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Photochemical mechanisms in intermolecular C-H bond activation reactions of organometallic complexes

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ABSTRACT

This article describes observations obtained from detailed investigations of the photochemistry of $(\eta^5\text{-}C_5R_5)Rh(CO)_2$ (R = H, Me) and $(HBPz^*_3)Rh(CO)_2$ (Pz* = 3,5-dimethylpyrazolyl) complexes in hydrocarbon solutions. Photochemical quantum efficiency data have been recorded for ligand photosubstitution and intermolecular Si-H/C-H bond activation processes following excitation at various wavelengths in the visible and near-UV regions. The results obtained, taken in conjunction with prior photochemical measurements (viz. matrix isolation, flash photolysis and low temperature studies in liquefied noble gases) lead to a proposed mechanistic scheme that explains both the ligand photosubstitution and C-H/Si-H bond activation reactions.

A. INTRODUCTION

Currently there is considerable interest in the photochemistry of $CpM(CO)_2$ and $Cp^*M(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$; M = Rh, Ir) complexes following the recognition that these and closely related molecules undergo light-induced intermolecular C-H bond activation reactions with saturated hydrocarbons [1-7]. In recent years, much effort has been devoted to establishing the nature and reactivity of the primary photoproducts that are formed [8-14]. Although coordinatively-unsaturated 16-electron CpRh(CO) and Cp*Rh(CO) species are believed to be key reaction intermediates in these processes they are extremely reactive and have not yet been spectroscopically observed in solution. Moreover, it is interesting to note that the thermal chemistry of $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ is understood to take place via an associative mechanism involving η^5-η^3 ring slippage of the cyclopentadienyl ligand [15-18].

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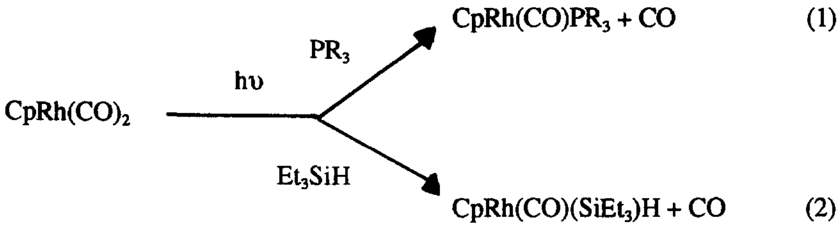
In contrast, there is relatively little photochemical information about the analogous $(HBPz^*_3)Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazolyl) complex which has been reported to readily activate both aromatic and saturated hydrocarbon molecules following photolysis in room-temperature solution [19]. This particular system is of significance because the intermolecular C-H bond activation appears to occur efficiently and with high thermodynamic selectivity. Moreover, the activation reaction is unusual in that it has been observed to proceed following irradiation in the visible region.

In this article we present evidence for the photochemical mechanisms that take place in the intermolecular C-H bond activation reactions of $CpRh(CO)_2$ [20,21] and $(HBPz^*_3)Rh(CO)_2$ [22] complexes.

B. RESULTS AND DISCUSSION

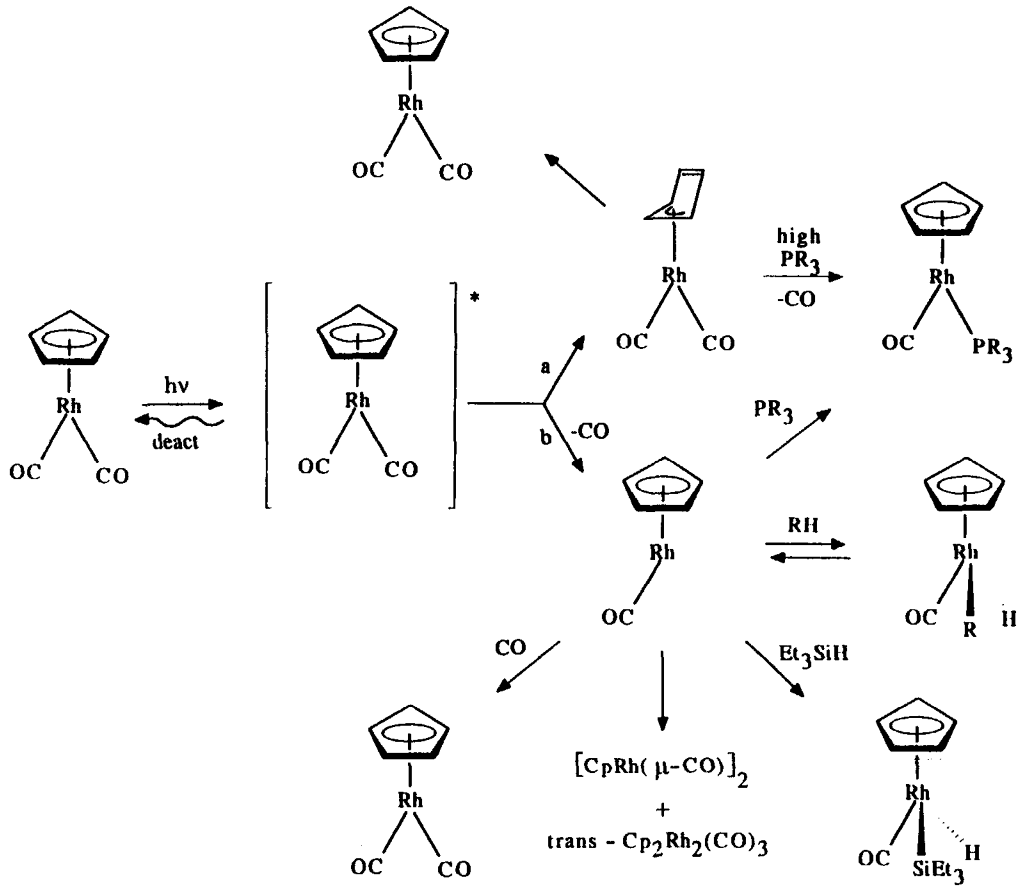
(i) $CpRh(CO)_2$

The photochemical reactions for the intermolecular C-H bond activation could not be measured directly as the oxidative addition products are not stable in solution [11]. Consequently, the photochemistry of ligand substitution (eq. 1) and Si-H oxidative addition (eq. 2) has been investigated.



Quantum efficiencies (ϕ_{cr}) have been determined for $CpRh(CO)_2$ in decalin solution as a function of substrate concentration, nature of the entering ligand (phosphine, phosphite) and irradiation wavelength (313, 458 nm) [20,21]. Similar measurements were carried out for $Cp^*Rh(CO)_2$ at 458 nm. Plots of the ϕ_{cr} values determined at 458 nm versus entering ligand (L) concentration of PPh_3 and Et_3SiH are shown in Fig. 1.

Several observations have been made from the photosubstitution (eq. 1) data. Firstly, the quantum efficiencies of both complexes measured at 458 nm increase linearly with phosphine concentration. Secondly, ϕ_{cr} data for the Cp* derivative are more than an order of magnitude lower than the Cp complex. Thirdly, the ϕ_{cr} values are not affected significantly by the addition of CO [20, 21]. Fourthly, the ϕ_{cr} results vary as the nature of the entering ligand is changed, the ϕ_{cr} values increasing as the phosphine cone angle decreases [21]. These observations are all consistent with a η^5-η^3 ring slippage mechanism and a ligand scavenging process which is competitive with the back η^3-η^5 process. However, the non-zero intercepts exhibited in Fig. 1 also suggest that there is a residual dissociative component to the reaction mechanism.



OC
CO
Rh
hν
deact
*
a
b
-CO
high
PR3
-CO
PR3
RH
Et3SiH
CO
R
H
SiEt3
[CpRh(μ-CO)]2
+
trans - Cp2Rh2(CO)3

Scheme 1

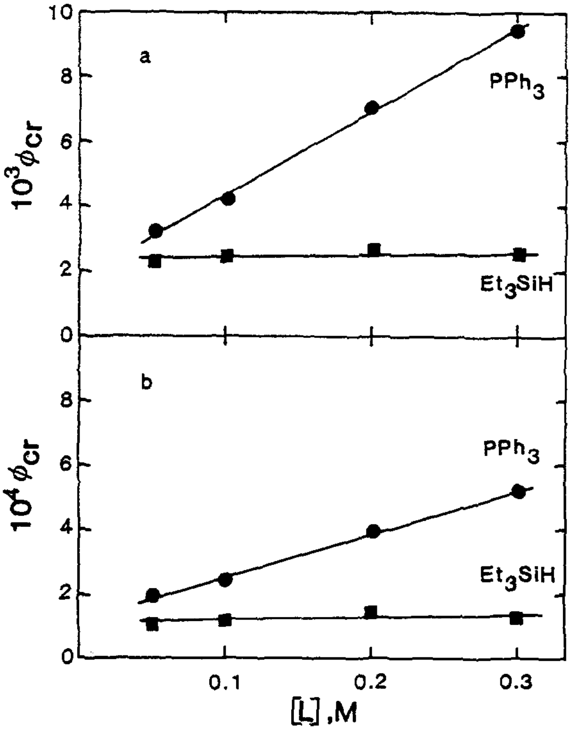


Fig. 1. Photochemical quantum efficiencies for the reactions of [a] $CpRh(CO)_2$ and [b] $Cp^*Rh(CO)_2$ with various concentrations of PPh_3 and Et_3SiH. (Reprinted, with permission, from ref. 21).

In contrast, the photochemical results for the Si-H activation reaction (eq. 2) are independent of the Et_3SiH concentration, although the observed intercepts for both complexes are, within experimental error, concordant with the photosubstitution data. Consequently, the oxidative addition reaction is concluded to proceed by a mechanism involving CO dissociation. Qualitatively similar results have been obtained following excitation at 313 nm, but the observed ϕ_{cr} values and the corresponding intercepts are approximately two orders of magnitude greater and significantly less dependent on PR_3 concentration and the nature of the entering nucleophile [21]. Hence, there appears to be a much larger contribution from the dissociative component in the mechanism at the shorter excitation wavelength.

Mechanistic pathways that represent these and prior experimental observations [8-14] are shown in Scheme I. The excitation wavelength dependence results illustrate that two ligand field (LF) excited states are populated which lead to different primary photoproducts. These excited levels are expected to be extremely short-lived in fluid solution [23] and are non-luminescent in 77 K glasses [24]. The quantum efficiency data implies that the higher energy excitation (313 nm) predominantly results in CO dissociation, whereas the lower energy excitation (458 nm) produces mainly η^5-η^3 ring slippages. The influence of Cp ring methylation on the ϕ_{cr} results further supports the involvement of a ring hapticity change. However, the low quantum efficiencies at 458 nm indicate that the back η^3-η^5 ring slippage process is very efficient. The key reaction intermediates are shown in Scheme 1; these are anticipated to be rapidly scavenged by solvent molecules (S) to form solvent coordinated species which subsequently react with the PR_3 ligands.

The ϕ_{cr} results also imply a dissociative route for the C-H/Si-H bond activation pathway; this is in accordance with earlier flash photolysis and low temperature measurements [8-14]. It is interesting to note that the (η^3-Cp)Rh(CO)$_2$ intermediate does not activate the R-H bond, whereas the CpRh(CO) species facilitates this reaction. It may be the electron withdrawing effect of the additional CO ligand in the former intermediate that makes the metal centre unable to perform the oxidative addition.

(ii) (HBPz*$_3$)Rh(CO)$_2$

Photochemical oxidative addition reactions in alkane solutions were monitored by recording UV-visible and FTIR spectra throughout photolysis; the spectral sequences are entirely in agreement with the intermolecular C-H bond activation reaction (eq. 3) first reported by Ghosh and Graham [19].

$$(HBPz^*_3)Rh(CO)_2 \xrightarrow[\text{n-pentane}]{h\nu} (HBPz^*_3)Rh(CO)(C_5H_{11})H + CO \qquad (3)$$

The photochemistry here is exceptionally clear and it is possible to achieve complete photoconversion to the hydrido product without any interference from secondary photoreactions. Moreover, spectra recorded from solutions kept in the dark at 293 K establish that there is a negligible contribution from thermal processes involving C-H bond activation during the course of these photochemical transformations.

Quantum efficiencies (ϕ_{CH}) for eq. 3 have been obtained following irradiation at 313, 366, 405 and 458 nm and are 0.34, 0.32, 0.15 and 0.01, respectively, illustrating a strong excitation wavelength dependence. Clearly, two electronically excited states with different reactivities are implicated in the photochemistry. It would appear reasonable to associate the reduced C-H bond activation from the lower energy level with the known thermal chemistry in which the tris(3,5-dimethylpyrazolyl)borate ligand undergoes facile η^3-η^2-η^3 interconversions [19]. Under such conditions visible excitation will result in a η^2 species and the determined ϕ_{CH} value will be low because of the rapid η^2-η^3 back reaction. On the other hand, the ϕ_{CH} data unequivocally demonstrate that population of an upper energy level leads to highly effective intermolecular C-H bond activation. This may be due to initial formation of a highly reactive monocarbonyl species, analagous to the above CpRh(CO)$_2$ system.

D. ACKNOWLEDGEMENT

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