configuration of the newly formed hydroxyl group of the products is noteworthy. Thus, the asymmetric hydrogenation of the 3-(aryloxy)-2-oxo-1-propylamine hydrochloride (**1b–e**) catalyzed by the (2*S*,4*S*)-MCCPM-Rh(I) complex gave the *S* product (**2b–e**) in 86.6–97.4% ee, whereas the same hydrogenation of 2-(*N*,*N*-diethylamino)acetophenone hydrochloride (**7**)[6c] yielded (*S*)-2-(*N*,*N*-diethylamino)-1-phenylethanol hydrochloride (**8**) in 97% ee. Therefore, the hydroxyl groups of **2a–e** have dramatically the opposite configuration to that of **8**.

For an understanding of the reason for the opposite stereoselectivity, the asymmetric hydrogenation of several types of amino ketones catalyzed by the (2*S*,4*S*)-MCCPM-Rh(I) complex was carried out. The results, listed in Table II, show that the α-amino ketone derivatives **1c**, **7**, **9**, and **11** are hydrogenated with higher enantioselectivities (86–97% ee) than the β-amino ketone derivatives [3-(*N*,*N*-dimethylamino)propiophenone hydrochloride, **13**] (63.6% ee) and that the asymmetric hydrogenations of (*N*,*N*-dimethylamino)acetone hydrochloride (**9**) and 1-phenyl-3-(*N*,*N*-diethylamino)-2-propanone hydrochloride (**11**)[8] bearing an alkyl group adjacent to the prochiral carbonyl group proceed with high enantioselectivities (85.7% ee and 91.2% ee, respectively) as well as 2-(*N*,*N*-diethylamino)acetophenone hydrochloride (**7**) having a phenyl ring (97% ee). With respect to the absolute stereochemistry of the hydroxyl groups of the hydrogenated products, all of them, except **2c**, have the same configuration. Because the 3-(aryloxy)-2-oxo-1-propylamine derivatives (**1**) contain an oxygen atom substituting on the α-position of the prochiral carbonyl group, the lone pair of electrons of the oxygen atom may play an important role in the stereoselectivity of these asymmetric hydrogenations.

The (2*S*,4*S*)-MCCPM-Rh(I) complex is a very efficient catalyst for the asymmetric hydrogenation of a variety of amino ketone derivatives leading to practical syntheses of chiral medicines such as (*S*)-propranolol, (*S*)-methoprolol, (*S*)-mephenoxalone, and (*S*)-metaxalone.

Acknowledgment. This work was partially supported by a Grant-in-Aid (No. 01470139) for Scientific Research for the Ministry of Education, Science, and Culture of Japan.

---

(8) Thomson, T.; Stevens, T. S. *J. Chem. Soc.* **1932**, 2607.

Photochemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in Phosphine Solutions: Evidence for an Associative Photosubstitution Mechanism

Denis P. Drolet and Alistair J. Lees*

Department of Chemistry
University Center at Binghamton
State University of New York
Binghamton, New York 13901

Received March 12, 1990

Over the past few years there has been much interest in the photochemistry of $(\eta^5\text{-}C_5R_5)ML_2$ and $(\eta^5\text{-}C_5R_5)ML(H)_2$ (M = Rh, Ir; R = H, CH_3; L = CO, PR_3, olefin) complexes leading to intermolecular activation of hydrocarbon C–H bonds.[1] Extensive matrix isolation, flash photolysis, and low-temperature solution studies have been performed on these systems, and they indicate that their C–H activation and photosubstitutional reactions proceed initially via ligand dissociation to yield a 16-electron species.[2] Recently, theoretical models of methane C–H bond activation have arisen based on this premise, i.e., that a coordinatively unsaturated 16-electron $(\eta^5\text{-}C_5R_5)ML$ complex is the key reactive intermediate.[3]

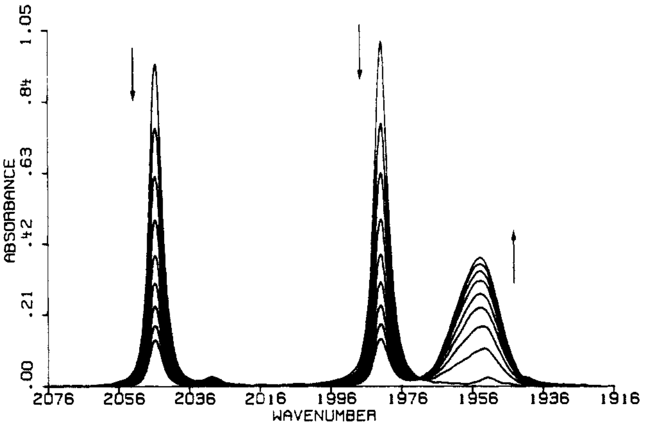

Figure 1. FTIR absorption spectral changes accompanying the 458-nm laser photolysis of 2.5 × 10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in deoxygenated decalin solution containing 0.05 M PPh_3 at 10 °C. Spectra are depicted following 0, 1, 2, 3, 4, 5, 6, 7, and 8 h irradiation time intervals.

In contrast, scant support has been given to the idea that associative processes play a role in these C–H bond activation mechanisms.[4] Although matrix isolation studies of $(\eta^5\text{-}C_5R_5)M(CO)_2$ (M = Rh, Ir) have provided preliminary evidence[5] for a ring slippage ($\eta^5 \rightarrow \eta^3$) step, this argument was later dropped in favor of a photochemically generated $(\eta^5\text{-}C_5R_5)M(CO)$ intermediate again.[6] Throughout these interpretations, however, many of which involve simple photosubstitution, there appears to be little weight attached to the known thermal reactivity of these molecules which have implicated ring slippage processes.[7] Our interest in the photoprocesses of $(\eta^5\text{-}C_5R_5)M(CO)_2$ has been stimulated by this apparent dichotomy. We present here a study of the solution photochemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in the presence of excess scavenging PPh_3 ligand; the results show unequivocally that this photoreaction proceeds via an *associative mechanism*.

Solutions (4 mL) of 2.5 × 10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in decalin containing excess PPh_3 (0.05–0.3 M) were rigorously deoxygenated, cooled to 10 °C, and then irradiated with the 458-nm line of an Ar ion laser. During photolysis the samples were rapidly stirred to ensure a uniform optical density throughout the solution. Laser powers of 50–200 mW were employed and accurately determined by means of a calibrated external power meter. Reactions were monitored throughout photolysis by UV–visible and FTIR spectroscopy; spectra were also recorded from solutions kept in the dark at 10 °C to assess the extent of thermal processes.

---

(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.* **1983**, *105*, 3929. (d) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508; *J. Am. Chem. Soc.* **1986**, *108*, 7332. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(2) (a) Haddleton, D. M. *J. Organomet. Chem.* **1986**, *311*, C21. (b) Belt, S. T.; Haddleton, D. M.; Perutz, R. N.; Smith, B. P. H.; Dixon, A. J. *J. Chem. Soc. Chem. Commun.* **1987**, 1347. (c) Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810. (d) Belt, S. T.; Grevels, F.-W.; Klotzbücher, W. E.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8373. (e) Wasserman, E. P.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1988**, *110*, 6076. (f) Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846. (g) Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841. (h) Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288.

(3) (a) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177. (b) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(4) Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1121.

(5) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624.

(6) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181.

(7) (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372; *J. Am. Chem. Soc.* **1984**, *106*, 5908. (c) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041. (d) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245. (e) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

0002-7863/90/1512-5878$02.50/0

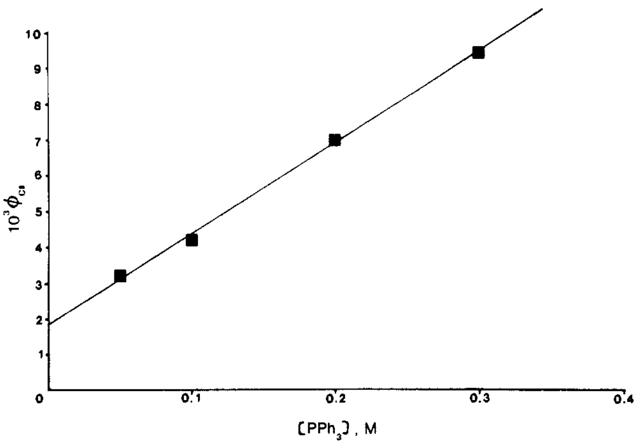

Figure 2. Plot of ϕ_{cr} vs PPh_3 ligand concentration for the 458-nm photochemical conversion of 2.5×10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ to $(\eta^5\text{-}C_5H_5)Rh(CO)PPh_3$ in deoxygenated decalin solution at 10 °C. Each ϕ_{cr} value represents a mean of at least three readings; estimated uncertainties on ϕ_{cr} are within ±5%.

Spectral changes recorded during a typical photolysis experiment are depicted in Figure 1. These FTIR absorption changes are entirely in accordance with simple ligand photosubstitution (eq 1), which is the same as the thermal reaction characterized by Basolo.[7a-c] The photochemistry here appears to be exceptionally clean as demonstrated by the retention of sharp isosbestic points throughout the reaction to completion; in addition, the $(\eta^5\text{-}C_5H_5)Rh(CO)PPh_3$ photoproduct is both thermally and photochemically stable under the conditions of the experiment. Moreover, there was no indication that other complexes are produced, such as the bridged $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ species formed during excitations of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in the absence of scavenging ligands.[8] Photochemical quantum efficiencies (ϕ_{cr}) were calculated by monitoring the disappearance of the reactant's ν(CO) bands (over at least 60% of reaction) and application of eq 2, which accounts for the changing degree of light absorption and inner-filter effects. Here, [R] is the concentration of the $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ complex at varying photolysis time t, I_0 is the incident light intensity per unit solution volume, b is the cell path length, D and ϵ_R are the optical density of the solution and molar absorptivity of the reactant complex at the irradiation wavelength, respectively, and ϕ_{cr} is the reaction quantum efficiency. Plots of $\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$ versus $\int_{t_0}^{t_i}[(1 - 10^{-D})/D]dt$, where A_0, A_t, and A_∞ are the infrared absorbance readings of the reactant's ν(CO) bands throughout photolysis, were observed to yield straight lines of slope α to reaction completion, where $\alpha = -\phi_{cr}\epsilon_R I_0 b$. In accordance with these photochemical conversions being complete and uncomplicated by side or subsequent reactions, the plots showed linearity when $A_\infty = 0$ and yielded coincident α values at both ν(CO) bands. Moreover, α values obtained by monitoring the increasing ν(CO) absorbance due to photoproduct formation were concordant. Determined ϕ_{cr} values were corrected for the small contribution (typically 4–8%) from the thermal process. Quantum efficiencies have been obtained for various concentrations of PPh_3 and are shown in Figure 2. Significantly, when the solutions were prior saturated with CO, there was no change in the observed spectral progressions or the measured quantum efficiency results.[9]

$$(\eta^5\text{-}C_5H_5)Rh(CO)_2 \xrightarrow[PPh_3]{h\nu} (\eta^5\text{-}C_5H_5)Rh(CO)PPh_3 + CO \quad (1)$$

$$d[R]/dt = -\phi_{cr}I_0(1 - 10^{-D})\epsilon_R b[R]/D \quad (2)$$

The observed linear dependence of ϕ_{cr} with $[PPh_3]$ and lack of an observed effect with added CO clearly implicate that the photosubstitutional chemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in PPh_3 solutions proceeds via an associative process. This knowledge is pertinent for developing a further understanding of reaction pathways in C–H activation chemistry. Although the current results do not yield specific information on the nature of the associative mechanism, a reasonable rationale is that the excited $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ complex undergoes a $\eta^5 \rightarrow \eta^3$ ring slippage which then reacts with the phosphine ligand, analogous to the thermal process[7a-c] and to a photochemical mechanism suggested for hydrocarbon activation by $(\eta^5\text{-}C_5H_5)Ir(CO)_2$.[4] Alternatively, a $\eta^5 \rightarrow \eta^1$ ring slippage or another type of complex deformation (such as a bending of the Rh–CO bonds) could be involved. It is also possible that there could be a direct reaction of the photoexcited complex with the incoming nucleophile, although our attempts to record luminescence from $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ have, to date, been unsuccessful (even at 77 K), implying that the excited state is very short-lived.[10] Finally, more complicated mechanisms such as bimolecular reaction of PPh_3 with initially photoproduced $(\eta^5\text{-}C_5H_5)Rh(CO)(R)H$ cannot be excluded at this time.

Presently, we are investigating whether associative photochemical mechanisms are more widespread in organometallic systems undergoing intermolecular C–H bond activation.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-89ER14039), for support of this research. We also thank Prof. Arthur W. Adamson for useful discussions.

---

(8) (a) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *10*, 337. (b) Hill, R.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2622.

(9) Saturated solutions were obtained by first bubbling CO through the solution for 30 min and then stirring the solution for a further 30 min under a sealed CO atmosphere. The concentration of CO in alkane solution at 10 °C is approximately 9×10^{-3} M; see: Lawson, D. D. *Appl. Energy* **1980**, *6*, 241.

(10) Rawlins, K. A.; Lees, A. J.; Bloyce, P. E.; Rest, A. J., unpublished observations.

Infrared Spectrum of Triplet Phenylnitrene. On the Origin of Didehydroazepine in Low-Temperature Matrices

James C. Hayes and Robert S. Sheridan*[,1]

Department of Chemistry, University of Nevada
Reno, Nevada 89557

Received April 12, 1990

Despite years of scrutiny,[2] the complete picture of the photochemistry of phenyl azide (**1**) has only recently begun to unfold. Beyond offering mechanistic novelty, this compound is an archetype for many photoaffinity labeling approaches[2,3] and photoresist[2,4] technologies. Early ESR investigations revealed that triplet phenylnitrene (**2**) is formed on irradiation of **1** in low-temperature glasses,[5] and UV/vis spectra were consequently attributed to this intermediate.[6] In a landmark observation in 1978, however, Chapman and LeRoux reported that photolysis of **1** in argon matrices at 10 K gave 1-aza-1,2,4,6-cycloheptatetraene (**3**), which was characterized by IR.[7] This unusual,

---

(1) Fellow of the Alfred P. Sloan Foundation, 1986–1990.

(2) *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984.

(3) Kanakarajan, K.; Goodrich, R.; Young, M. J. T.; Soundararajan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6536.

(4) Meijer, E. W.; Nijhuis, S.; van Vroonhoven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, *110*, 7209.

(5) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

(6) Reiser, A.; Frazer, V. *Nature (London)* **1965**, *208*, 682. Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162.

(7) Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282.