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Photochemistry and C−H Bond Activation Reactivity of $(HBPz^*_3)Rh(CO)_2$ (Pz^* = 3,5-Dimethylpyrazolyl) in Hydrocarbon Solution

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Currently, there is considerable interest in the photochemistry of complexes of the general formulas $(\eta^5\text{-}C_5R_5)ML_2$ and $(\eta^5\text{-}C_5R_5)ML(H)_2$ (R = H, Me; M = Rh, Ir; L = CO, PR_3, olefin) following the recognition that these molecules undergo light-induced intermolecular C−H bond activation processes with saturated hydrocarbons.[1] In recent years much effort has been devoted to establishing the nature and reactivity of the primary photoproducts that are formed in these cyclopentadienyl systems.[2−5] On the other hand, there is relatively little photochemical information about the dicarbonyl(tris(3,5-dimethylpyrazolyl)borato)rhodium(I) complex, $(HBPz^*_3)Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazolyl), which has been reported to readily activate both aromatic and saturated hydrocarbons following photolysis (even with daylight) in room-temperature solution.[6] This particular system is especially significant because the intermolecular C−H bond activation appears to take place efficiently and with high thermodynamic selectivity; however, to date, the photochemical and photophysical mechanisms taking place in room-temperature solution are not understood.

In this article, we report the results of our measurements of the solution photochemistry of $(HBPz^*_3)Rh(CO)_2$, including a determination of the absolute quantum efficiencies for intermolecular C−H bond activation at several excitation wavelengths.[7,8] The results reveal that the C−H bond activation reaction proceeds exceptionally cleanly in room-temperature solution following photolyses in either the near-UV or visible region. Moreover, the obtained quantum efficiencies demonstrate that the C−H bond activation process is strongly dependent on the wavelength of light excitation and that high conversion efficiencies can be attained.

The photochemical reactions were monitored by recording diode-array UV−visible and FTIR spectra throughout photolysis; typical results are shown in Figure 1. These results are entirely in agreement with the intermolecular C−H bond activation reaction (eq 1) reported by Ghosh and Graham,[6] the

$$(HBPz^*_3)Rh(CO)_2 \xrightarrow[n\text{-pentane}]{h\nu} (HBPz^*_3)Rh(CO)(C_5H_{11})H + CO \quad (1)$$

FTIR spectra revealing that there is a smooth conversion from the dicarbonyl complex (ν(CO) at 2054 and 1980 cm^{-1}) to the monocarbonyl hydrido photoproduct (ν(CO) at 2029 cm^{-1}, lit.[6c] 2031 cm^{-1}). The photochemistry here is extraordinarily clean and complete photoconversions can be achieved to the hydrido product at each of the excitation wavelengths without any interferences from secondary photoreactions. Moreover, spectra recorded from solutions kept in the dark at 293 K have established that there are negligible contributions from thermal processes during the course of these photochemical transformations.

Recorded absolute quantum efficiencies for the C−H bond activation process at the various excitation wavelengths are shown in Table 1. The ϕ_{CH} results are clearly strongly dependent on the irradiation wavelength, and they illustrate that the oxidative addition reaction proceeds very effectively following excitation in the near-UV region. It is also unusual to note that there is a reduced efficiency on long wavelength photolysis while still exciting into the lowest absorption band. Although absolute quantum efficiencies are not yet available for most photochemically-induced C−H activating systems, it is worthwhile commenting that recent determinations of activation efficiencies for the $(\eta^5\text{-}C_5R_5)M(CO)_2$ (M = Rh, Ir) complexes on visible excitation are approximately 1 order of magnitude lower.[5]

Investigations have also been made into the thermal chemistry of this system. In room-temperature solution the $(HBPz^*_3)Rh(CO)_2$ complex exists as an equilibrium mixture of two molecules in which the tris(3,5-dimethylpyrazolyl)borate ligand undergoes facile tridentate (η^3)−bidentate (η^2) interconversion (see eq 2). Estimates of $K_{eq} \approx 0.01$ and $\Delta G° \approx 3.0$ kcal mol^{-1}

$$(\eta^3\text{-}HBPz^*_3)Rh(CO)_2 \rightleftarrows (\eta^2\text{-}HBPz^*_3)Rh(CO)_2 \quad (2)$$

(at 298 K) have been obtained for this equilibrium in CH_2Cl_2,

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(1) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (c) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *J. Am. Chem. Soc.* **1983**, *105*, 3929. (d) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. (e) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. (f) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovak, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13. (g) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984** , *106*, 7272.

(2) (a) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624; *J. Chem. Soc., Dalton Trans.* **1987**, 1181. (b) Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846.

(3) (a) Haddleton, D. M. *J. Organomet. Chem.* **1986**, *311*, C21. (b) Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1372; *J. Chem. Soc., Chem. Commun.* **1986**, 1734. (c) Haddleton, D. M.; McCramley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810. (d) Belt, S. T.; Haddleton, D. M.; Perutz, R. N.; Smith, B. P. H.; Dixon, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1347. (e) Belt, S. T.; Grevels, F.-W.; Koltzbücher, W. E.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8373. (f) Haddleton, D. M.; Perutz, R. N.; Jackson, S. A.; Upmacis, R. K.; Poliakoff, M. *J. Organomet. Chem.* **1986**, *311*, C15. (g) Bell, T. W.; Brough, S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933.

(4) (a) Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841. (b) Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288. (c) Weiller, B. H.; Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 4326.

(5) (a) Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1121. (b) Drolet, D. P.; Lees, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5878; **1992**, *114*, 4186.

(6) (a) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (b) Bloyce, P. E.; Mascetti, J.; Rest, A. *J. Organomet. Chem.* **1993**, *444*, 223. (c) Ghosh, C. K. Ph.D. Dissertation, University of Alberta, Edmonton, Alberta, Canada, 1988.

(7) The $(HBPz^*_3)Rh(CO)_2$ complex was prepared via reaction of potassium hydrotris(3,5-dimethylpyrazolyl)borate with chlorodicarbonylrhodium(I) dimer, according to the procedure described by Ghosh.[6c]

(8) Photochemical procedures and kinetic analyses were performed as reported previously.[5b]

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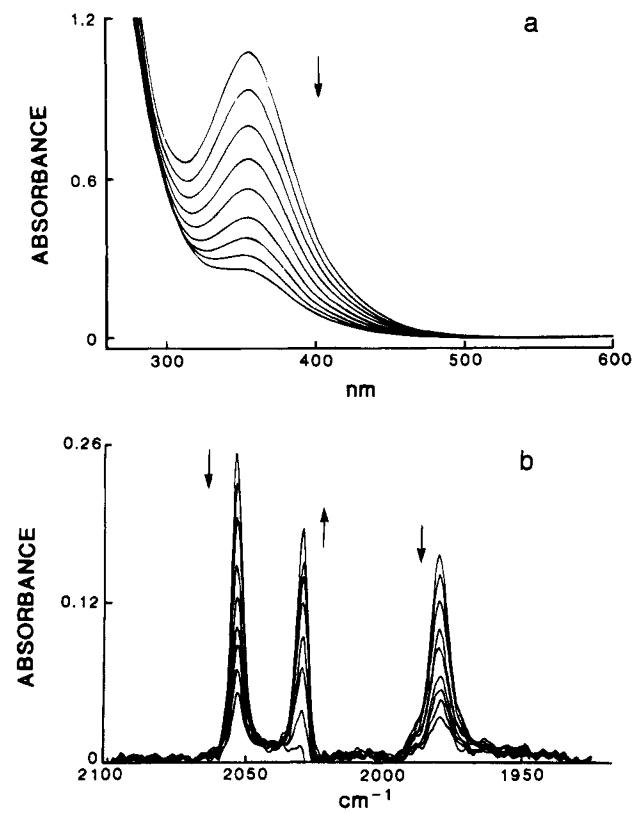

Figure 1. (a) UV–visible absorption and (b) FTIR absorption spectral changes accompanying the 366-nm photolysis of 3.4×10^{-4} M $(HBPz^*_3)Rh(CO)_2$ in deaerated *n*-pentane at 293 K. Initial spectra are recorded prior to irradiation; subsequent spectra are depicted following 45 s irradiation time intervals.

Table 1. Absolute Photochemical Quantum Efficiencies (ϕ_{CH}) for the Intermolecular C–H Bond Activation Reaction of $(HBPz^*_3)Rh(CO)_2$ in Deaerated *n*-Pentane at 293 K

excitation wavelength	ϕ_{CH}[a]	excitation wavelength	ϕ_{CH}[a]
313	0.34	405	0.15
366	0.32	458	0.01

[a] Values were determined in triplicate and were reproducible to within ±5%.

and weak IR bands at 2078 and 2009 cm^{-1} are observable, representing the η^2-species.[6c] Furthermore, the η^2-form has actually been isolated as the protonated complex $[(\eta^2\text{-}(HBPz^*_2)(Pz^*H)Rh(CO)_2]BF_4$ and its crystal structure determined.[9] The rate of $\eta^3 \rightarrow \eta^2 \rightarrow \eta^3$ interconversion of $(HBPz^*_3)Rh(CO)_2$ in solution is apparently very fast, because even at 183 K ^{1}H NMR spectra in CD_2Cl_2 have yielded no evidence for the η^2-complex.[6c] Despite the facile η^3–η^2 process, it is crucial to recognize that no oxidative addition was observed to take place from $(HBPz^*_3)Rh(CO)_2$ in the dark at 298 K, eliminating the simple ligand dechelation as the key step in the photochemical activation mechanism.

The unusual wavelength dependence of ϕ_{CH} implies that two electronically excited states with very different reactivities are involved in the photochemistry because the reaction quantum efficiency reduces with decreasing excitation energy on photolysis into the lowest absorption band.[10] These excited states are believed to be ligand field (LF) levels because of the weak absorbance and solvent insensitivity of the lowest energy absorption band. Moreover, no luminescence has been detected from the complex in 2-MeTHF at 77 K, consistent with the LF assignment.[11] Quantum efficiencies following excitation at 458 nm have been measured at various temperatures: 0.009 (273 K), 0.011 (283 K), 0.011 (293 K), and 0.012 (303 K). The least-squares line of an Arrhenius-type plot of ln ϕ_{CH} versus $1/T$ yields an apparent activation energy of $E_a = 5.4$ kJ mol^{-1}, clearly too small to invoke thermal activation from the lower LF state to the upper LF level. Furthermore, when the solutions were prior saturated with CO gas (ca. 9×10^{-3} M), there was no effect on the ϕ_{CH} results at any of the excitation wavelengths.

Interestingly, the lower energy state must be producing a reaction intermediate with a much reduced C–H bond activation reactivity. The $(\eta^2\text{-}HBPz^*_3)Rh(CO)_2$ species is implicated because the thermal results have revealed that this complex is unable to oxidatively add to RH; hence the long wavelength photochemistry is apparently dominated by the facile $\eta^2 \rightarrow \eta^3$ back-reaction. In sharp contrast, the ϕ_{CH} results reveal that the population of an upper excited state leads to highly efficient C–H bond activation. Obviously, the key reaction intermediate produced here is of a very different nature. At these shorter excitation wavelengths, CO extrusion is known to readily take place in metal carbonyl complexes[11,12] and, thus, the photochemical results strongly suggest that the intermediate which is so highly reactive toward hydrocarbon C–H bonds is the monocarbonyl $(HBPz^*_3)Rh(CO)$ species. The lack of an observable effect of CO concentration on ϕ_{CH} is consistent with an extremely rapid reaction of the photoproduced intermediate with the hydrocarbon substrate.

In this connection, the recent study of $(HBPz^*_3)Rh(CO)_2$ in methane matrices at 12 K and in Nujol mulls at 12 and 77 K did not find any evidence for C–H bond activation, although this reaction did proceed on warming the mull to 298 K.[6b] Both CO loss and ligand dechelation products were determined to form in low yield at 12 K, suggesting that at low temperature there is insufficient thermal energy to remove CO from the matrix cage. On the other hand, in solution the CO dissociation reaction takes place readily and, as shown here, the C–H activation proceeds with high efficiency. Furthermore, the high C–H activation efficiency in this complex, as compared to the corresponding cyclopentadienyl systems, may relate to the differences in the photophysical pathways of these metal complexes. Presently, we are further investigating the nature of the excited states and primary photoproducts in this important system and also carrying out a more extensive study of the photoreactivity in different hydrocarbon solvents.

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(9) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341.

(10) If only a single excited state was being formed, then the observed ϕ_{CH} values would be independent of excitation wavelength as the quantum efficiency measurement takes into account variations in the light absorption. Consequently, the results clearly establish two different excited states within the lowest energy absorption band envelope.

(11) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

(12) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.