)_2 > Cp'Rh(CO)_2 > Cp^*Rh(CO)_2 \gg (acac)Rh(CO)_2 > (ind)Rh(CO)_2$ and vary by over 3 orders of magnitude depending on the complex chosen and the excitation wavelength employed. The results obtained indicate that the photoefficiencies of these complexes are predominantly determined by radiative and nonradiative decay processes of neighboring excited states and the electronic and steric properties of the unique ligand.

Introduction

Millions of dollars are wasted every year due to the burn off of methane gas, which is a byproduct of the fossil fuel industry. Methane gas is an extremely rich energy resource, but unfortunately, it is very difficult to transport in an economical fashion. It would be advantageous if methane could be converted into a material that would be more easily utilized. In the early 1980s a series of compounds were discovered that might assist in performing this task. A variety of cyclopentadienyliridium hydride and carbonyl complexes were observed to have the ability to photochemically activate alkane C−H bonds under relatively mild conditions. Subsequently, the photochemical mechanisms occurring in these types of organometallic complexes have been the focus of considerable attention.[1] A more complete mechanistic understanding may make it possible to better utilize these systems in a wide spectrum of areas, such as homogeneous catalysis, synthetic chemistry, reduction in greenhouse gases, and extension of energy resources.

A variety of photochemical techniques have been employed in an effort to determine the mechanisms operating in these organometallic systems. The photochemistry of complexes with the general formula XML_2, where X = η^5-C_5H_5, η^5-C_5Me_5, or $HBPz^*_3$ (Pz* = 3,5-dimethylpyrazolyl), M = Rh or Ir, and L = CO, H_2, C_2H_4, or PR_3, has been studied under competitive ligand-scavenging conditions,[1,2] by low-temperature matrix isolation[3] and ultrafast spectroscopy,[4] and in low-temperature liquid noble gases.[5,6] Recently we have performed detailed

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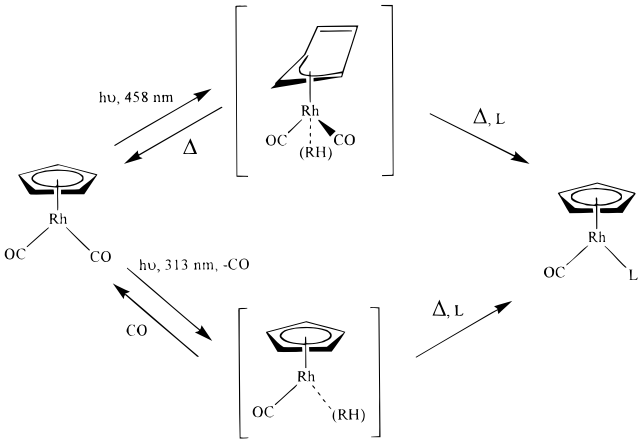
Scheme 1



experiments to determine the influence of different hydrocarbon substrates on the photoefficiencies of $CpRh(CO)_2$, $Cp^*Rh(CO)_2$, and $(HBPz^*_3)Rh(CO)_2$.[7] Quantitative photochemical measurements have revealed that these systems possess a substantial wavelength-dependent reaction photoefficiency. The primary photoproduced intermediate responsible for intermolecular C−H bond activation has been concluded to be the XRh(CO) coordinatively unsaturated species, in agreement with the time-resolved and low-temperature studies.[4−6] However, the strong wavelength dependence observed in the ligand substitution studies has implicated an additional reaction intermediate following excitation in the visible region. Apparently, each of these rhodium complexes possesses two ligand field (LF) states with distinct reactivities. A higher-lying state is accessed via excitation at shorter wavelengths ($\lambda_{ex} = 313$ nm) and results in predominantly CO dissociation and effective C−H activation, and a lower-lying energy state is populated via excitation at longer wavelengths ($\lambda_{ex} = 458$ nm), which is understood to lead to dechelation of the unique ligand (suggested to be ring slippage) and inefficient C−H activation (see Scheme 1).[7a−i]

While it has been shown that complexes of the general formula $XRh(CO)_2$ have a very interesting photochemistry, there is still much to be learned about the optimum conditions for photoreactivity and intermolecular C−H bond activation chemistry. Consequently, the objective of this study was to investigate the influence on the quantitative photochemistry for a series of related molecules (see Figure 1), using a recently developed photokinetic procedure.[8] Here, we report the results of detailed measurements of absolute photoefficiencies for these rhodium dicarbonyl derivatives following three modifications to the unique ligand. First, the effect of increased electron-donating substituents on the cyclopentadienyl ring by different degrees of methylation has been explored. In our earlier work only comparisons between the Cp and Cp* derivatives at two excitation wavelengths were obtained.[7b,d,h] Second, the effect of replacing the cyclopentadienyl ring with an indenyl ring has been investigated. Third, the influence of changing from a cyclopentadienyl complex to the pseudo-square-planar structure of the $(acac)Rh(CO)_2$ (acac = acetylacetonato) complex has been studied. In all of the systems investigated we have quantitatively measured the photochemistry at three different excitation wavelengths in the 313−458 nm region.

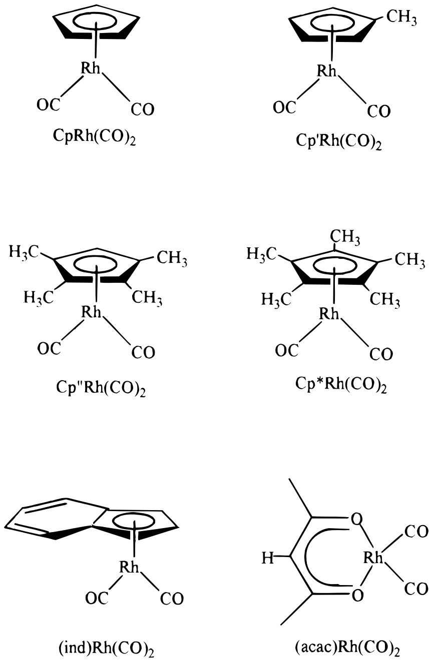


Figure 1. $XRh(CO)_2$ systems investigated in this work.

Experimental Section

Materials. Dicarbonylchlororhodium(I) dimer and dicarbonylbis(ethylene)rhodium(I) dimer were obtained in high purity (>99%) from Pressure Chemical Co. and used as received. Acetylacetonatodicarbonylrhodium(I) was obtained from Pressure Chemical Co. in high purity (>99%). Dicarbonylpentamethylcyclopentadienylrhodium(I) and cyclopentadienylthallium were purchased from Aldrich Chemical Co. in high purity (97%) and used without further purification. Triethylsilane was obtained from Aldrich Chemical Co. and used after triple distillation under nitrogen. Methylcyclopentadienyl dimer was obtained from Aldrich Chemical Co. and freshly cracked prior to synthesis to yield the monomer methylcyclopentadiene. Tetramethylcyclopentadienylpotassium was obtained from Aldrich Chemical Co. and used as received. Tetrahydrofuran and hexanes used in syntheses were obtained as reagent grade from Fisher Chemical Co. and were dried and deoxygenated via sodium/benzophenone and potassium/benzophenone distillation, respectively. Spectroscopic grade *n*-hexane used in photochemical studies was obtained from Aldrich Chemical Co. and used after deoxygenation via nitrogen purging. Indene was obtained as technical grade (>90%) from Aldrich Chemical Co. and was freshly distilled prior to use. The entering ligand *cis*-cyclooctene was purchased from Aldrich Chemical Co. in high purity (>99%). Neutral alumina chromatographic adsorbant (80−200 mesh) and Brockman Activity I neutral alumina (80−200 mesh) were obtained from Fisher Chemical Co.

The argon and nitrogen gases used for solvent deoxygenation and synthesis were purchased as high research grade (>99.99% purity) and were deoxygenated and dried by passage over potassium hydroxide

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(Fisher Chemical Co.), 5 Å molecular sieves, and a pelletized copper catalyst (BASF R3-11, Schweizerhall, Inc.), according to a previously described procedure.[9] Carbon monoxide 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 alternating segments of calcium sulfate and 5 Å molecular sieves.

Syntheses. The $CpRh(CO)_2$, $Cp'Rh(CO)_2$ ($Cp' = \eta^5$-C_5H_4Me), $Cp''Rh(CO)_2$ ($Cp'' = \eta^5$-C_5HMe_4), and $(ind)Rh(CO)_2$ ($ind = \eta^5$-C_9H_7) were synthesized by methods previously described in the literature with modification.[10] $Cp^*Rh(CO)_2$ was obtained from Aldrich Chemical Co. and purified via recrystallization from *n*-pentane. $(acac)Rh(CO)_2$ was obtained from Pressure Chemical Co. and used as received. All syntheses were carried out under an inert atmosphere unless otherwise stated. THF and hexanes were freshly distilled prior to syntheses from their respective sodium and potassium ketyls. Sodium methylcyclopentadienide was generated fresh prior to synthesis via reaction of the freshly cracked methylcyclopentadiene with sodium metal in THF. Sodium indenide was prepared in a similar fashion with freshly distilled indene. All compounds were synthesized via reaction of either dicarbonylchlororhodium(I) or bis(ethylene)chlororhodium(I) dimer with their respective cyclopentadienyl or indenyl salts. Approximately stoichiometric conditions were followed (a 2:1 mole ratio of salt:dimer). $(ind)Rh(CH_2{=}CH_2)_2$ was prepared in high yield in accordance with a previously reported procedure in the literature.[10f]

$CpRh(CO)_2$. To a well-stirred solution of dicarbonylchlororhodium(I) dimer, $[Rh(CO)_2Cl]_2$, in hexanes (0.25 g, 0.64 mmol in 150 mL) was added cyclopentadienylthallium (1.75 g, 6.5 mmol). This solution was refluxed with stirring under a nitrogen atmosphere for 48 h. The product was purified via filtration and elution of a single bright yellow band from a 20 cm neutral alumina column with hexanes to yield a bright yellow oil (0.21 g, 73%). ^1H NMR (C_6D_6): δ 5.48 (s). IR (ν_{CO}, *n*-hexane): 2048, 1985 cm^{-1} (lit.[10a,b] (as liquid) 2051, 1987 cm^{-1}). UV−vis (λ_{max}, *n*-hexane): 221 nm ($\epsilon = 9600\ M^{-1}\ cm^{-1}$), 284 nm ($\epsilon = 3820\ M^{-1}\ cm^{-1}$), 320 nm (sh) ($\epsilon = 390\ M^{-1} cm^{-1}$), 420 nm (sh) ($\epsilon = 78\ M^{-1}\ cm^{-1}$) (lit.[7b] 420 nm (sh) ($\epsilon = 78\ M^{-1}\ cm^{-1}$)).

$Cp'Rh(CO)_2$. A 250 mL round-bottom Schlenk flask equipped with a stirbar was charged with 0.25 g (0.64 mmol) of the dicarbonylchlororhodium(I) dimer, $[Rh(CO)_2Cl]_2$. Using a syringe, 50 mL of THF was added to the flask, and the resulting solution was stirred to dissolve the solid. This solution was added via cannula transfer to a freshly prepared solution of sodium methylcyclopentadienide (in excess) in THF. The formation of a brown product was observed on mixing. After the solution was stirred for 12 h, the solvent was removed under vacuum to yield a dark brown residue. The product was extracted with hexanes and purified on a 20 cm Brockman Activity I neutral alumina column eluting with hexanes to yield a yellow oil (0.18 g, 58%). ^1H NMR (C_6D_6): δ 1.61 (s, 3H), 5.26 (d, 2H), 5.46 (d, 2H). IR (ν_{CO}, *n*-hexane): 2043, 1981 cm^{-1} (lit.[10d] (in hexane) 2043, 1981 cm^{-1}). UV−vis (λ_{max}, *n*-hexane): 220 nm ($\epsilon = 9900\ M^{-1}\ cm^{-1}$), 288 nm ($\epsilon = 3960\ M^{-1}\ cm^{-1}$), 400 nm ($\epsilon = 110\ M^{-1}\ cm^{-1}$).

$Cp''Rh(CO)_2$. A 250 mL round-bottom Schlenk flask equipped with a stirbar was charged with 0.25 g (0.64 mmol) of the dicarbonylchlororhodium(I) dimer, $[Rh(CO)_2Cl]_2$. Using a syringe, 50 mL of THF was added to the flask, and the resulting solution was stirred to dissolve the solid. In a drybox a second 250 mL Schlenk flask was charged with potassium tetramethylcyclopentadienide $[K^+(C_5Me_4H)^-]$ (0.21 g, 1.31 mmol). This flask was taken out of the drybox, and 50 mL of THF was added via syringe to dissolve the potassium salt. The two solutions were combined via cannula transfer with continuous stirring of the receiving solution. The mixture was left to stir overnight at room temperature and resulted in a dark orange/brown slurry. The solvent was removed and the product extracted from the resulting residue with hexanes. The product was purified via a 20 cm Brockman Activity I neutral alumina column, eluting with hexane/toluene (50:50 by volume) to yield an orange/red oil (0.2 g, 56%). ^1H NMR (C_6D_6): δ 1.99 (s, 6H), 2.05 (s, 6H), 5.29 (s, 1H). IR (ν_{CO}, *n*-hexane): 2030, 1967 cm^{-1} (lit.[10e] (as liquid) 2039, 1976 cm^{-1}). UV−vis (λ_{max}, *n*-hexane): 257 nm ($\epsilon = 9500\ M^{-1}\ cm^{-1}$), 303 nm ($\epsilon = 3800\ M^{-1}\ cm^{-1}$), 430 nm ($\epsilon = 130\ M^{-1}\ cm^{-1}$).

$(ind)Rh(CO)_2$. A 250 mL single-neck round-bottom flask was charged with $(ind)Rh(CH_2{=}CH_2)_2$ (0.25 g, 0.91 mmol) dissolved in 100 mL of *n*-pentane. This solution was purged with carbon monoxide in a well-ventilated fume hood. The reaction was monitored with IR spectroscopy, and a clean conversion to the dicarbonyl product was verified by ^1H NMR spectroscopy. The product was purified via precipitation from *n*-pentane at −78 °C. A fine yellow powder was obtained (0.20 g, 80%). ^1H NMR ($CDCl_3$): δ 5.792 (d, 2H), 6.075 (q, 1H), 7.130 (m, 2H), 7.285 (m, 2H). IR (ν_{CO}, *n*-hexane): 2048, 1991 cm^{-1} (lit.[10g] (in heptane) 2048, 1990 cm^{-1}). UV−vis (λ_{max}, *n*-hexane): 253 nm ($\epsilon = 21152\ M^{-1}\ cm^{-1}$), 305 nm ($\epsilon = 7856\ M^{-1}\ cm^{-1}$), 340 nm ($\epsilon = 5940\ M^{-1}\ cm^{-1}$) (lit.[10h] (in toluene) 340 nm ($\epsilon = 5940\ M^{-1}\ cm^{-1}$)).

$Cp^*{}_2Rh_2(CO)_3$. A solution of $Cp^*Rh(CO)_2$ in hexanes (0.074 g, 0.25 mmol in 50 mL) was refluxed with stirring under a nitrogen atmosphere for 72 h. The product was purified via column chromatography on a 10 cm neutral alumina column with hexanes. Two bands eluted off the column, the first orange due to the starting material and the second darker orange due to the binuclear species (i.e., $Cp^*{}_2Rh_2(CO)_3$). The infrared spectrum in a KBr pellet yielded two characteristic bands at 1939 and 1983 cm^{-1} which agreed well with the literature reported values.[10i]

$(ind)_2Rh_2(CO)_3$ and $(ind)_3Rh_3(CO)_3$. A 250 mL round-bottom Schlenk flask equipped with a stirbar was charged with 0.25 g (0.64 mmol) of the dicarbonylchlororhodium(I) dimer, $[Rh(CO)_2Cl]_2$. Using a syringe, 50 mL of THF was added to the flask, and the resulting solution was stirred to dissolve the solid. This solution was added via cannula transfer to a freshly prepared solution of sodium indenide (in excess) in THF. The formation of a brown product was observed on mixing. After the solution was stirred for 12 h, the solvent was removed under vacuum to yield a dark brown residue. The product was extracted with hexanes and purified on a 20 cm Brockman Activity I neutral alumina column. Three bands eluted from the column, the first being yellow, the second red, and the final a dark green. These bands corresponded to the mono-, di-, and trinuclear species: $(ind)Rh(CO)_2$, $(ind)_2Rh_2(CO)_3$, and $(ind)_3Rh_3(CO)_3$. The complex $(ind)Rh(CO)_2$ provided the same data as recorded above. ^1H NMR $[(ind)_2Rh_2(CO)_3]$ ($CDCl_3$): δ 5.57 (d, 4H), 5.815 (q, 2H), 6.955 (m, 4H), 7.155 (m, 4H). IR $[(ind)_2Rh_2(CO)_3]$ (ν_{CO}, *n*-hexane): 1988, 1848 cm^{-1}. IR $[(ind)_3Rh_3(CO)_3]$ (ν_{CO}, CH_2Cl_2): 1854, 1809 cm^{-1} (lit.[10g] (in CH_2Cl_2) 1852, 1805 cm^{-1}).

CpRh(CO)cy. To a well-stirred solution of $CpRh(CO)_2$ in hexanes (0.056 g, 0.25 mmol in 50 mL) was added *cis*-cyclooctene (cy; 0.03 g, 0.26 mmol). This solution was refluxed with stirring under a nitrogen atmosphere for 72 h. The product was purified via column chromatography on a 10 cm neutral alumina column with hexanes. A single light orange band eluted off the column due to the CpRh(CO)cy. On removal of solvent an orange powder was obtained with a single carbonyl vibrational mode at 1979 cm^{-1} in the infrared spectrum. Use of a 10 cm column ensured elution of any residual of unreacted *cis*-cyclooctene.

Cp*Rh(CO)cy. To a well-stirred solution of $Cp^*Rh(CO)_2$ in hexanes (0.074 g, 0.25 mmol in 50 mL) was added *cis*-cyclooctene (0.03 g, 0.26 mmol). This solution was refluxed with stirring under a nitrogen atmosphere for 120 h. The product was purified via column chromatography on a 10 cm neutral alumina column with hexanes. A single light orange band eluted off the column and was identified as Cp*Rh(CO)cy. On removal of solvent an orange powder was obtained with a single carbonyl vibrational mode at 1962 cm^{-1} in the infrared

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spectrum. Use of a 10 cm column ensured elution of any residual unreacted *cis*-cyclooctene.

(ind)Rh(CO)cy. To a well-stirred solution of (ind)Rh$(CO)_2$ in hexanes (0.069 g, 0.25 mmol in 50 mL) was added *cis*-cyclooctene (0.03 g, 0.26 mmol). This solution was refluxed with stirring under a nitrogen atmosphere for 120 h. The product was purified via column chromatography on a 10 cm neutral alumina column with hexanes and eluted as a single light orange band. On removal of solvent an orange powder was obtained with a single carbonyl vibrational mode at 1981 cm^{-1} in the infrared spectrum. Use of a 10 cm column enabled elution of unreacted *cis*-cyclooctene.

(acac)Rh(CO)cy. To a well-stirred solution of (acac)Rh$(CO)_2$ in hexanes (0.065 g, 0.25 mmol in 50 mL) was added *cis*-cyclooctene (0.03 g, 0.26 mmol). This solution was refluxed with stirring under a nitrogen atmosphere for 168 h. However, little conversion to product was observed. A cuvette of the above solution was irradiated with 313 nm light. Slow conversion to product was observed, and after one week the solvent was evaporated and the residue passed through a micro neutral alumina column. Two bands eluted with hexanes, the first being the parent (acac)Rh$(CO)_2$ (yellow) and the second the photoproduct (acac)Rh(CO)cy (more orange and darker). The infrared spectrum displayed a single ν_{CO} mode at 2002 cm^{-1}, similar to that observed in the photochemical experiments. The spectral data agree well with analogous data previously reported in the literature.[11]

Equipment and Procedures. 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 reported are considered accurate to ±2 nm. Infrared spectra were recorded on a Nicolet model 20SXC Fourier transform infrared (FTIR) spectrometer. Spectra were obtained from solutions using NaCl cells of 0.5 and 1.0 mm path length, and the reported band maxima are considered accurate to ±0.5 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 for the isolated complexes. NMR spectra were recorded on a Brücker AM-360 NMR spectrometer. Emission spectra were recorded on a SLM 48000 fluorimeter which incorporates a Hamamatsu R928 photomultiplier tube and photon counting facilities. Low-temperature emission measurements were performed using an Oxford Instruments model DN1704K variable-temperature liquid-nitrogen cryostat.

A Lexel Corp. model 95-4 argon-ion laser (4W-all lines) was used to perform the visible photolyses at 458 nm; incident laser light intensity was determined by means of an Ophir Optronics Ltd. external power meter with a Nova display. Typically, laser powers between 60 and 90 mW were employed, although measurements were also obtained with much lower powers (20−30 mW), and the data were found to be reproducible. The photochemistry was monitored by recording UV−vis and FTIR spectra at regular time intervals throughout the irradiation procedure (the overall photolysis time took between 4 and 72 h for each run). Irradiations at 313 and 366 nm were carried out with light from an Ealing Corp. medium-pressure 200 W mercury arc lamp using interference filters (Ealing Corp., 10 nm band-pass) to isolate the excitation wavelength. Incident light intensities at 313 and 366 nm were determined by Aberchrome 540 and ferrioxalate actinometry.[12,13] 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 for at least five readings and were found to be reproducible to within ±5% in all cases. The stated uncertainties of ±10% for the absolute quantum efficiency values incorporate the systematic errors involved in measuring the light intensity. All reactions were also performed in the dark to assess the extent of thermal processes, which were found to be negligible under our experimental conditions.

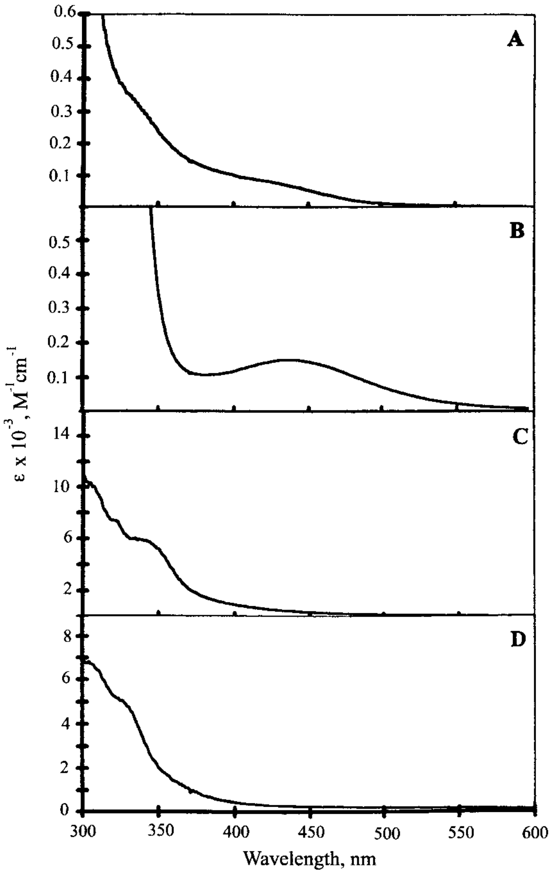

Figure 2. Electronic absorption spectra of (A) CpRh$(CO)_2$, (B) Cp*Rh$(CO)_2$, (C) (ind)Rh$(CO)_2$, and (D) (acac)Rh$(CO)_2$ in deoxygenated *n*-hexane solution at 293 K.

Table 1. Electronic Absorption Bands and Assignments for XRh$(CO)_2$ Complexes in *n*-Hexane Solution at 293 K

	λ_{max}, nm (ϵ, M^{-1} cm^{-1})		
complex	E_2, $\pi-\pi^*$	M → CO CT, M → Cp CT, LF[a]	LF
CpRh$(CO)_2$	221 (9600)	284 (3820)	320 (390),[b] 420 (78)[b]
Cp′Rh$(CO)_2$	220 (9900)	288 (3960)	400 (110)[b]
Cp″Rh$(CO)_2$	257 (9500)	303 (3800)	430 (130)
Cp*Rh$(CO)_2$	237 (9120)	314 (3800)	438 (152)
(ind)Rh$(CO)_2$	253 (21200)	305 (7860)	340 (5940)
(acac)Rh$(CO)_2$	259 (12300)	303 (6750)	357 (5110)

[a] The bands in the region 284−314 nm also possess some absorption due to B-type $\pi-\pi^*$ and carbonyl n−π^* character (see ref 14). [b] Observed as a shoulder.

During irradiation and emission experiments, the solution temperatures were controlled to within ±0.1 K by circulating a thermostated ethylene glycol−water mixture through a jacketed cell holder mounted on an optical rail. Solutions were stringently filtered through 0.22 μm Millipore filters and deoxygenated by purging with prepurified nitrogen gas for 15 min prior to irradiation. Emission data for solid samples were acquired with the sample oriented at an angle of 20−25° to the incident light.

Results

Electronic Absorption Spectra. Figure 2 depicts electronic absorption spectra of several of the XRh$(CO)_2$ complexes, and the data obtained from all the complexes are summarized in Table 1. Typically, the complexes exhibit three absorption bands in the region 200−500 nm. The lowest-energy band for each of the cyclopentadienyl derivatives appears in the visible region

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[11] Serron, S.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534.
[12] Heller, H. G.; Langan, J. N. *J. Chem. Soc., Perkin Trans.* **1981**, 341.
[13] (a) Parker, C. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 104. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518. (c) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966.

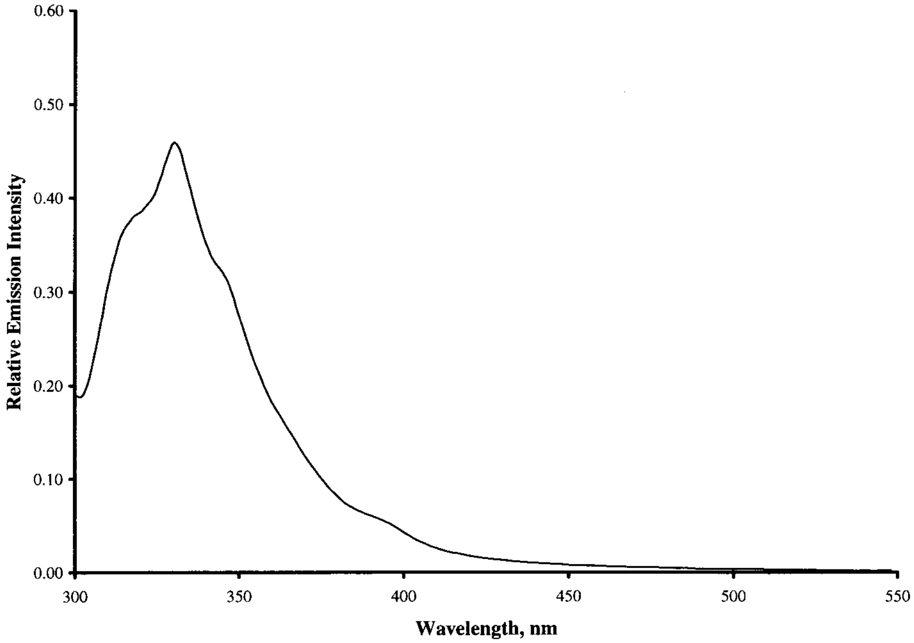


Figure 3. Emission spectrum of (ind)Rh(CO)$_2$ in deoxygenated CH_2Cl_2 solution at 293 K following excitation at 290 nm.

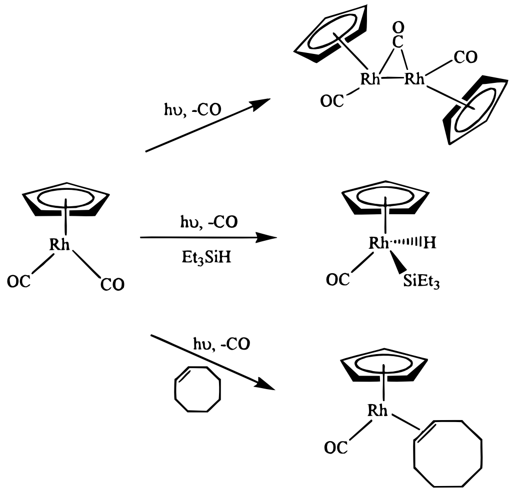
Table 2. Infrared Carbonyl Stretching Bands for the Various XRh(CO)$_2$ Complexes and Their Photochemical Products

complex	solvent	ν(CO), cm^{-1}	complex	solvent	ν(CO), cm^{-1}
CpRh(CO)$_2$	*n*-hexane	2048, 1985	Cp*$_2$Rh$_2$(CO)$_3$	KBr pellet	1984, 1940
Cp$_2$Rh$_2$(CO)$_3$	*n*-hexane	1981, 1834	Cp*Rh(CO)(SiEt$_3$)H	*n*-hexane	1996
CpRh(CO)(SiEt$_3$)H	*n*-hexane	2012	Cp*Rh(CO)cy	*n*-hexane	1962
CpRh(CO)cy	*n*-hexane	1979	(ind)Rh(CO)$_2$	*n*-hexane	2048, 1991
Cp′Rh(CO)$_2$	*n*-hexane	2044, 1981	(ind)$_2$Rh$_2$(CO)$_3$	*n*-hexane	1988, 1848
Cp′Rh(CO)(SiEt$_3$)H	*n*-hexane	2007	(ind)Rh(CO)cy	*n*-hexane	1981
Cp″Rh(CO)$_2$	*n*-hexane	2030, 1967	(acac)Rh(CO)$_2$	*n*-hexane	2083, 2014
Cp*Rh(CO)$_2$	*n*-hexane	2026, 1963	(acac)Rh(CO)cy	*n*-hexane	2002

of the spectrum, and the corresponding bands for the indenyl and acac systems are observed at somewhat higher energies. Generally, methylation of the cyclopentadienyl ring results in a red shift for the lowest-energy absorption band. For the Cp and Cp′ complexes this band appears as a shoulder with significant overlap of the higher-energy band. However, in the Cp* derivative this band is red shifted further and is a more distinctive feature. There also appears to be an increase in the extinction coefficients of these lowest-energy bands with increased methylation. Moreover, the longest-wavelength bands for the indenyl and acac complexes have substantially higher extinction coefficients compared to the other systems.

Infrared Spectra. The infrared spectra for all six complexes exhibit two strong carbonyl stretching vibrational modes (ν_{CO}) accompanied by their respective isotope peaks at lower energy (see Figure 3 and Table 2). On increasing methylation of the cyclopentadienyl ring, these vibrational modes shift to lower frequency, and the average vibrational frequency of the two bands moves from 2017 cm^{-1} (in the Cp complex) to 1995 cm^{-1} (in the Cp* complex). On replacing the cyclopentadienyl ring by an indenyl group, there is a shifting of the ν_{CO} bands to higher frequency (the average frequency is 2020 cm^{-1}). In the acac derivative, there is an even greater shift in the ν_{CO} bands to much higher frequencies (the average frequency is 2049 cm^{-1}).

Photochemical Reactions. Three different photochemical reactions (each involving CO dissociation) were observed to take place in the XRh(CO)$_2$ system, depending on the reaction conditions. These were a binucleation process (eq 1), silyl hydride activation of added Et$_3$SiH (eq 2), and photochemical substitution by added *cis*-cyclooctene (eq 3). The reactions (eqs 1−3), while shown for CpRh(CO)$_2$, are representative for all of the XRh(CO)$_2$ complexes investigated. In the case of the binucleation reactions (eq 1), the electronic and infrared spectra observed during photolysis clearly indicate the formation of metal-bridged tricarbonyl complexes, concordant with previous literature data.[4b,d,7b−i,10f,g] These photochemical transformations were observed to take place slowly (over a period of several hours); the indenyl and acac complexes underwent especially slow photochemical reactions. When Et$_3$SiH was incorporated in the solution, Si−H bond activation was observed to occur



(1)
(2)
(3)

Table 3. Photochemical Quantum Efficiencies (ϕ_{cr}) for Conversion of $XRh(CO)_2$ to Their Corresponding Photoproducts in Deoxygenated *n*-Hexane at 293 K[a,b]

	ϕ_{cr}		
reaction product	$\lambda_{ex} = 313$ nm	$\lambda_{ex} = 366$ nm	$\lambda_{ex} = 458$ nm
$Cp_2Rh_2(CO)_3$	0.30	0.078	
$CpRh(CO)(SiEt_3)H$	0.29[c]	0.078[c]	0.0032[c]
$CpRh(CO)cy$	0.30	0.078	
$Cp'Rh(CO)(SiEt_3)H$			0.0023
$Cp^*{}_2Rh_2(CO)_3$	0.15	0.033	
$Cp^*Rh(CO)(SiEt_3)H$	0.15	0.032	0.00017
$Cp^*Rh(CO)cy$	0.15	0.034	
$(ind)_2Rh_2(CO)_3$	0.019	0.0084	
$(ind)Rh(CO)cy$	0.018	0.0074	
$(acac)_2Rh_2(CO)_3$	0.042	0.0082	
$(acac)Rh(CO)cy$	0.041	0.0083	

[a] All values are accurate to ±10%. [b] The concentration of the entering ligand is 0.05 M in each case. [c] Data are taken from ref 7i.

photochemically (eq 2) with the formation of the corresponding silyl hydride photoproducts.[3d,7b−i] When *cis*-cyclooctene was used as an entering ligand, the corresponding monosubstituted photoproducts were formed photochemically (eq 3).[3c−e,15] In the absence of light, the $XRh(CO)_2$ complexes were observed to be thermally stable under the same experimental conditions. Infrared data recorded from the parent complexes and their corresponding photoproducts are summarized in Table 2.

Luminescence Observations. Luminescence measurements performed on the $(ind)Rh(CO)_2$ complex in deoxygenated CH_2Cl_2 at 293 K following excitation at 290 nm resulted in the observation of a structured emission band in the region 300−500 nm (see Figure 3). The emission band ($\lambda_{max} = 331$ nm) displays characteristic $\pi-\pi^*$ emission with features at 313, 331, 348, 367, and 389 nm. This band structure yields an average vibrational spacing of 1485 cm^{-1} which is assigned to the indenyl ligand's C═C stretching mode. An emission lifetime of 2.5 ns was determined for $(ind)Rh(CO)_2$ in deoxygenated CH_2Cl_2 solution at 293 K; this is also consistent with the $\pi-\pi^*$ assignment. Similar studies performed on $(acac)Rh(CO)_2$ as a solid at 293 and 77 K resulted in a weak structured band in the region 320−420 nm following excitation at 300 nm; this is again characteristic of $\pi-\pi^*$ emission. The emission spectrum was found to be independent of the excitation wavelength in the region 300−360 nm, but an emission lifetime was not resolved due to light scatter from the sample.

Quantum Efficiencies. Absolute quantum efficiencies (ϕ_{cr}) have been determined for each of the binucleation, silyl hydride activation, and ligand substitution photochemical reactions in accordance with a previously described photokinetic procedure.[8] This method is ideally suited to studying these processes as it accounts for increasing inner filter effects due to the light absorption by photoproducts during the progress of the reactions. Table 3 summarizes the quantum efficiencies obtained for each of the investigated reactions in deoxygenated *n*-hexane at various excitation wavelengths. Two significant observations can be made: (i) the efficiencies of these systems are substantially influenced by changes in the unique ligand, and (ii) there is a significant wavelength dependence on the efficiency for each of the molecules studied. Taking the unsubstituted cyclopentadienyl complex, $CpRh(CO)_2$, as the basic template for comparison, some clear observations can be made about the modifications on this system. First, there is a substantial reduction in the photoefficiencies at all wavelengths on increased methylation of the cyclopentadienyl ligand. Indeed, complete methylation of the cyclopentadienyl ring causes a 50% drop in photoefficiency on excitation at 313 nm and an approximately 58% reduction at 366 nm. This reduction is even more pronounced at the longer excitation wavelength of 458 nm where there is a 95% drop in photochemical efficiency on replacing Cp by Cp*. Second, replacement of a Cp ring by an indenyl group produces an even greater reduction in the quantum efficiencies following excitation at either 313 or 366 nm. Photolysis of the indenyl molecule resulted in an approximately 90−94% reduction in quantum efficiency from that observed in the $CpRh(CO)_2$ species for the binucleation and *cis*-cyclooctene substitution reactions following 313 and 366 nm excitation. Finally, quantum efficiencies for the *pseudo*-square-planar $(acac)Rh(CO)_2$ complex reveal a drop in efficiency of approximately 86−89% for the binucleation and photochemical substitution reactions at 313 and 366 nm compared with those obtained for the analogous reactions in $CpRh(CO)_2$.

Discussion

Electronic Absorption Spectra. This photochemical study, with excitations at 313, 366, and 458 nm, is predominantly concerned with the chemistry arising from the two lowest-energy excited states. Previously, these have been assigned as ligand field (LF) in nature due to the low extinction coefficients and lack of solvent dependence of their absorption bands, the lack of luminescence at low temperature, and the rapid CO dissociative photochemistry originating from these states.[3,4,7b] On examination of the data in Table 1 and the spectra in Figure 2, there are some similarities that exist for all of these cyclopentadienyl complexes. For each of the $XRh(CO)_2$ (X = Cp, Cp′, Cp″, Cp*) derivatives, the lowest-energy absorption band is weak and has an extinction coefficient that does not exceed 152 M^{-1} cm^{-1}. As the cyclopentadienyl ring is increasingly methylated there is an enhancement in the magnitude of the extinction coefficient for this lowest-energy band. Also, methylation of the ring causes an overall red-shifting of this band, and it appears at longest wavelength for the permethylated $Cp^*Rh(CO)_2$ complex. In the case of $CpRh(CO)_2$, a second LF band is observed at higher energy ($\lambda_{max} = 320$ nm (sh), $\epsilon = 390$ M^{-1} cm^{-1}); this band is understood to also be present in the substituted Cp molecules but is apparently masked by the overlap of higher-energy M → CO and M → Cp charge-transfer features (see Table 1 and Figure 2).[4e,16,17]

Clearly, changing the unique ligand substantially influences the electronic absorption spectra, as exemplified by a comparison of the data from the cyclopentadienyl complexes with the $(ind)Rh(CO)_2$ and $(acac)Rh(CO)_2$ complexes. Replacement of the cyclopentadienyl group with an acac or indenyl ligand leads to significantly higher extinction coefficients for the lowest absorption bands in these complexes compared to those observed in the Cp and methylated Cp ring complexes. This is because in the acac and indenyl derivatives there is a substantial absorption overlap by the $\pi-\pi^*$ states in this region of the

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(14) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; 5th ed.; Wiley: New York, 1991. (b) Braude, E. A. *Determination of Organic Structures by Physical Methods*; Academic Press: New York, 1955.

(15) Belt, S. T.; Duckett, S. B.; Haddleton, D. M.; Perutz, R. N. *Organometallics* **1989**, *8*, 748.

(16) Methylation of benzene is known to red shift the $\pi-\pi^*$ B bands (ref 14). Therefore, some contribution to the absorption in this region may be due to a partial overlap with the long-wavelength tail of the $\pi-\pi^*$ state in $Cp^*Rh(CO)_2$.

(17) (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

spectrum.[18] For the cyclopentadienyl complexes, the $\pi-\pi^*$ absorptions are found at much higher energies, and they do not significantly contribute to the absorption in the region of the lowest-energy absorption bands.

Wavelength Dependence of the Photochemistry. From previous studies it has been concluded that there is a distinct reactivity observed from the two lowest-energy LF excited states in the $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ complexes.[7a,b,i] A higher-energy LF state has been concluded to be responsible for CO dissociation, and a lower-energy LF state has been postulated to lead to a photochemical $\eta^5 \rightarrow \eta^3$ ring-slippage (see Scheme 1). The current results lend support to the notion of distinct photochemical pathways, as revealed by the wavelength-dependent quantum efficiencies obtained for $CpRh(CO)_2$ and the other derivatives under a variety of reaction conditions (see Table 3). All of the molecules studied exhibit photoefficiencies which are substantially dependent on the excitation wavelength. With the exception of the $(acac)Rh(CO)_2$ complex, the most reasonable explanation for this wavelength dependence is that photolysis at shorter wavelength leads to the generation of the 16-electron carbonyl dissociative product, XRh(CO), whereas excitation at longer wavelengths involves a ring-slippage process ($\eta^5 \rightarrow \eta^3$).[4-7] For the acac complex, short-wavelength excitation similarly leads to a CO dissociation product, but longer-wavelength excitation leads to ligand dechelation analogous to that observed in $(HBPz^*_3)Rh(CO)_2$.[7c-h,11,19]

It should be noted that, in cases where excitation leads to exclusively ring-slippage or dechelation-type processes, a quantum efficiency (ϕ_{cr}) of zero should be obtained. This is because such mechanisms do not lead to any dissociative loss of CO and the photoproduct intermediates are thermally able to revert to starting complex. Hence, the net effect is that they effectively result in the dissipation of energy from the excited states with no overall net photochemistry occurring. In our results it is interesting that we still observe finite quantum efficiency values for each complex studied, although the drop in ϕ_{cr} at longer wavelength of excitation is very substantial. Our explanation for this is that there is substantial overlap between the two lowest-lying LF bands and it is not feasible to populate one excited state exclusively on excitation at 313, 366, or 458 nm. The absorption band that represents the higher-energy LF state (which is responsible for CO dissociation) appears to substantially tail into the lower-energy region, and it is apparently still accessed by the excitation at long wavelength. Indeed, the electronic absorption spectrum of $CpRh(CO)_2$ reveals that the two lowest-energy bands appear as shoulders at 320 and 420 nm (see Figure 2 and Table 1). In $CpRh(CO)_2$, it is obviously not possible to selectively excite into either the upper or lower LF states exclusively.

However, in the case of the $Cp^*Rh(CO)_2$ complex, the lower-energy LF state is significantly red-shifted (see Figure 2) and somewhat separated, so that the higher-energy LF state is not so readily populated on long-wavelength excitation. This observation is clearly supported by the ϕ_{cr} data (see Table 3). Comparing the photoefficiencies at 313 and 458 nm for $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$, the Cp complex shows a reduction in ϕ_{cr} of less than 2 orders of magnitude, whereas in the Cp* complex this drop is almost 3 orders of magnitude. On comparing the efficiency data at 458 nm for the two molecules, the value observed in the Cp* derivative is seen to be approximately 5% of that observed in the Cp derivative. These results again support the notion that the lower state undergoes a different photochemical mechanism that essentially serves to dissipate the energy absorbed by the molecule. The data for excitation at 366 nm also support the idea that the states are not exclusively populated because the efficiency data are intermediate between those obtained for 313 and 458 nm excitation (see Table 3).

Influence of Cyclopentadienyl Ligand Methylation. The reduction in ϕ_{cr} on going from the Cp derivative to the Cp* derivative is clearly related to the degree of methylation of the cyclopentadienyl ring. It can be seen from the absorption data (see Figure 2 and Table 1) that as the Cp ring is methylated the higher energy LF state is no longer observable and the absorbance in the 284−320 nm region significantly increases. This is due to a substantially greater amount of overlap by the nearby M → CO and M → Cp charge-transfer (CT) states with the higher energy LF state.[4e,16,17] The net effect of this is that on excitation of $Cp^*Rh(CO)_2$ at 313 nm much less of the total energy is absorbed by the upper LF state, and this results in a significantly lower reaction photoefficiency (see Table 3). Clearly, most of the energy is being absorbed into the CT states, which leads to polarization of the molecule, less CO dissociation, and effective nonradiative deactivation. However, as noted above, the wavelength dependence of ϕ_{cr} is even more pronounced for the permethylated system, apparently because there is a greater separation between the two lower-lying ligand field absorption bands in $Cp^*Rh(CO)_2$. In this molecule, almost all of the energy appears to be dissipated via the thermal back slip processes and very little CO dissociation actually takes place (the photoefficiency at long wavelength becomes nearly zero). For the $Cp'Rh(CO)_2$ complex, the results are intermediate between those of the Cp and Cp* derivatives. We recognize that other photophysical processes may also contribute to the reduction of the photoefficiency values on methylation. Increased vibrational deactivation of the LF excited state can be anticipated as the Cp ring is methylated. Here, the number of vibrational modes in the molecule is increased and there will be many more routes for intramolecular nonradiative deactivation and for intermolecular nonradiative decay via solvent interaction.[7g,i]

Additionally, there is the possibility of a new mechanistic pathway in these methylated Cp derivatives, such as competitive intramolecular C−H bond activation (see Scheme 2). Until the discovery of intermolecular C−H bond activation, it was believed that intramolecular processes were the only ones that existed as they were more favorable entropically.[1,2,20] Bearing this in mind, it is certainly possible that the ϕ_{cr} values are reduced because of increased intramolecular interactions as the Cp ring is methylated.[1c,2f] Such interaction has been reported in the literature by Bercaw et al. for bis(pentamethylcyclopentadienyl)zirconium dihydride, where one of the methyl groups was activated, and in the bis(neopentyltetramethylcyclopentadienyl)zirconium dichloride, where the neopentyl group has been reported to be intramolecularly activated.[20] Moreover, matrix isolation work on $CpIr(CO)_2$ has led to the postulation of an η^4 intermediate, where one of the protons from the generated η^4-cyclopentadiene is exchanged for the proton of the activated CH_4;[3f] this observation again provides evidence of intramolecular interaction between the metal center and a

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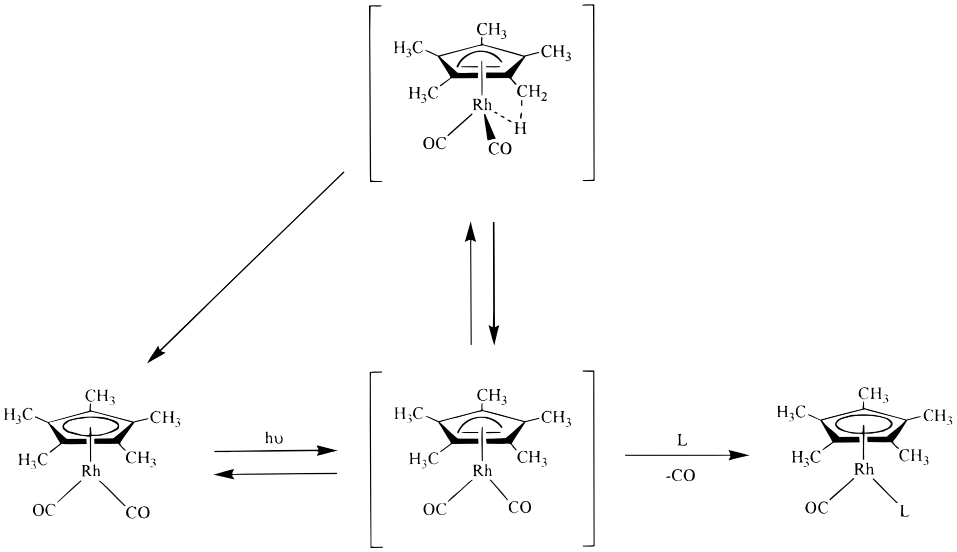
(18) The increased conjugation of the indenide group leads to substantial red shifting of the $\pi-\pi^*$ E_2 band and significant absorption in the lowest-energy region for $(ind)Rh(CO)_2$ (ref 14). Assignments of $\pi-\pi^*$ states have been made, but these orbitals may be considerably mixed with the orbitals deriving from the transition metal.

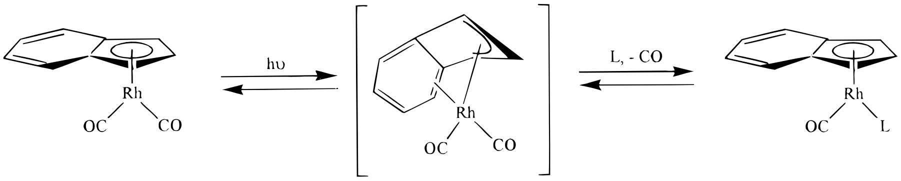
(19) Brouwers, A. M. F.; Oskam, A.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1777.

(20) McAlistair, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

Scheme 2



Scheme 3



proton on the cyclopentadienyl ring. An intramolecular mechanism involving the unique ligand, such as that depicted in Scheme 2, could also contribute to the significant lowering of the ϕ_{cr} values (upon 458 nm excitation) in the Cp* complex compared to the Cp complex. This type of mechanism would effectively trap the photoproduced ring-slipped intermediate and return it to the parent species via a reverse ring-slippage process, thereby reducing the overall reaction photoefficiency.

Influence of the Indenyl Ligand. Replacement of the Cp ring with an indenyl ring dramatically affects the quantitative photochemistry of the system under investigation. Upon excitation at 313 nm, the observed ϕ_{cr} values drop by greater than an order of magnitude in comparison with those of the Cp derivative (see Table 3). To explain this, one needs to recognize that in the indenyl complex the LF bands are substantially blue shifted and the upper LF state (responsible for CO dissociation) may not be as readily accessed even at this relatively high energy excitation of 313 nm (see Figure 2 and Table 1). Also, in the indenyl complex, there may be an additional overlapping absorbance at 313 nm due to the neighboring $\pi-\pi^*$ state, which is not the case for the Cp complex.[18] Strong support for this idea is provided by the observation of the structured $\pi-\pi^*$ luminescence band (see Figure 3) and the determination of a typical $\pi-\pi^*$ fluorescence lifetime from this complex in room-temperature solution, which sharply contrasts with the photophysical behavior of the Cp and Cp* complexes where no luminescence was observed even at 77 K.[7a,b,d] Consequently, for (ind)Rh(CO)$_2$, it can be concluded that a large portion of the energy that might be expected to reach the photochemically reactive LF manifold is dissipated via the $\pi-\pi^*$ level.

There are, of course, other possible factors that could contribute to the observed reduction in photoefficiency for (ind)Rh(CO)$_2$, including the increased ability of the indenyl ligand to undergo ring-slippage.[21] A more effective $\eta^5 \rightarrow \eta^3$ ring-slippage process in the indenyl complex would reduce the photoefficiency, especially at longer wavelengths of excitation. As noted above for the methylated Cp derivatives, the indenyl complex could also be anticipated to have additional vibrational deactivation modes from the LF excited states, leading to more efficient nonradiative return to the ground state and lower ϕ_{cr} values. One should again consider intramolecular effects in the (ind)Rh(CO)$_2$ molecule that might lead to a reduction in photoefficiency. It is well-known that when a slip occurs in a Cp or ind ring system a buckling occurs with a loss of planarity.[21] However, in the case of the indenyl ring slip there is an accompanying aromatization of the six-membered ring. Clearly, if the ring were to bend sufficiently toward the metal center (see Scheme 3), then there is a possibility of coordination of the six-membered ring in an η^2 fashion to the vacant site on the slipped (η^3-ind)Rh(CO)$_2$ molecule. This would provide steric hindrance at the metal center and effectively reduce ϕ_{cr}. An analogous mechanism has been postulated in the thermal chemistry of (η^5-ind)Mo(CO)$_3$X, where X = Cl, Br, or I.[22]

In summary, the results have revealed that in the indenyl complex the reaction efficiency is significantly lower than in the cyclopentadienyl derivatives. This is attributed to ineffective population of the LF excited states because of substantial overlap of the low-lying $\pi-\pi^*$ state and intramolecular effects involving the indenyl group.

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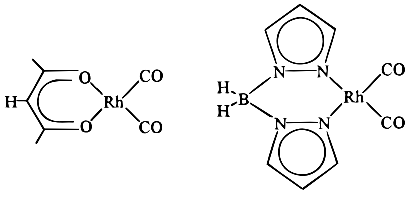
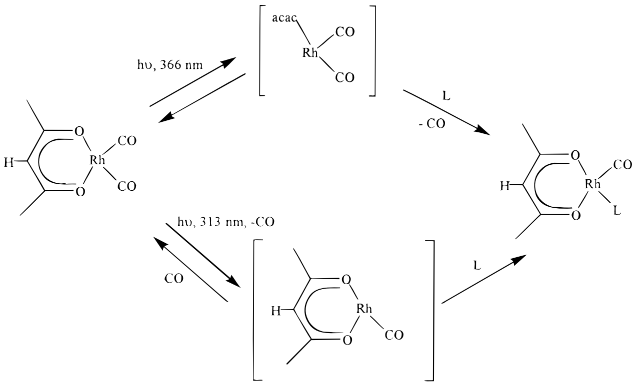
Influence of Dechelation/Rechelation Processes. Comparing the quantum efficiency data for the (acac)Rh(CO)$_2$ complex with those of any of the cyclopentadienyl derivatives reveals that there is also a substantial reduction in the observed ϕ_{cr} values. The lower quantum efficiencies are again thought to be brought about by efficient loss of energy into neighboring $\pi-\pi^*$ and M−CO CT states. The $\pi-\pi^*$ state in the acac complex is at a much lower energy compared to the Cp derivative, and it is clear that it is effectively populated following excitation at 313 and 366 nm. The presence of this state is further supported by the detection of weak luminescence from solid (acac)Rh(CO)$_2$ at room temperature and at 77 K. Although weak, this spectrum is typical of $\pi-\pi^*$ emission with a structured band in the 430−530 nm region that is independent of the excitation wavelength over the 300−360 nm region.

Interestingly, the inefficient photochemistry of (acac)Rh(CO)$_2$ appears to be analogous to earlier observations from (H$_2$BPz$_2$)-Rh(CO)$_2$ (Pz = pyrazolyl), which is also a 16 electron stable complex and *pseudo*-square-planar in structure (see below). In fact, this pyrazolyl derivative was found to be virtually photochemically inert, yet it readily undergoes thermal substitution as does (acac)Rh(CO)$_2$.[7f,11] However, (acac)Rh(CO)$_2$, like the other complexes in this study, exhibits a strong wavelength dependence in its photochemistry, as revealed by the quantum efficiencies (see Table 3). This result again suggests that there are two different photochemical reaction pathways taking place.



Indeed, the presence of two different reaction pathways is strongly supported by previous ultrafast and other time-resolved spectroscopy investigations and matrix isolation studies.[4d,19,23] Ultrafast spectroscopy on a picosecond time scale has detected the initial production of a monocarbonyl solvated product following high-energy excitation (λ_{ex} = 289 nm). Independent time-resolved infrared (TRIR) studies have detected the formation of an initial monocarbonyl product which subsequently forms the bridged dinuclear species, (acac)$_2$Rh$_2$(CO)$_2$(μ-CO), on a microsecond time scale. Matrix isolation studies, carried out at excitation wavelengths longer than 280 nm, have detected the formation of the monocarbonyl species and a monodentate dicarbonyl product. Unfortunately, ultrafast studies were not able to directly detect the formation of this monodentate dicarbonyl species, because it is only formed effectively upon long-wavelength excitation. Scheme 4 summarizes the two postulated photochemical routes for the (acac)Rh(CO)$_2$ complex based upon the observed quantum efficiency data and previous spectroscopic measurements.

Scheme 4



Summary of Energy Dissipation Processes. Several processes appear to strongly influence the photochemical reactivity of these XRh(CO)$_2$ derivatives. On higher-energy excitation the carbonyl dissociation mechanism is predominant, and this is characterized by high reaction quantum efficiencies and supported by ample spectroscopic evidence via earlier ultrafast and matrix isolation studies. However, in all the complexes studied here, there is a distinct reduction in photochemical efficiencies, suggesting that a different reaction pathway takes place at longer-wavelength excitation. The drop in photoefficiency is understood to be associated with the different nature of the reaction intermediates occurring on excitation into the lower-energy absorption bands of these complexes. For the CpRh-(CO)$_2$ complex, this has been assigned to the presence of a ring-slippage ($\eta^5 \rightarrow \eta^3$) mechanism occurring at lower-energy excitation. A similar argument is put forward for the methylated cyclopentadienyl derivatives, but the reduction in ϕ_{cr} over the whole wavelength manifold studied is thought to be due to other factors that lead to enhanced nonradiative deactivation of the excited state, including increased vibrational deactivation and the possibility of intramolecular agostic interactions. For the (ind)Rh(CO)$_2$ complex, a ring-slippage intermediate, along with the possibility of an intramolecular η^2 interaction occurring in the formation of the slipped (η^3-ind)Rh(CO)$_2$ species, may also contribute to the quantitative photochemical observations. Finally, the quantitative photochemistry of (acac)Rh(CO)$_2$ is rationalized with the incorporation of a dechelation/rechelation pathway occurring at long-wavelength excitation.

There is, however, other photophysical behavior that could contribute to lower reaction quantum efficiencies at long wavelength. If the lowest-energy reactive level is simply intrinsically less reactive than the upper level, then a wavelength dependence will result. One possibility is that the upper and lower levels correspond to singlet and triplet LF states. Recently, separate photochemical pathways have been observed from lowest-energy singlet and triplet LF excited states of W(CO)$_5$L (L = pyridine and piperidine),[24] W(CO)$_4$(en) (en = ethylenediamine),[7j] and [CpFe(η^6-ipb)]PF$_6$ (ipb = isopropylbenzene).[25] Moreover, the application of ultrafast spectroscopic techniques has facilitated direct identification of reactive singlet and triplet LF excited states in CpMn(CO)$_3$[26] and CpV(CO)$_4$.[27] The differences in the reactivities of the singlet and triplet species appear to be brought about by statistical and thermodynamic influences in the solvation process.[25−28] Another possibility is that the lowest-lying band in the XRh(CO)$_2$ system is actually a Rh → CO MLCT transition, rather than a LF band, which would certainly account for the reduced reactivity. Recent

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theoretical work on $Cr(CO)_6$[29] and ultrafast studies on $Cr(CO)_4$(bpy) (bpy = 2,2′-bipyridine)[30] support this notion. Finally, the distinct reactivities may result from an avoided crossing between the potential energy curves of the lower- and higher-energy reactive levels. Recent calculations on $Mn_2(CO)_{10}$,[31] $MnCl(CO)_5$,[32] and $Mn(H)(CO)_3$(H-DAB) (DAB = 1,4-diaza-1,3-butadiene)[33] have provided evidence for this concept.

Conclusion

Absolute quantum efficiency (ϕ_{cr}) measurements have proven to be an excellent way to probe the reactivity of excited states in a range of related rhodium dicarbonyl derivatives. The differences in the photoefficiencies across this range of complexes have been rationalized by radiative and nonradiative decay processes of neighboring excited states and the mechanistic influence of the unique ligand.

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Supporting Information Available: A figure depicting a representative infrared sequence obtained during 458 nm photolysis of $CpRh(CO)_2$ in deoxygenated *n*-hexane containing 0.05 M *cis*-cyclooctene at 293 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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