ELSEVIER

Journal of Organometallic Chemistry 554 (1998) 1–11

Journal of Organometallic Chemistry

Photochemical features of intermolecular C–H bond activation [1]

Alistair J. Lees *

Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

Received 25 November 1996; received in revised form 26 February 1997

Abstract

The photophysical and photochemical properties of the C–H activating $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$, $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ and $(HBPz_3^*)Rh(CO)_2$ ($Pz^* = 3,5$-dimethylpyrazolyl) complexes in room-temperature hydrocarbon solutions are compared and contrasted. Recent quantitative measurements of the solution photochemistry and kinetic analyses of the reaction pathways are discussed. The data reveal that the C–H and Si–H activation reactions occur via similar photochemical routes, whereas the ligand photosubstitution reaction proceeds by a different pathway. Several key mechanistic features of the light-induced intermolecular C–H bond activation process are identified. © 1998 Elsevier Science S.A.

Keywords: Photochemistry; Photophysics; Excited states; Rhodium; C–H bond activation

1. Introduction

Saturated hydrocarbons, in the form of alkanes and alkyl groups, constitute a substantial fraction of natural carbon materials and so it is really not surprising that C–H bonds are among the strongest and most inert of single bonds. Consequently, it is a major challenge to chemists to ‘‘activate’’ these normally unreactive C–H bonds and to convert them to organic functional groups that are more useful.

Alkanes are not entirely inert, of course, and it is well recognized that they undergo many different reactions involving free-radical intermediates in both solution and gas phases. Significantly, though, these processes are generally not that useful for two reasons. The first, is that the cleavage of different types of C–H bonds (primary, secondary and tertiary) is usually rather unselective. The second is that alkane reactivity rarely leads to more useful functionalized compounds, as the products themselves are prone to undergo further reaction (e.g., oxidation of methane to methanol which is very inefficient because of further decomposition to carbon dioxide and water). Thus, at the heart of C–H activation research is a need to comprehend the key features of the reactivity and not simply to discover new systems. If such an understanding can be obtained then it may be feasible to develop new reagents and/or catalysts that have the capability to selectively transform molecules containing saturated C–H bonds into more reactive materials.

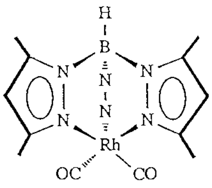
The most progress in this area has been made using organometallic complexes as reagents in oxidative addition processes involving hydrocarbon substrates [1]. For instance, there has been considerable attention paid to the photochemical reactivity of $CpML_2$ and Cp^*ML_2 ($M = Rh$, Ir; $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$; $L =$ CO, PR_3, olefin) following the discovery that these types of molecules can activate C–H bonds of alkane solvents on UV irradiation [2]. Following early mechanistic studies of these systems in which competitive relative rates of C–H bond activation were established [2,3], a variety of photochemical methods have been used to investigate these important reactions. These have involved: matrix isolation [4], laser-flash photolysis (including ultrafast spectroscopy) [5], solvation in liquefied noble gases [6], and quantum efficiency determination [7]. Recently, the photochemistry of the analogous $(HBPz_3^*)Rh(CO)_2$ ($HBPz^* = 3,5$-dimethylpyrazolyl) complex (see below) has also been investigated [8], since it was found that this molecule

---

* Tel.: +1-607-7772362; fax: +1-607-7774478; e-mail: alees@bingvmb.cc.binghamton.edu.

[1] Invited article for Special Issue on the State of the Art in Organometallic Photochemistry and Photophysics.

activates hydrocarbons, including methane, in daylight [9].



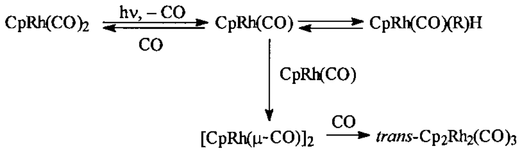
N-N = third pyrazolyl ring

A good understanding has now been achieved concerning the photochemical mechanisms in several of these d^8 organometallic complexes. Indeed, spectroscopic measurements on $CpML_2$ and Cp^*ML_2 have convincingly demonstrated that the primary photoproduct is a coordinatively-unsaturated 16-electron species (CpML or Cp^*ML) which is extremely reactive and rapidly forms a solvent adduct complex (CpML...S or Cp^*ML...S) in even weakly coordinating solvent (S), before undergoing C–H bond activation [4–7]. Furthermore, the rates of C–H activation of alkane to $Cp^*Rh(CO)X$ (X = Kr, Xe) in liquefied rare gas solutions at low temperature [10] and to CpRh(CO) in the vapor phase [11] have now been determined and these processes are also rapid.

In recent years we have reported spectroscopic data and quantum efficiency values for photosubstitution and intermolecular C–H/Si–H activation reactions involving $CpRh(CO)_2$, $Cp^*Rh(CO)_2$, $CpIr(CO)_2$ and $(HBPz_3^*)Rh(CO)_2$ in various room-temperature solutions [7,8]. This approach has made it possible to not only obtain the quantitative data for these light-induced conversions but also to elucidate a number of key features of the photophysical and photochemical properties leading to C–H activation of alkanes in solution. The purpose of this review is to illustrate the current progress made in understanding the quantitative photochemistry of these systems and to provide a comparison of the behavior of the cyclopentadienyl and tris(pyrazolyl)borate complexes. Particular attention is drawn to a number of common elements in the photophysical and photochemical mechanisms involved in the C–H activation process.

2. Photochemical reactivity

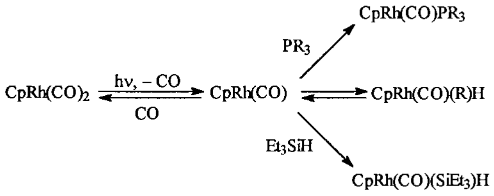
The photochemistry of $CpRh(CO)_2$ in room-temperature alkane (RH) following either UV or visible photolysis is characterized by a slow decomposition reaction and formation of a rather insoluble red carbonyl-bridged *trans*-$Cp_2Rh_2(CO)_3$ complex [5b, 7b]. However, the alkyl hydrido complex, CpRh(CO)(R)H, has been identified as a reaction intermediate via flash photolysis measurements; in the absence of a scavenging ligand this species has a lifetime on the order of milliseconds and it subsequently undergoes reductive elimination to form $[CpRh(\mu\text{-}CO)]_2$ and then more slowly to the above binuclear complex [5b]. Under these solution conditions the primary photoproduct (formally a 16-electron CpRh(CO) species) is rapidly solvated prior to the C–H activation reaction [4–7]. Consequently, the photoreactivity of $CpRh(CO)_2$ in hydrocarbon solution can be represented by an initial CO dissociation step followed by rapid solvation and then competing C–H activation and binucleation processes (see Eqs. (1) and (2)).



(1)

(2)

Although the photoproduced C–H activated alkyl hydrido CpRh(CO)(R)H derivatives are unstable it has been shown that it is possible to stabilize monocarbonyl photoproducts with the addition of an excess concentration of entering ligand [7]. Phosphine and phosphite ligands have been found to be excellent scavenging ligands for the solvated monocarbonyl intermediate, forming stable $CpRh(CO)PR_3$ and $Cp^*Rh(CO)PR_3$ complexes. Similarly, triethylsilane has been found to be effective at scavenging the monocarbonyl complex, forming a stable silyl hydrido $CpRh(CO)(SiEt_3)H$ derivative that is analogous to the C–H activated product (see Eqs. (3), (4) and (5)).



(3)

(4)

(5)

In the presence of these added scavenging ligands the solution photoreactions are exceptionally clean [7b]. Indeed, spectra recorded during the course of these reactions reveal that essentially complete conversions can be achieved without interference from secondary photoreactions or thermal processes. Examples of such spectra are shown in Figs. 1 and 2 which depict UV–visible and FTIR data acquired during laser photolysis at 458 nm of $CpRh(CO)_2$ in deoxygenated decalin solution containing excess PPh_3. The photochemical reaction proceeds cleanly, forming the $CpRh(CO)PPh_3$ photoproduct ($\nu(CO) = 1954\ cm^{-1}$) with the retention of isobestic points throughout the irradiation. Similarly,

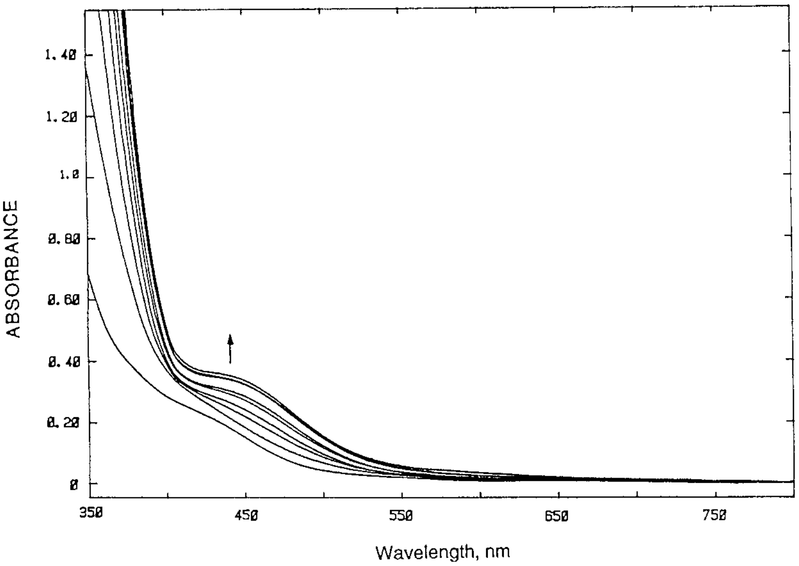


Fig. 1. UV–visible absorption spectral changes accompanying the 458-nm photolysis of $\mathrm{CpRh(CO)_2}$ in deoxygenated decalin solution containing 0.05 M $\mathrm{PPh_3}$ at 283 K. Spectra are depicted following irradiation intervals of 1h; initial spectrum recorded prior to irradiation. Data taken from Ref. [7b].

in triethylsilane solutions the reaction is able to proceed without complication (see Figs. 3 and 4), forming the corresponding $\mathrm{CpRh(CO)(SiEt_3)H}$ complex ($\nu(\mathrm{CO}) = 2009\ \mathrm{cm}^{-1}$) in almost complete conversion.

The $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)_2}$ complex provides a most interesting contrast because the UV or visible photochemistry in room-temperature alkane (RH) is clean without the need to add a scavenging ligand [8]. Here, the photochemical reaction in hydrocarbon solution involves complete conversion to the corresponding alkyl hydrido photoproduct, $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)(R)H}$, which is itself stable under the photolysis conditions. Once again the initial CO extrusion has been shown to be extremely fast, forming a monocarbonyl fragment which is solvated within 10 ps [12]. Consequently, the photochemistry of $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)_2}$ in hydrocarbon solution is represented by rapid CO dissociation and solvation followed by the C–H bond activation step (see Eq. (6)).

$$(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)}_2 \underset{\mathrm{CO}}{\overset{h\nu,-\mathrm{CO}}{\rightleftarrows}} (\mathrm{HBPz}_3^*)\mathrm{Rh(CO)} \rightarrow (\mathrm{HBPz}_3^*)\mathrm{Rh(CO)(R)H} \qquad (6)$$

Spectra obtained during the course of the photolysis of $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)_2}$ illustrate the exceptionally clean C–H activation process taking place in alkane solution. Representative UV–visible and FTIR spectra are depicted in Fig. 5; these were recorded during the 366-nm irradiation of $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)_2}$ in deoxygenated *n*-pentane solution at room temperature. The C–H activation reaction proceeds completely, forming the $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)(C_5H_{11})H}$ photoproduct ($\nu(\mathrm{CO}) = 2029\ \mathrm{cm}^{-1}$) with the retention of isosbestic points throughout the irradiation. Similar spectroscopic observations have been made in other hydrocarbons, including several arene solvents [8c].

The C–H activation photochemistry of $\mathrm{CpIr(CO)_2}$ in solution takes place with some of the features of both the above $\mathrm{CpRh(CO)_2}$ and $(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)_2}$ systems [7b,e]. In the absence of an added scavenging ligand, UV photolysis of the parent dicarbonyl complex in hydrocarbon solution results in conversion to the corresponding alkyl hydrido complex (see Eq. (7)), again via the solvated monocarbonyl species [4–7]. The CpIr(CO)(R)H photoproduct is somewhat more stable

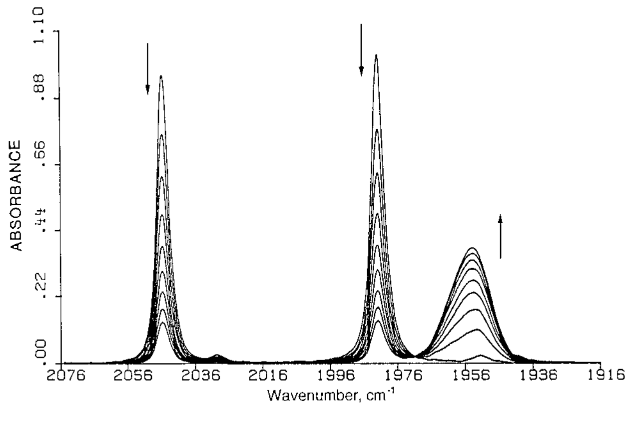


Fig. 2. FTIR absorption spectral changes accompanying the 458-nm photolysis of $\mathrm{CpRh(CO)_2}$ in deoxygenated decalin solution containing 0.05 M $\mathrm{PPh_3}$ at 283 K. Spectra are depicted following irradiation intervals of 1h; initial spectrum recorded prior to irradiation. Data taken from Ref. [7b].

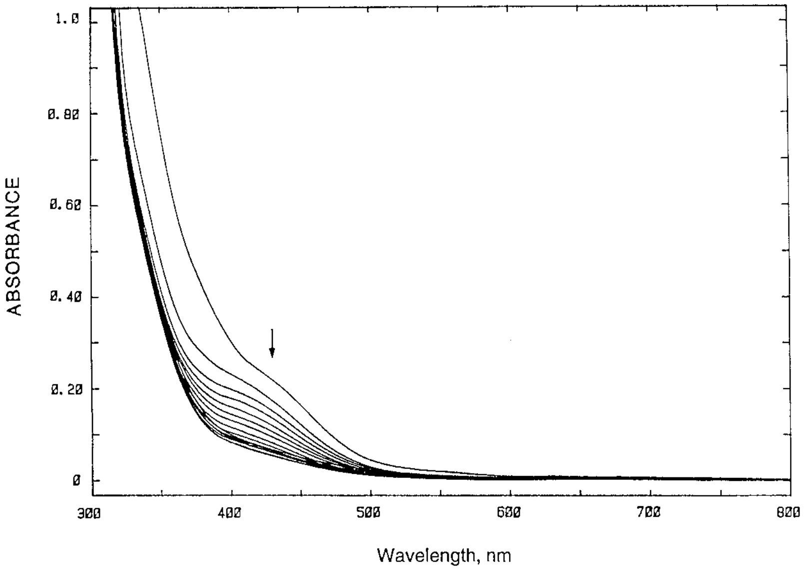


Fig. 3. UV–visible absorption spectral changes accompanying the 458-nm photolysis of $\mathrm{CpRh(CO)_2}$ in deoxygenated decalin solution containing 0.1 M $\mathrm{Et_3SiH}$ at 298 K. Spectra are depicted following irradiation intervals of 30 min; initial spectrum recorded prior to irradiation. Data taken from Ref. [7b].

than the corresponding rhodium complex, but it is itself light sensitive and readily decomposes (see Eq. (8)) [7f].

$$\begin{tikzcd} \mathrm{CpIr(CO)_2} \arrow[r, shift left, "h\nu,\ -\mathrm{CO}"] & \mathrm{CpIr(CO)} \arrow[l, shift left, "\mathrm{CO}"] \arrow[r] & \mathrm{CpIr(CO)(R)H} \arrow[d, "h\nu"] & (7) \\ & & \text{decomposition products} & (8) \end{tikzcd}$$

It should also be noted that the same C–H activation products can be reached by irradiation of substituted derivatives of $\mathrm{CpM(CO)_2}$. Photolysis of $\mathrm{CpRh(CO)(C_2H_4)}$ [4c,e] and $\mathrm{CpIr(CO)(C_2H_4)}$ [4g] offer the advantage of higher photochemical conversions, although once again there are competing products in the case of the iridium complex. Importantly, though, the studies of $\mathrm{CpIr(CO)(C_2H_4)}$ provide supporting evi-

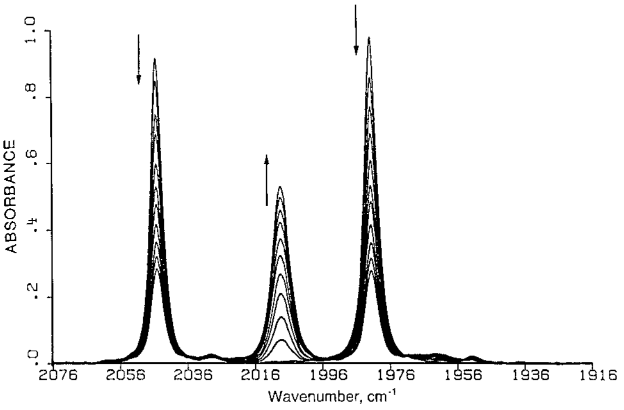


Fig. 4. FTIR absorption spectral changes accompanying the 458-nm photolysis of $\mathrm{CpRh(CO)_2}$ in deoxygenated decalin solution containing 0.1 M $\mathrm{Et_3SiH}$ at 298 K. Spectra are depicted following irradiation intervals of 30 min; initial spectrum recorded prior to irradiation. Data taken from Ref. [7b].

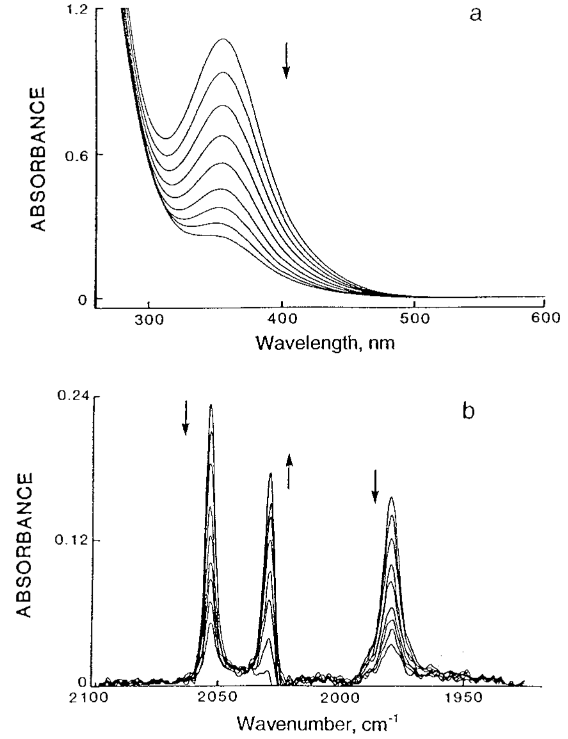


Fig. 5. (a) UV–visible and (b) FTIR absorption spectral changes accompanying the 366-nm photolysis of $\mathrm{(HBPz_3^*)Rh(CO)_2}$ in deoxygenated *n*-pentane at 293 K. Spectra are depicted following 45 s irradiation time intervals; initial spectra recorded prior to irradiation. Data taken from Ref. [8b].

dence for a dissociative pathway in the intermolecular C–H bond activation mechanism.

3. Quantum efficiencies

Both the photochemistry of the cyclopentadienyl and tris(pyrazolyl)borate systems have been investigated quantitatively with the determination of absolute photochemical quantum efficiencies at excitation wavelengths between 313 and 458 nm [7b, 8]. In the case of the $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ complexes the photochemical reaction quantum efficiencies (ϕ_{cr}) have been measured as a function of the entering ligand concentration for both the PR_3 photosubstitution and Si–H bond activation reactions (Eqs. (3) and (5)). These ϕ_{cr} results are shown in Figs. 6 and 7. In the case of $(HBPz_3^*)Rh(CO)_2$ the absolute quantum efficiencies for C–H bond activation (ϕ_{CH}) have been determined directly from the photochemical reactions in the hydrocarbon solutions (Eq. (6)). Table 1 summarizes ϕ_{CH} data obtained for $(HBPz_3^*)Rh(CO)_2$ in several alkane and arene solvents.

It can be seen that the quantum efficiencies for each of the complexes are strongly dependent on the exciting wavelength with the ligand substitution and C–H/Si–H bond activation reactions proceeding much more efficiently following UV excitation (313 or 366 nm) than visible irradiation (405 or 458 nm). The high quantum efficiencies recorded upon UV photolysis are entirely

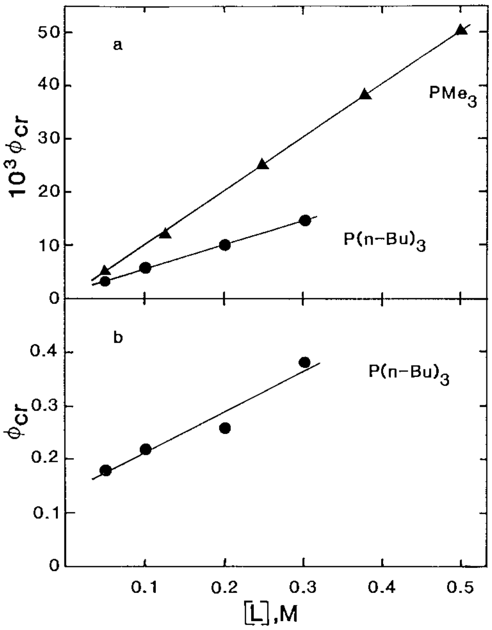


Fig. 7. Plots of photochemical quantum efficiencies (ϕ_{cr}) for the reaction of $CpRh(CO)_2$ with various concentrations of entering ligand, L = PMe_3 and $P(n\text{-}Bu)_3$, at 268 K. Excitation is at (a) 458 and (b) 313 nm. Each ϕ_{cr} value represents the mean of at least three readings; estimated uncertainties are within (a) ±5% and (b) ±10%. Data taken from Ref. [7b].

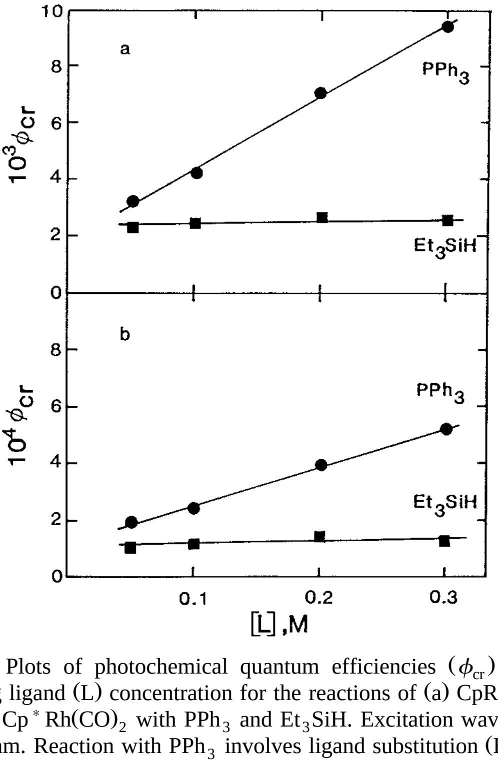


Fig. 6. Plots of photochemical quantum efficiencies (ϕ_{cr}) versus entering ligand (L) concentration for the reactions of (a) $CpRh(CO)_2$ and (b) $Cp^*Rh(CO)_2$ with PPh_3 and Et_3SiH. Excitation wavelength is 458 nm. Reaction with PPh_3 involves ligand substitution (Eq. (3)) and reaction with Et_3SiH involves Si–H bond activation (Eq. (5)). In (a) the photosubstitution data were obtained at 283 K and the Si–H bond activation data was recorded at 293 K. In (b) the data were obtained at 268 K. Each ϕ_{cr} value represents the mean of at least three readings; estimated uncertainties on ϕ_{cr} are within ±5%. Data taken from Ref. [7b].

Table 1
Absolute photochemical quantum efficiencies for the intermolecular C–H bond activation reaction of $(HBPz_3^*)Rh(CO)_2$ in deoxygenated hydrocarbon solutions at 293 K[a,b]

Solvent	λ_{ex} (nm)	ϕ_{CH}
Benzene	366	0.13
	458	0.0059
Toluene	366	0.14
	458	0.0073
p-xylene	366	0.17
	458	0.0086
Mesitylene	366	0.22
	458	0.0092
n-pentane	313	0.34
	366	0.32
	405	0.15
	458	0.011
n-hexane	366	0.31
	458	0.011
n-heptane	366	0.31
	458	0.010
Isooctane	366	0.31
	458	0.010

[a] Estimated errors ±8%.

[b] Data taken from Refs. [8b] and [8c].

consistent with an effective CO dissociation mechanism, as indeed is generally found for the primary photoprocesses of metal carbonyl complexes [13,14]. On the other hand, the reduced quantum efficiencies observed at longer excitation wavelengths in either system are unusual and indicate that an additional process must take place.

One rationale is that there are two overlapping excited states with different photochemical reactivities in both the cyclopentadienyl and tris(pyrazolyl)borate complexes. As different photochemical pathways appear to be involved, it is necessary to view their kinetics separately. The following represents a kinetic analysis for the rapid CO dissociation reaction from an upper excited state of $\mathrm{CpRh(CO)_2}$. This derives an expression of the quantum efficiency (ϕ) for the case when $\mathrm{Et_3SiH}$ is present as the scavenging ligand in excess concentration.

$$\mathrm{CpRh(CO)_2} \xrightarrow{I_{\mathrm{abs}}} \mathrm{CpRh(CO)} + \mathrm{CO} \tag{9}$$

$$\mathrm{CpRh(CO)} + \mathrm{CO} \xrightarrow{k_1} \mathrm{CpRh(CO)_2} \tag{10}$$

$$\mathrm{CpRh(CO)} + \mathrm{CpRh(CO)} \xrightarrow{k_2} [\mathrm{CpRh}(\mu-\mathrm{CO})]_2 \tag{11}$$

$$\mathrm{CpRh(CO)} + \mathrm{Et_3SiH} \xrightarrow{k_3} \mathrm{CpRh(CO)(SiEt_3)H} \tag{12}$$

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{CpRh(CO)}]}{\mathrm{d}t} &= I_{\mathrm{abs}} - k_1[\mathrm{CpRh(CO)}][\mathrm{CO}] \\ &\quad - k_2[\mathrm{CpRh(CO)}][\mathrm{CpRh(CO)}] \\ &\quad - k_3[\mathrm{CpRh(CO)}][\mathrm{Et_3SiH}] = 0\end{aligned} \tag{13}$$

$$[\mathrm{CpRh(CO)}] = \frac{I_{\mathrm{abs}}}{k_1[\mathrm{CO}] + k_2[\mathrm{CpRh(CO)}] + k_3[\mathrm{Et_3SiH}]} \tag{14}$$

$$\frac{\mathrm{d}[\mathrm{CpRh(CO)(SiEt_3)H}]}{\mathrm{d}t} = \frac{k_3[\mathrm{Et_3SiH}]\, I_{\mathrm{abs}}}{k_1[\mathrm{CO}] = k_2[\mathrm{CpRh(CO)}] + k_3[\mathrm{Et_3SiH}]} \tag{15}$$

hence

$$\phi = \frac{k_3[\mathrm{Et_3SiH}]}{k_1[\mathrm{CO}] + k_2[\mathrm{CpRh(CO)}] + k_3[\mathrm{Et_3SiH}]} \tag{16}$$

and

$$\phi = 1 \text{ when } \{k_1[\mathrm{CO}] + k_2[\mathrm{CpRh(CO)}]\} \ll k_3[\mathrm{Et_3SiH}] \tag{17}$$

This kinetic analysis assumes that the intermediate CpRh(CO) is produced with unity efficiency on light absorption and it does not account for nonradiative deactivation mechanisms from the upper energy excited state. In fact, the actual quantum yield for photoproduct formation (ϕ_{cr}) will be represented by the branching ratio $k_{\mathrm{CO}}/(k_{\mathrm{CO}} + k_{\mathrm{nr}})$, 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. Consequently, the above kinetic expression, which is based on rapid CO dissociation from an upper excited state, predicts that ϕ_{cr} will be independent of ligand concentration at low concentrations of CpRh(CO) and CO, as actually revealed by the experimental data for $\mathrm{Et_3SiH}$ (see Fig. 6). A similar analysis can be performed for the ligand substitution reaction with $\mathrm{PR_3}$ accounting for the small values of ϕ_{cr} at low $\mathrm{PR_3}$ concentration (here $\mathrm{PR_3}$ simply replaces $\mathrm{Et_3SiH}$ in the above Eqs. (12)–(17). It should be noted that the reaction of CpRh(CO) with RH is not incorporated in the above analysis, as CpRh(CO)(R)H is unstable and is inconsequential to the net photochemistry or the quantum efficiency. Also, prior saturation of the hydrocarbon solution with CO gas (ca. 9×10^{-3} M) was not observed to influence the measured ϕ_{cr} values [7b]; this is consistent with a negligible extent of back reaction with CO and the kinetic conditions shown in Eq. (17).

Considering the other pathway now, the following kinetic analysis represents an initial ring slippage ($\eta^5 \rightarrow \eta^3$) reaction from the lower excited state of $\mathrm{CpRh(CO)_2}$. It derives a quantum efficiency (ϕ) for the situation when $\mathrm{PR_3}$ is present as a scavenging ligand in high concentration.

$$\mathrm{CpRh(CO)_2} \xrightarrow{I_{\mathrm{abs}}} (\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2} \tag{18}$$

$$(\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2} \xrightarrow{k_1} \mathrm{CpRh(CO)_2} \tag{19}$$

$$(\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2} + \mathrm{PR_3} \xrightarrow{k_2} \mathrm{CpRh(CO)PR_3} + \mathrm{CO} \tag{20}$$

$$\begin{aligned}\frac{\mathrm{d}[(\eta_3-\mathrm{Cp})\mathrm{Rh(CO)_2}]}{\mathrm{d}t} &= I_{\mathrm{abs}} - k_1[(\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2}] \\ &\quad - k_2[(\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2}][\mathrm{PR_3}]\end{aligned} \tag{21}$$

$$[(\eta^3-\mathrm{Cp})\mathrm{Rh(CO)_2}] = \frac{I_{\mathrm{abs}}}{k_1 + k_2[\mathrm{PR_3}]} \tag{22}$$

$$\frac{\mathrm{d}[\mathrm{CpRh(CO)(PR_3)}]}{\mathrm{d}t} = \frac{k_2[\mathrm{PR_3}]\, I_{\mathrm{abs}}}{k_1 + k_2[\mathrm{PR_3}]} \tag{23}$$

hence

$$\phi = \frac{k_2[\mathrm{PR}_3]}{k_1 + k_2[\mathrm{PR}_3]} \tag{24}$$

and

$$\phi = \frac{k_2[\mathrm{PR}_3]}{k_1} \text{ when } k_2[\mathrm{PR}_3] \ll k_1. \tag{25}$$

This kinetic analysis again does not account for quantum inefficiencies and it assumes that $(\eta^3-$Cp)Rh(CO)$_2$ is formed in unity efficiency on excitation without competing nonradiative relaxation processes. The actual quantum efficiency for photoproduct formation (ϕ_{cr}) will be represented by the above expression for ϕ (Eq. (25)) multiplied by the branching ratio $k_{slip}/(k_{slip}+k_{nr})$, where k_{slip} is the rate constant for the cyclopentadienyl ring slippage ($\eta^5 \rightarrow \eta^3$) process (itself a dissociative step) and k_{nr} is the summation of the rate constants for nonradiative decay from the excited state. It is important to recognize that this kinetic analysis is based on a competitive process involving the back ring slip ($\eta^3 \rightarrow \eta^5$) with the ligand scavenging of the photoproduced intermediate. Notably, similar conclusions can be reached even if a more extensive $\eta^5 \rightarrow \eta^1$ hapticity change is considered. In either case, a ring slippage mechanism occurring from a lower excited state does predict the linear dependence of ϕ_{cr} on [PR$_3$], which is experimentally observed at high concentrations of scavenging ligand (see Figs. 6 and 7). It should be noted, though, that the reaction quantum efficiencies must be low for Eq. (25) to hold and for the linear dependence of ϕ_{cr} with [L] to occur. This is indeed the case for the excitations at 458 nm. Clearly, such kinetic behavior also rationalizes why the quantum efficiencies are influenced by the different scavenging abilities of the various PR$_3$ ligands (see Figs. 6 and 7) and the correlation with entering ligand cone angle [7b].

It is also noted that one could reach a similar kinetic conclusion if the excited state of the complex, [CpRh(CO)$_2$]*, is considered to react directly with the entering ligand to form a 20-electron species in an associative process. However, this pathway is unrealistic because ultrafast spectroscopic measurements have confirmed that the ligand scavenging even at diffusion controlled rates is not competitive with the CO dissociation process or the rapid solvation of the monocarbonyl primary photoproduct [4–7].

The photochemistry of Cp*Rh(CO)$_2$ appears to be analogous to CpRh(CO)$_2$, although it is interesting that the ϕ_{cr} values at 458 nm in the Cp* system are lower by more than an order of magnitude (see Fig. 6). Clearly, the nature of the cyclopentadienyl ligand substantially influences the quantum efficiency of the C–H activation mechanism. This is attributed to more effective nonradiative relaxation pathways from the excited states involved in the Cp* system, as the methyl substituents introduce many more vibrational modes. If this is the case then it is essentially the branching ratio of the excited state, representing the dissociative step relative to the nonradiative relaxation processes, that is being reduced. Noticeably, the experimentally determined slope of ϕ_{cr} versus [PPh$_3$] is lower in the case of the Cp*Rh(CO)$_2$ molecule (compare Figs. 6a and 6b) suggesting that the bimolecular reaction with PPh$_3$ is somewhat inhibited, presumably because of the increased steric hindrance about the Cp* ring. Thus, the quantum efficiency data appears to indicate that both components of the photochemical mechanism are affected by replacing Cp with Cp*.

In considering the photochemistry of (HBPz$_3^*$)Rh(CO)$_2$ it is helpful to first recognize its thermal reactivity. The complex is known to exist in room-temperature solution as an equilibrium mixture of two isomers in which the tris(3,5-dimethylpyrazolyl)borate ligand undergoes facile interconversions between tridentate (η^3) and bidentate (η^2) coordination (Eq. (26)). At 298 K the η^3 complex is predominant and estimates of $\Delta G \approx 12.6$ kJ mol^{-1} and $K_{eq} \approx 0.01$ have been obtained for this equilibrium in CH$_2$Cl$_2$ [9b]. The rate of ligand $\eta^3 \leftrightarrow \eta^2$ interconversion is apparently fast as ^{1}H NMR spectra of (HBPz$_3^*$)Rh(CO)$_2$ in CD$_2$Cl$_2$ at 183 K have revealed no evidence for the η^2 complex [9b]. However, IR spectra of the complex in CH$_2$Cl$_2$ at 298 K exhibit weak features at 2078 and 2009 cm^{-1}, attributed to the ν(CO) bands of the η^2 species; these are virtually isoenergetic with the ν(CO) bands at 2084 and 2020 cm^{-1} of the square planar (H$_2$BPz$_2$)Rh(CO)$_2$ complex [8b]. The η^2 species has also been isolated in its protonated form, [{η^2-HBPz$_2^*$)(Pz*H)}Rh(CO)$_2$]BF$_4$, exhibiting analogous ν(CO) bands at 2090 and 2026 cm^{-1} [8b,15].

$$(\eta^3-\mathrm{HBPz}_3^*)\mathrm{Rh(CO)}_2 \leftrightarrow (\eta^2-\mathrm{HBPz}_3^*)\mathrm{Rh(CO)}_2 \tag{26}$$

Significantly, although the $\eta^3 \leftrightarrow \eta^2$ interconversions are extremely facile in (HBPz$_3^*$)Rh(CO)$_2$, it was determined that C–H activation does not occur in the dark during the course of the photolysis experiment [8]. This observation eliminates a simple ligand $\eta^3 \rightarrow \eta^2$ dechelation as the key step in the photochemical C–H activation. The wavelength dependence of the quantum efficiencies (see Table 1), however, leads one to infer that the tris(pyrazolyl)borate ligand is perhaps not innocent in the photochemical mechanism and that it may undergo a $\eta^3 \rightarrow \eta^2$ ligand dechelation process upon long wavelength excitation. After all, the Rh–N bond is the weakest coordination bond in the molecule and a ligand dechelation route will effectively reduce the quantum efficiency as the $\eta^3 \rightarrow \eta^2$ pathway is inconsequential with respect to the C–H activation reactivity. Here the photoproduced η^2-complex simply returns to the parent species with no net photochemical conversion (see Eq. (27)). Actually, in the strictest sense of this mechanism the quantum efficiencies for C–H activation (ϕ_{CH}) should be zero, but clearly the lowest lying absorption band envelope is broad (see Fig. 5a) and visible excitation is not able to exclusively populate a lower energy excited state. Hence, C–H activation can still proceed (albeit less effectively) via the CO dissociative mechanism (Eq. (6)) from the upper energy level.

$$(\mathrm{HBPz}_3^*)\mathrm{Rh(CO)}_2 \overset{h\nu}{\rightleftarrows} (\eta^2-\mathrm{HBPz}_3^*)\mathrm{Rh(CO)}_2 \qquad (27)$$

Consequently, the wavelength dependence of the quantum efficiencies of both the cyclopentadienyl and tris(pyrazolyl)borato systems can be explained by invoking a second primary photoproduct that is formed upon visible light absorption. A photophysical scheme representing this postulation and assuming ligand field (LF) reactivity (vide infra) is shown in Fig. 8. In the case of CpRh(CO)$_2$, the lifetime of the (η^3-Cp)Rh(CO)$_2$ intermediate (presumably in the solvated form again) can be estimated from the scavenging data. Noting that the obtained ϕ_{cr} results already rise above the value for the CO dissociation reaction when [PR$_3$] = 0.05 M (see Fig. 6), and assuming that the scavenging process is diffusion controlled (with k$_{diff}$ between 10^9 and 10^{10} M^{-1} s^{-1}), then the lifetime of this reaction intermediate will lie between 2 and 20 ns. However, it should be recognized that time-resolved studies have not yet revealed the presence of this second reaction intermediate, although this is perhaps not surprising considering that all these investigations were carried out at shorter excitation wavelengths than the 405–458 nm region and, hence, are focused on the monocarbonyl primary photoproduct. Moreover, a solvated ring slipped species, (η^3-Cp)Rh(CO)$_2$ . . . S, may be more difficult to identify spectroscopically (either in transient UV–visible or TRIR spectra) than the monocarbonyl complex if it is initially produced in a low formation efficiency. Significantly, though, there is other spectroscopic evidence for a η^3-Cp species. In recent matrix isolation work it has been determined that (η^3-Cp)Rh(CO)$_3$ is generated upon prolonged long wavelength (> 400 nm) irradiation of CpRh(CO)$_2$ in CO matrices [16] and there is considerable support for the formation of (η^3-Cp)Rh(CO)$_2$PR$_3$ intermediates in the thermal chemistry of CpRh(CO)$_2$ [17,18].

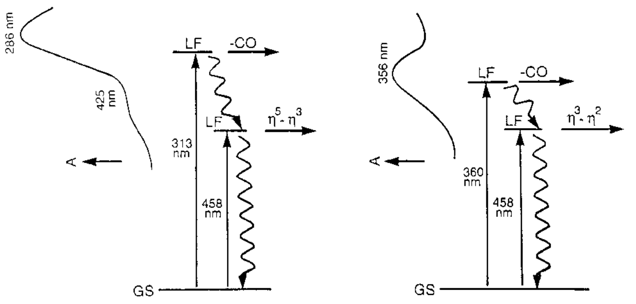


Fig. 8. Photophysical schemes for (a) CpRh(CO)$_2$ and (b) (HBPz$_3^*$)Rh(CO)$_2$ portraying different reactivities from two ligand field excited states. Figure reproduced from Ref. [7d].

For CpRh(CO)$_2$ and Cp*Rh(CO)$_2$ the irradiations at 313 and 458 nm roughly correspond to the positions of the lowest energy absorption feature, which is essentially a long tail with a shoulder in the visible region (see Fig. 1). Hence, it is entirely reasonable to associate these quantum efficiency results with the population of two different excited states. For (HBPz$_3^*$)Rh(CO)$_2$, however, the lowest energy absorption band is broad and unstructured and provides no spectral evidence for two different excited states (see Fig. 5a). Moreover, unlike the CpRh(CO)$_2$ and Cp*Rh(CO)$_2$ systems there is no specific evidence from the ϕ_{CH} results for a different type of reactivity upon long-wavelength excitation. And, again, the postulated (η^2-HBPz$_3^*$)Rh(CO)$_2$ intermediate has not yet been identified spectroscopically in the photoreactivity [19], despite the fact that it is prevalent in the thermal chemistry. Perhaps the long-wavelength photochemistry of (HBPz$_3^*$)Rh(CO)$_2$ may not be quite so analogous to the cyclopentadienyl system and it is worthwhile considering some other possibilities that could also give a quantum efficiency wavelength dependence.

Firstly, it may be that while two excited states are involved, the lower state is actually unreactive but leads to CO dissociation via thermal activation to the upper level. While this hypothesis certainly has ample precedent in organometallic photophysics [13b], recent measurements of the temperature dependence of quantum efficiency following long-wavelength excitation of (HBPz$_3^*$)Rh(CO)$_2$ do not support it in this case, however. For instance, measurements of the C–H activation reaction of (HBPz$_3^*$)Rh(CO)$_2$ in *n*-pentane has resulted only in low apparent activation energies of 8.3 (±2.5) and 5.4 (±2.5) kJ mol^{-1} following excitation at 366 and 458 nm, respectively [8b]. Such low activation energies are more consistent with the replacement of solvent in the solvated (η^2-HBPz$_3^*$)Rh(CO)$_2$ . . . S intermediate, rather than portraying a thermal activation process between two different excited states. Moreover, low activation energies have been obtained from the 458-nm ligand photosubstitution reaction of CpRh(CO)$_2$ with PPh$_3$, which yielded a value of 15.5 (±2.5) kJ mol^{-1} [7b]. Also, recent studies of the reactions of Cp*Rh(CO)X with hydrocarbons in liquefied rare gas solvents (X = Kr, Xe) are relevant, having revealed similarly low activation energies [6c,d, 10].

Secondly, the long-wavelength reactivity may arise from a triplet state with reduced reactivity. This situation would be analogous to that of $W(CO)_5$(pyridine), where convincing evidence has been obtained for more efficient reactivity taking place directly from a neighboring ligand field singlet state [20]. Thirdly, the wavelength dependence of the quantum efficiencies can be rationalized by implicating a third lower energy ''dark'' state that is itself unreactive but leads to ground state recovery. Such a mechanism has been suggested for other transition metal complexes, including several Co(III) systems [21]. Finally, the distinct photochemical mechanisms may not occur via two different excited states at all, but could take place on one excited-state potential surface. Excitation at higher energy might lead to a prompt CO dissociation reaction, whereas shorter energy irradiation may populate a lower part of the potential which undergoes more effective radiationless deactivation and, hence, the reaction proceeds via a less efficient CO dissociative pathway. Clearly, these aspects of the primary photochemistry are still to be resolved.

It is also interesting to see that the ϕ_{CH} results for $(HBPz^*_3)Rh(CO)_2$ at a common excitation wavelength are lower for the aromatic solutions than in the alkanes (see Table 1) [8]. This observation is rather intriguing as the CO back-reaction to form the starting complex is not a competitive mechanism under the experimental conditions, as revealed by the lack of a [CO] dependence on ϕ_{CH}. Consequently, the variations in the C–H activation quantum efficiencies cannot be explained on the premise of differing kinetic reactivities of the hydrocarbon substrates. Furthermore, the solvent viscosities for the range of hydrocarbons studied are similar so it would not appear that geminate CO recombination via solvent cage effects are influencing the ϕ_{CH} values. In this regard, recent ultrafast spectroscopic measurements on $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ have also eliminated the possibility of both geminate and diffusional CO processes affecting the quantum efficiencies [5f]. Thus, the variations of ϕ_{CH} over the range of hydrocarbons would seem to be influenced predominantly by photophysical effects and, specifically, the extent of nonradiative relaxation from the excited state of $(HBPz^*_3)Rh(CO)_2$. Once again, it is apparently the branching ratio between the dissociative and nonradiative routes that ultimately determines the C–H activation photochemical efficiency.

4. Excited states

In each of the above photosubstitution and C–H activation reactions of $CpRh(CO)_2$, $Cp^*Rh(CO)_2$ and $(HBPz^*_3)Rh(CO)_2$ the UV and visible excitations are into their lowest (or second lowest) energy absorption bands (see Table 2). The electronically-excited states in these complexes would appear to be ligand field (LF) transitions for several reasons. For instance, it is notable that the energy positions of these absorption bands are in accordance with the ligand field strengths of the d^8 metals (the analogous $CpCo(CO)_2$ complex is red) [13a]. Also, their molar absorptivities are relatively low, although in the case of $(HBPz^*_3)Rh(CO)_2$ the lowest energy absorption band is significantly more intense than the corresponding feature of the other complexes and suggests that a charge transfer component may be overlapping. Moreover, the energies of all these lowest energy transitions exhibit negligible solvent dependence [7b, 8b,c], consistent with assignment of LF transitions [13,22]. Additionally, low-temperature luminescence measurements carried out on these complexes as EPA glassy solutions and solids at 77 K have yielded no discernible emission features [7b, 8b], concordant with rapid nonradiative deactivation of the excited states and the LF assignments [13b]. Finally, the quantum efficiency data described above have confirmed that the excited states in these molecules are highly dissociative in nature, which is again consistent with them being LF levels [13a,b]. Indeed, recent ultrafast (fs) spectroscopy on several of these dicarbonyl complexes has revealed the dissociative properties of the lowest lying excited states [5c–f, 12]. These experiments have shown that the unsolvated monocarbonyl species is formed promptly and then solvated within a matter of a few ps.

Table 2
Lowest lying electronic absorption bands of $CpM(CO)_2$, $Cp*M(CO)_2$ and $(HBPz^*_3)Rh(CO)_2$ complexes in decalin at 298 K[a,b]

Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$CpRh(CO)_2$	425 (sh)	78
$Cp^*Rh(CO)_2$	505	152
$CpIr(CO)_2$	355 (sh)	144
$Cp^*Ir(CO)_2$	380 (sh)	67
$(HBPz^*_3)Rh(CO)_2$	356	2100

[a] Data taken from Ref. [7d].
[b] Recorded in *n*-pentane for $(HBPz^*_3)Rh(CO)_2$.

5. Conclusion

A comparison of the solution photochemistry of $CpRh(CO)_2$, $Cp^*Rh(CO)_2$ and $(HBPz^*_3)Rh(CO)_2$ complexes has identified a number of common features in the C–H activation chemistry. In each instance, the photochemical reactivity upon UV irradiation is characterized by extremely fast and efficient CO dissociation from excited states, which are apparently LF in nature. There is also now convincing evidence that the intermolecular C–H bond activation step takes place following the formation of a solvated monocarbonyl complex.

Additionally, it is significant that the back reaction of the photoproduced intermediate with CO to reform the parent complex does not take place effectively, so the photochemical quantum efficiencies for C–H activation are influenced predominantly by the extent of CO dissociation relative to the nonradiative relaxation processes from the excited state. On the other hand, it is noticeable that in either system a reduced photoreactivity occurs following visible photolysis; kinetic analysis of the absolute quantum efficiencies obtained suggests that these reaction mechanisms may involve ligand ring-slippage or dechelation processes.

Acknowledgements

Gratitude is extended to the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy (Grant DE-FG02-89ER14039) for support of this research.

References

[1] For recent reviews see: (a) A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, Reidel, Boston, MA, 1984; (b) R.H. Crabtree, Chem. Rev. 85 (1985) 245; (c) C.L. Hill, Activation and Functionalization of Alkanes, Wiley, New York, 1989; (d) W.D. Jones, F.J. Feher, Acc. Chem. Res. 22 (1989) 91; (e) J.A. Davies, P.L. Watson, L.F. Liebman, A. Greenberg, Selective Hydrocarbon Activation, VCH Publishers, New York, 1990; (f) A.D. Ryabov, Chem. Rev. 90 (1990) 403; (g) R.H. Crabtree, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Alkanes and Cycloalkanes, Wiley, New York, 1992, p. 653; (h) R.N. Perutz, Chem. Soc. Rev. (1993) 361; (i) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., Wiley-Interscience, New York, 1994, p. 321; (j) B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154; (k) B.A. Arndtsen, R.G. Bergman, Science 270 (1995) 1970; (l) A.A. Bengali, B.A. Arndtsen, P.M. Burger, R.H. Schultz, B.H. Weiller, K.R. Kyle, C.B. Moore, R.G. Bergman, Pure Appl. Chem. 67 (1995) 281.

[2] (a) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352. (b) J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723; (c) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 3929; (d) J.K. Hoyano, A.D. McMaster, W.A.G. Graham, J. Am. Chem. Soc. 105 (1983) 7190; (e) R.A. Periana, R.G. Bergman, Organometallics 3 (1984) 508; (f) M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac, R.G. Bergman, J. Am. Chem. Soc. 106 (1984) 1211; (g) A.H. Janowicz, R.A. Periana, J.M. Buchanan, C.A. Kovak, J.M. Stryker, M.J. Wax, R.G. Bergman, Pure Appl. Chem. 56 (1984) 13; (h) R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 106 (1984) 7272; (i) B.A. Arndtsen, R.G. Bergman, A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 156.

[3] (a) W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 104 (1982) 4240; (b) W.D. Jones, F.J. Feher, Organometallics 2 (1983) 562; (c) W.D. Jones, F.J. Feher, Organometallics 2 (1983) 686; (d) W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 106 (1984) 1650; (e) W.D. Jones, F.J. Feher, Inorg. Chem. 23 (1984) 2376; (f) W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 107 (1985) 620.

[4] (a) A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano, A.D. McMaster, J. Chem. Soc., Chem. Commun. (1984) 624; (b) D.M. Haddleton, R.N. Perutz, J. Chem. Soc., Chem. Commun. (1985) 1372; (c) D.M. Haddleton J. Organomet. Chem. 311 (1986) C21; (d) A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano, A.D. McMaster, J. Chem. Soc., Dalton Trans. (1987) 1181; (e) D.M. Haddleton, A. McCamley, R.N. Perutz, J. Am. Chem. Soc. 110 (1988) 1810; (f) P.E. Bloyce, A.J. Rest, I. Whitwell, W.A.G. Graham, R. Holmes-Smith, J. Chem. Soc., Chem. Commun. (1988) 846; (g) T.W. Bell, S.-A. Brough, M.G. Partridge, R.N. Perutz, A.D. Rooney, Organometallics 12 (1993) 2933.

[5] (a) S.T. Belt, D.M. Haddleton, R.N. Perutz, B.P.H. Smith and A.J. Dixon, J. Chem. Soc. Chem. Commun., (1987) 1347; (b) S.T. Belt, F.-W. Grevels, W.E. Koltzbücher, A. McCamley and R.N. Perutz, J. Am. Chem. Soc., 111 (1989) 8373; (c) T.P. Dougherty and E.J. Heilweil, J. Chem. Phys., 100 (1994) 4006; (d) W.T. Grubbs, T.P. Dougherty and E.J. Heilweil, Chem. Phys. Letts., 227 (1994) 480; (e) T.P. Dougherty, W.T. Grubbs and E.J. Heilweil, J. Phys. Chem., 98 (1994) 9396; (f) S.E. Bromberg, T. Lian, R.G. Bergman and C.B. Harris, J. Am. Chem. Soc., 118 (1996) 2069.

[6] (a) D.M. Haddleton, R.N. Perutz, S.A. Jackson, R.K. Upmacis, M. Poliakoff, J. Organomet. Chem. 311 (1986) C15; (b) M.B. Sponsler, B.H. Weiller, P.O. Stoutland, R.G. Bergman, J. Am. Chem. Soc. 111 (1989) 6841; (c) B.H. Weiller, E.P. Wasserman, R.G. Bergman, C.B. Moore, G.C. Pimentel, J. Am. Chem. Soc. 111 (1989) 8288; (d) B.H. Weiller, E.P. Wasserman, C.B. Moore, R.G. Bergman, J. Am. Chem. Soc. 115 (1993) 4326.

[7] (a) D.P. Drolet, A.J. Lees, J. Am. Chem. Soc. 112 (1990) 5878; (b) D.P. Drolet, A.J. Lees, J. Am. Chem. Soc. 114 (1992) 4186; (c) A.A. Purwoko, A.J. Lees, Coord. Chem. Rev. 132 (1994) 155; (d) A.A. Purwoko, A.J. Lees, J. Organomet. Chem. 504 (1995) 107; (e) D.E. Marx, A.J. Lees, Inorg. Chem. 27 (1988) 1121; (f) D.P. Drolet, A.J. Lees, unpublished results.

[8] (a) A.A. Purwoko, A.J. Lees, Inorg. Chem. 34 (1995) 424; (b) A.A. Purwoko, A.J. Lees, Inorg. Chem. 35 (1996) 675; (c) A.A. Purwoko, S.D. Tibensky, A.J. Lees, Inorg. Chem. 35 (1996) 7049.

[9] (a) C.K. Ghosh, W.A.G. Graham, J. Am. Chem. Soc. 109 (1987) 4726; (b) C.K. Ghosh, PhD Dissertation, University of Alberta, Edmonton, Alberta, Canada, 1988; (c) P.E. Bloyce, J. Mascetti, A.J. Rest, J. Organomet. Chem. 444 (1993) 223; (d) S. Trofimenko, Chem. Rev. 93 (1993) 943.

[10] (a) R.H. Schultz, A.A. Bengali, M.J. Tauber, B.H. Weiller, E.P. Wasserman, K.R. Kyle, C.B. Moore, R.G. Bergman, J. Am. Chem. Soc. 116 (1994) 7369; (b) A.A. Bengali, R.H. Schultz, C.B. Moore, R.G. Bergman, J. Am. Chem. Soc. 116 (1994) 9585.

[11] E.P. Wasserman, C.B. Moore, R.G. Bergman, Science 255 (1992) 315.

[12] T. Lian, S.E. Bromberg, H. Yang, G. Proulx, R.G. Bergman, C.B. Harris, J. Am. Chem. Soc. 118 (1996) 3769.

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

[14] (a) R. Bonneau, J.M. Kelly, J. Am. Chem. Soc. 102 (1980) 1220; (b) A.J. Lees, A.W. Adamson, Inorg. Chem. 20 (1981) 4381; (c) J.M. Kelly, C. Long, R. Bonneau, J. Phys. Chem. 87 (1983) 3344; (d) J.D. Simon, X. Xie, J. Phys. Chem. 90 (1986) 6751; (e) J.D. Simon, X. Xie, J. Phys. Chem. 90 (1986) 6751; (f) J.D. Simon, X. Xie, J. Phys. Chem. 91 (1987) 5538; J.D. Simon, X. Xie, J. Phys. Chem. 93 (1989) 291; (h) L. Wang, X. Zhu, K.G. Spears, J. Am. Chem. Soc. 110 (1988) 8695; (i) A.G. Joly, K.A. Nelson, J. Phys. Chem. 93 (1989) 2876; (j) M. Lee, C.B. Harris, J. Am. Chem. Soc. 111 (1989) 8963; (k) X. Xie, J.D. Simon, J. Am. Chem. Soc. 112 (1990) 1130; (l) S.-C. Yu,

X. Xu, R. Lingle, J.B. Hopkins, J. Am. Chem. Soc. 112 (1990) 3668; (m) E. O'Driscoll, J.D. Simon, J. Am. Chem. Soc. 112 (1990) 6580.

[15] R.G. Ball, C.K. Ghosh, J.K. Hoyano, A.D. McMaster, W.A.G. Graham, J. Chem. Soc., Chem. Commun. (1989) 341.

[16] R.N. Perutz, unpublished results.

[17] (a) H.G. Schuster-Woldan, F. Basolo, J. Am. Chem. Soc. 88 (1996) 1657; (b) R. Cramer, L.P. Seiwell, J. Organomet. Chem. 92 (1975) 245; (c) M.E. Rerek, F. Basolo, Organometallics 2 (1983) 372; (d) M.E. Rerek, F. Basolo, J. Am. Chem. Soc. 106 (1984) 5908; (e) L. Ji, M.E. Rerek, F. Basolo, Organometallics 3 (1984) 740; (f) M. Cheong, F. Basolo, Organometallics 7 (1988) 2041; (g) D.L. Lichtenberger, S.K. Renshaw, F. Basolo, M. Cheong, Organometallics 10 (1991) 148.

[18] J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307.

[19] No evidence for the η^2-species has been observed in 458-nm irradiation experiments in liquefied xenon at 228 K; S.D. Tibensky, A.J. Lees, T.L. Snoeck, D.J. Stufkens, unpublished results.

[20] C. Moralejo, C.H. Langford, D.K. Sharma, Inorg. Chem. 28 (1989) 2205.

[21] (a) L. Moggi, F. Bolletta, V. Balzani, F. Scandola, J. Inorg. Nucl. Chem. 28 (1966) 2589; (b) R.A. Pribush, C.K. Poon, C.M. Bruce, A.W. Adamson, J. Am. Chem. Soc. 96 (1974) 3027; (c) R.B. Wilson, E.I. Solomon, J. Am. Chem. Soc. 102 (1980) 4085; (d) C.H. Langford, Acc. Chem. Res. 17 (1984) 96; (e) J.K. McCusker, K.N. Walda, D. Magde, D.N. Hendrickson, Inorg. Chem. 32 (1993) 394.

[22] D.M. Manuta, A.J. Lees, Inorg. Chem. 25 (1986) 3212.