# Photochemical Dehydrogenation of Alkanes Catalyzed by trans-Carbonylchlorobis(trimethylphosphine)rhodium: Aspects of Selectivity and Mechanism

John A. Maguire, William T. Boese, and Alan S. Goldman*

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. Received January 3, 1989

Abstract: The photochemical dehydrogenation of alkanes is catalyzed in solution by $trans$-$Rh(PMe_3)_2(CO)Cl$ with high efficiency; quantum yields up to 0.10 and turnover numbers as high as 5000 are achieved with cyclooctane as substrate. The intramolecular regioselectivity of the reaction is investigated with methyl-, ethyl-, and isopropylcyclohexane. In competition experiments, cyclooctane is found to be 17 times as reactive as cyclohexane; under carbon monoxide atmosphere, the selectivity is enhanced to a factor of 130. A kinetic isotope effect, $k_H/k_D = 5.3$, is found for the dehydrogenation of C_6H_{12}/C_6D_{12}. Both intra- and intermolecular selectivities are consistent with a pathway involving a reversible C–H oxidative addition followed by a β-hydrogen elimination. $trans$-$Rh(PMe_3)_2(CO)Cl$ is demonstrated to be the only significant photoactive species in solution. The dehydrogenation reaction is quenched by carbon monoxide with Stern–Volmer kinetics. On the basis of these results, a mechanism is proposed in which the energy needed to drive these thermodynamically unfavorable dehydrogenations is obtained only from Rh–CO bond photolysis.

The selective and catalytic functionalization of alkanes remains one of the most important and challenging goals of organometallic chemists.[1] Many homogeneous transition-metal alkane activation reactions have been discovered in the past 10 years, but there have been relatively few examples of catalytic derivatizations.[2-8] Recently, Tanaka reported[9] the development of a photochemical rhodium system, related to Eisenberg's benzene carbonylation systems,[10] which effects the terminal carbonylation of n-pentane with moderate efficiency.

$$CO + n\text{-}C_5H_{12} \xrightarrow{Rh(PMe_3)_2(CO)Cl,\ h\nu} n\text{-}C_5H_{11}CHO \qquad (1)$$
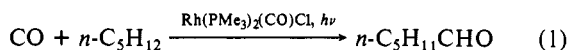
In addition to the potential value of carbonylation, our interest in this system was spurred by the observation that the mechanism of reaction 1 probably involves a 16-electron rhodium alkyl hydride.[9,10,11a] Such species may be expected to display other forms of catalytic reactivity, which have not been observed with the more familiar 18-electron alkyl hydride insertion products. We have therefore begun a systematic study of the alkane chemistry of $trans$-$RhP_2(CO)Cl$ (**1**, P = PMe_3) and derivatives. In the course of this study, we have found a much more photoefficient alkane reaction, photodehydrogenation.[12]

$$alkane \xrightarrow{1,\ h\nu} alkene + H_2 \qquad (2)$$
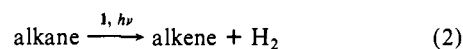
Reaction 2 has since been independently reported elsewhere.[13] In this paper, we discuss features of the mechanism of reaction 2. In particular, we identify the photochemical step necessary to drive this thermodynamically unfavorable reaction. We also examine the intra- and intermolecular selectivity of reaction 2 and find a pattern that is quite unusual in view of the known selectivity patterns of related alkane transfer–dehydrogenation catalysts.

Results and Discussion

The catalytic system in eq 2 can yield high turnover numbers and rates. For example, when a cyclooctane solution of **1** (2.0 mM) was irradiated ($\lambda > 320$ nm, 500-W Hg-arc lamp, 50 °C), the initial rate of cyclooctene formation was 122 mM/h (61 turnovers/h). After 48 h, 58% conversion to cyclooctene was observed. A lower concentration of catalyst (0.4 mM) afforded the same rate of cyclooctene formation (120 mM/h, which expressed as a turnover rate is 300/h). Total turnover numbers up to 5000 have been achieved.

General Properties of the Catalyst. Complex **1** is an air-sensitive, pale-yellow compound which is thermally stable in alkane solutions at 135 °C. The lowest energy electronic absorption appears at 360 nm ($\epsilon = 4500$ M^{-1} cm^{-1}). The assignment of an analogous absorption exhibited by homologous phosphine analogues has been discussed elsewhere.[14] No change in the ^1H NMR or electronic spectra is observed under an atmosphere of carbon monoxide or an atmosphere of dihydrogen. In the presence of less than ca. 1 equiv of trimethylphosphine, exchange of free and coordinated phosphine is rapid on the NMR time scale. The addition of ethylene, cyclooctene, cyclohexene, or trimethylphosphine (up to 1 equiv) has no affect on the electronic or infrared spectrum of **1**.

(1) For reviews of this area see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819, and ref 1–11 therein.

(2) Other notable alkane functionalizations catalyzed by soluble transition-metal systems include those recently reported by Felkin,[3] Crabtree,[4,5] Jones,[6] Hill,[7] and Sen[8] and for the important class of oxygen transfer reactions, see: Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898–6900, and references therein.

(3) (a) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243–1244. (b) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 788–789. (c) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Lin, Y. *Tetrahedron Lett.* **1985**, *26*, 1999–2000. (d) Cameron, C.; Felkin, H.; Fillebeen-Khan, T.; Forrow, N. J.; Guittet, E. *J. Chem. Soc., Chem. Commun.* **1986**, 801–802.

(4) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816–817.

(5) (a) Burk, M. J.; Crabtree, R. H.; McGrath, D. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1829–1830. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032.

(6) (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (b) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047.

(7) (a) Renneke, R. F.; Hill, C. *J. Am. Chem. Soc.* **1986**, *108*, 3528–3529. (b) Renneke, R. F.; Hill, C. *J. Am. Chem. Soc.* **1988**, *110*, 5461–5470.

(8) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109–8111.

(9) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758–759.

(10) (a) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764–767. (b) Kunin, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 535–536. (c) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124–2129.

(11) (a) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1794–1796. (c) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5566–5567. (d) Spillett, C. T.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1932–1933.

(12) Alkane photodehydrogenation has previously been reported for one other system; ref 5.

(13) (a) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. *Chem. Lett.* **1988**, 263–264. (b) Nomura, K.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 161.

(14) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485–1488.

Intramolecular Selectivity. The regioselectivity of reaction 2 is highly unusual, particularly in view of the close relationship it bears to transfer–dehydrogenation catalysts and the photo-dehydrogenation system reported by Crabtree.[5] Those systems display a preference for dehydrogenations involving primary C–H bonds. This is considered to be a reflection of the selectivity (thermodynamic, and in some cases kinetic) shown by transition-metal complexes in the stoichiometric insertion into C–H bonds: primary > secondary ≫ tertiary.[1,15]
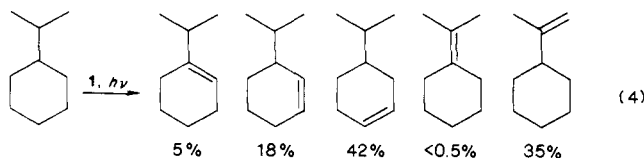
Irradiation of **1** (2.0 mM) in a methylcyclohexane solution affords the distribution of alkenes shown in eq 3. This contrasts
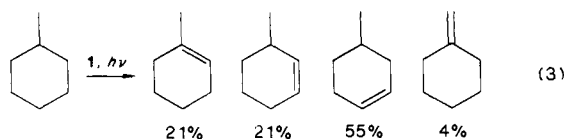
with the order of thermodynamic stability: 1-methylcyclohexene > 3-methylcyclohexene > 4-methylcyclohexene > methylene-cyclohexane.[3,16] The observed product distribution was time-independent over a period of 22.5 h of irradiation during which a total of 3.9% conversion (157 turnovers) was effected. The addition of 4-methylcyclohexene (1%) to a methylcyclohexane solution of **1** did not measurably affect the net rate of formation of any of the products upon irradiation. Reaction 3 is therefore apparently under kinetic control. The system of reaction 3 is unusual in this respect, as other dehydrogenation catalysts also catalyze isomerization. The product distribution was the same when the reaction was carried out under 50 Torr of CO (which reduced the reaction rate by a factor of 8). Note that the most minor isomeric product, methylenecyclohexane, is the major kinetic product when methylcyclohexane dehydrogenation is catalyzed by $(PR_3)_2IrH_5$ (thermally)[3] or by $(PR_3)_2IrH_2(O_2CCF_3)$[5] (photochemically and probably thermally as well).

The dehydrogenation of ethylcyclohexane shows a selectivity pattern similar to that observed for methylcyclohexane. After irradiation for 72 h under CO (50 Torr),[17] the total conversion to alkene was 1.0% with the following distribution: 4-ethyl-cyclohexene (54%), 3-ethylcyclohexene (18%), 1-ethylcyclohexene (15%), ethylidenecyclohexane (12%), vinylcyclohexane (2%). The distribution of isomers was unchanged during the course of the reaction, and when a similar solution with added vinylcyclohexane (0.2%) was irradiated, there was no significant loss of vinyl-cyclohexane. Furthermore, when vinylcyclohexane (0.2%) was added to a methylcyclohexane solution of **1** (under 50 Torr of CO), 93% of the vinylcyclohexane remained after 48 h of irradiation (which resulted in 1.7% dehydrogenation of the methylcyclo-hexane). We conclude that the observed C_8H_{14} isomer distribution is under kinetic control. The low rate of vinylcyclohexane formation underscores the observation that steric factors are not dominant in determining the selectivity of **1**, in contrast with the known transfer–dehydrogenation systems.

The dehydrogenation of isopropylcyclohexane affords a distribution of isopropylcyclohexene isomers consistent with the methyl and ethyl analogues (eq 4). The complete lack of iso-

propylidenecyclohexane is the most notable point of this experiment. In general, with the alkylcyclohexanes, we observe a trend toward formation of the more substituted, more thermodynam-ically stable olefins. However, the formation of a tetrasubstituted olefin like isopropylidenecyclohexane, via a β-elimination step, would require a *tert*-alkyl hydride intermediate. There are no precedents for the oxidative addition of a tertiary C–H bond to a metal center, and thus the failure of the catalyst to give iso-propylidenecyclohexane is suggestive of an oxidative addition/β-elimination pathway. In particular, it may be noted that radical or carbonium ion mechanisms would be expected to yield iso-propylidenecyclohexane as the major product.

Intermolecular Selectivity. The modest degree of intramolecular selectivity from the alkylcyclohexane catalyses contrasts with a high degree of intermolecular selectivity among cycloalkanes. When **1** was irradiated in a 50:50 mixture of cyclooctane/cy-clohexane, the ratio of cyclooctene/cyclohexene formed was 17:1. Surprisingly, the presence of CO influenced the selectivity. When an otherwise identical solution was irradiated under 400 Torr of CO, the cyclooctene/cyclohexene ratio increased to 130:1. This represents a kinetic product ratio, as demonstrated by the observation that irradiation (16 h) of a cyclooctane solution of **1** and cyclohexene (25 mM) afforded no detectable (<0.2 mM) cyclohexane; i.e., cyclohexene is not hydrogenated under the conditions of the reaction. Note that Bergman has found that the insertion of $(C_5Me_5)IrP$ into C–H bonds favors *cyclohexane over cyclooctane* by a factor of 11.[15]

Although under kinetic control, the cycloalkane and alkyl-cyclohexane reactions show a preference for formation of the thermodynamically more stable olefins, with some effect of steric factors (e.g., 4-methylcyclohexene is the major product of reaction 3, although less stable than 1-methylcyclohexene). This pattern strongly suggests that the turnover-limiting (irreversible) step of the dehydrogenations is not the initial C–H bond activation. Instead, a subsequent β-elimination step may be turnover-limiting, or alternatively, a reversible β-elimination step would also tend to favor the formation of thermodynamically stable olefins as "kinetic" products.

$$M + RH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M(R)(H) \qquad (5)$$

$$M(R)(H) \underset{k_{-3?}}{\overset{k_3}{\rightleftharpoons}} M(olefin)H_2 \overset{k_4}{\longrightarrow} products \qquad (6)$$

Irradiation of **1** in a 1:1 (v:v) mixture of C_6D_{12}/C_6H_{12} revealed an unusually high isotope effect for reaction 2, $k_H/k_D = 5.3$. Kinetic isotope effects for C–H oxidative additions in other systems[18-20] are found to be much lower than this. Thus, the large effect we observe is not easily reconciled with C–H addition as the turnover-limiting step. It is consistent with a pathway such as that of eq 5 and 6, involving a reversible C–H oxidative addition and a subsequent β-elimination, which would yield an overall isotope effect $(K_{2H}/K_{2D})(k_{3H}/k_{3D})$. Jones[18a] has found an equilibrium isotope effect of 2.7 for the addition of a benzene C–H bond to $(C_5Me_5)RhP$. If K_{2H}/K_{2D} is likewise approximately 2.7, then a kinetic isotope effect, k_{3H}/k_{3D}, of approximately 2 would give the resulting overall value of 5.3.

The very high reactivity of cyclooctane versus cyclohexane is consistent with the alkylcyclohexane selectivity pattern and would appear to be attributable to the much more favorable $\Delta H°$ of cyclooctane dehydrogenation (23.3 versus 28.2 kcal mol⁻¹).

(15) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352–354. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. (c) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508–510.
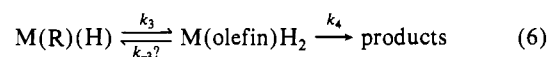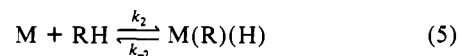
(16) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermo-dynamics of Organic Compounds*; Robert E. Kreiger Publishing: Malabar, FL, 1987.

(17) In the case of the alkylcyclohexane and cyclohexane (but not cyclo-octane) reactions, formation of some white precipitate was observed after extended irradiation in the absence of CO. Thus, although the reaction rate for these substrates is greatly reduced by a CO atmosphere, we preferred to conduct the selectivity studies under CO to maintain the purity of the solution.

(18) (a) For the oxidative addition of cyclohexane C–H(D) bonds to $(C_5Me_5)IrP$, a kinetic isotope effect $k_H/k_D = 1.38$ has been found: ref 15b. (b) For the insertion into the C–H(D) bonds of benzene, $k_H/k_D = 1.4$: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819. (b) For insertion of $(C_5Me_5)RhP$ into hexane C–H(D) bonds, $k_H/k_D = 1.1$: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346.

(19) Similarly large values of k_H/k_D (4.4–7.7) have been reported for cyclohexane photodehydrogenation and transfer–dehydrogenation catalyzed by $Ir(PR_3)_2(O_2CF_3)(H)_2$: ref 5.

(20) For an intramolecular C–H oxidative addition, the cyclization of $Pt(PEt_3)_2(CH_2CMe_3)_2$, k_H/k_D is approximately 3: Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732–2733.
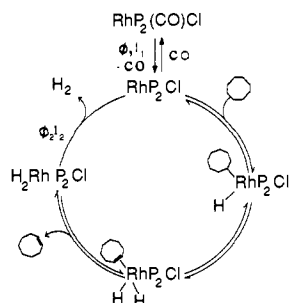
Figure 1. Example of a hypothetical class I photochemical cycle for cyclooctane dehydrogenation.
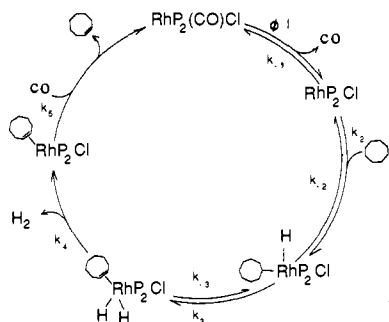

Figure 2. Proposed class II mechanism for cyclooctane dehydrogenation.

However, there also appears to be an additional contribution from purely kinetic factors. When **1** was irradiated in alkene solutions, for example, cycloctene/cyclohexene (50:50, mol:mol; 1200 Torr of CO/H$_2$), the reverse reaction, hydrogenation, was found to occur and, surprisingly, to proceed more rapidly with cyclooctene than with cyclohexene (1.5 versus 0.65 mM/h). This suggests

$$\text{cycloalkene} + H_2 \xrightarrow{1,\ h\nu} \text{cycloalkane} \qquad (7)$$
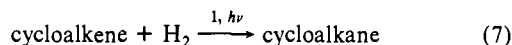
that the greater rate of dehydrogenation of cyclooctane versus cyclohexane is not due solely to the relatively low ΔH° of cyclooctane dehydrogenation but is due also to a relative lowering of the kinetic barrier. Although the mechanisms of reactions 2 and 7 cannot be identical, they very likely have thermal steps in common (in opposite directions). Possibly, one of these steps is rate-limiting (e.g., β-elimination/olefin insertion), and the catalyst is more effective for this step (in both directions) with cyclooctane/cyclooctene than with cyclohexane/cyclohexene.

Identification of the Photoactive Species. Several hypothetical mechanisms for reaction 2 can be constructed based on precedents such as Ford's flash photolysis work[11] and Halpern's study of olefin hydrogenation with Wilkinson's catalyst.[21] We can divide such mechanisms into two major categories. The first, which we will call class I (see, for example, Figure 1), is a photochemical cycle of the type proposed by Crabtree. This involves the familiar steps found in an olefin hydrogenation cycle such as that of Wilkinson's catalyst, proceeding in the "reverse" direction with one of the steps being photochemical. In Crabtree's case, the photochemical step is loss of dihydrogen. An alternative photochemical step is rhodium–olefin dissociation. Note that, for reaction 2, a plausible class I catalytic cycle must be photochemically initiated, i.e., one photon is necessary to enter the cycle and another photon is necessary to perpetuate it.

The second type of cycle, class II, does not involve photoextrusion of either of the components of a dehydrogenation (i.e., H$_2$ or olefin). Instead, the photochemical step is loss of an ancillary ligand, in this case loss of CO from **1**. Reaction with alkane then gives either a metal–olefin or metal dihydride complex, which then reacts with CO to regenerate **1** (see Figures 2 and 3).

The example of a class I mechanism shown in Figure 1 involves RhP$_2$H$_2$Cl as the photoactive intermediate. Known analogues of
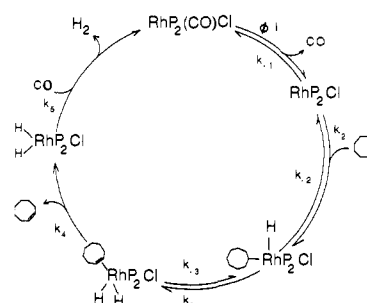

Figure 3. Alternative class II mechanism for cyclooctane dehydrogenation. This cycle is not consistent with the behavior of the triphenylphosphine analogue of RhP$_2$(CO)Cl.

this complex are orange[22] and therefore likely absorb light in the visible region more strongly than does the pale-yellow **1**. Thus, it would be plausible that in experiments using a cutoff filter (e.g., Pyrex, $\lambda > 300$ nm) and a typical UV irradiation source (e.g., a Hg-arc lamp) the UV light irradiates precursor **1**, while the "catalytically active" intermediate can absorb the remaining visible light. To test this hypothesis, we irradiated a cyclooctane solution of **1** (under 800 Torr of CO) with two beams of light simultaneously. One beam was of UV light (366 nm), which is strongly absorbed by **1**. The second beam was of visible light ($\lambda > 430$ nm) to which **1** is completely transparent. There was no significant acceleration from the visible light as compared with the UV light alone.

In the case of monochromatic irradiation (366 nm), we can demonstrate that a class I catalytic cycle for reaction 2 is not operative. Such a pathway requires an intermediate that absorbs 366-nm light strongly enough to be competitive with **1**. Because the quantum yield of reaction 2 is fairly high, such an intermediate must absorb fairly strongly, for example, 8% of the incident light under 50 Torr of CO at 50 °C $\Phi_{obs} = 0.08$). It would therefore be easily detectable by UV–visible spectroscopy. However, we have found that, upon 366-nm irradiation of a cyclooctane solution of **1** (4.0 × 10^{-4} M) in a specially modified UV–visible spectrophotometer, no significant change (<±0.5%) of absorption at 366 nm (or 333 and 450 nm) is observed approximately 1.5 s after the termination of irradiation.

It would still be plausible, a priori, that a strongly UV-absorbing species is the photoactive intermediate but that it undergoes thermal decay too fast to be observed by our techniques. However, the quantum yield of reaction 2 is found to be independent of light intensity (1.3 × 10^{-9}–2.8 × 10^{-8} einstein s^{-1}) and of the concentration of **1** (0.2–5.0 mM). These observations enable us to rule out the possibility of a photoactive intermediate, X, which undergoes a competing thermal decay (eq 8 and 9).

$$1 \underset{k_{-8}\ (\Delta)}{\overset{h\nu}{\rightleftharpoons}} X \qquad (8)$$

$$X \xrightarrow{h\nu} \text{products} \qquad (9)$$
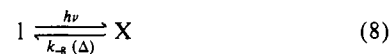
If the thermal decay of X (k_{-8}) is significant (relative to the forward photoprocess of eq 9), then Φ_{obs} must decrease with increasing [**1**] due to competitive absorption by the major species **1**. Similarly, decreasing irradiation intensity would decrease Φ_{obs} since the rate of reaction 9 would decrease relative to the thermal decay, contrary to our observations.

If, on the other hand, the thermal decay of X were much slower than the forward photoprocess (eq 9), we would be able to observe X in spite of the time delay between irradiation and observation. This is proven as follows. With a solution volume of 1.6 mL and an irradiation intensity of 1.30 × 10^{-9} einstein s^{-1}, for example, reaction 9 (product formation) proceeds at a rate of 6.5 × 10^{-8} mol L^{-1} s^{-1}. A thermal process much slower than reaction 9 would

(21) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11–19.

(22) (a) Empsall, H. D.; Hyde, E. M.; Mentzer, E.; Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2069–2074. (b) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (c) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *196*, 145.
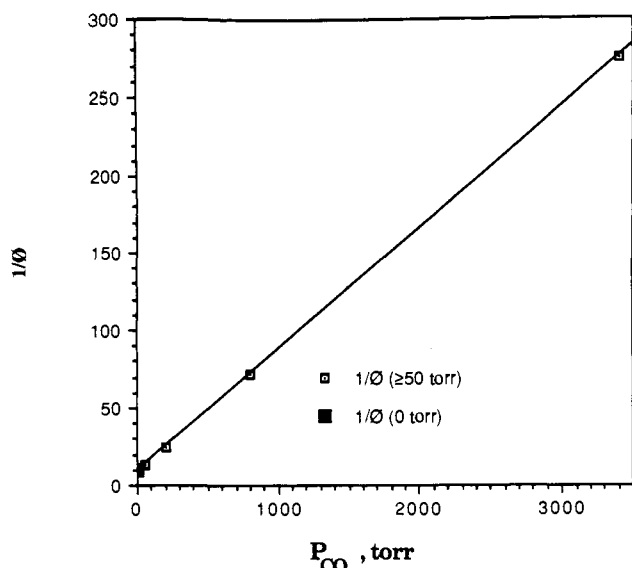
Photochemical Dehydrogenation of Alkanes

J. Am. Chem. Soc., Vol. 111, No. 18, 1989 7091

Figure 4. Dependence of quantum yield of reaction 2 (λ = 366 nm; 50 °C) on P_{CO}; [RhP$_2$(CO)Cl] = 2.0 mM; P_{H_2} = 400 Torr; neat cyclooctane.[29]

destroy much less than 9.8×10^{-8} mol L^{-1} of X in a delay time of 1.5 s; therefore, the concentration of X during irradiation must be much less than this value in order to escape detection 1.5 s subsequently. For a species in such a concentration to absorb 8% of the incident light in competition with **1** (which is present at levels of $(4.0–20) \times 10^{-4}$ M, ϵ = 4500 M^{-1} cm^{-1}) would require an extinction coefficient, $\epsilon_x \gg 1.5 \times 10^6$ M^{-1} cm^{-1},[23] an implausibly high value.[24]

A simpler argument can be made which does not invoke the lack of dependence of Φ_{obs} on intensity and [**1**]. A maximum steady-state value of X according to the scheme of eq 8 and 9 can be calculated, based on two assumptions: (1) The *maximum* rate of formation of X is equal to the rate at which photons enter the reaction vessel (with a correction factor of 0.08 to allow for the minimum quantity of light necessary to induce reaction 9 to give an overall Φ_{obs} of 0.08). (2) The rate of thermal decay of X is equal to k_{-8} X (where k_{-8} is a first-order or pseudo-first-order rate constant[25a]). At the lowest experimental light intensity (I = 1.3 $\times 10^{-9}$ einstein s^{-1}), we find

$$[X] = (\phi_8 - 0.08)(I/V)/k_{-8} \leq (0.92)(8.13 \times 10^{-7} \text{ M s}^{-1})/k_{-8}$$
$$(10)$$

(V = solution volume, 1.6 mL). In order to escape detection by our methods, a species that absorbs 8% of the incident light during

(23) The fraction of incident light absorbed by X in a solution of **1** and X is equal to $(1 - T_{total})\epsilon_x c_x/(\epsilon_x c_x + \epsilon_1 c_1)$. Since $T < 0.016$ in all cases (due to the absorption by **1**), this term is approximately equal to $\epsilon_x c_x/(\epsilon_x c_x + \epsilon_1 c_1)$. We know that $c_1 \geq 4 \times 10^{-4}$ M, and $\epsilon_1 = 4500$ M^{-1} cm^{-1}. If the thermal reaction is much slower than the forward photoreaction (6.5×10^{-8} M s^{-1}), the concentration disappearance of X is $\ll 9.8 \times 10^{-8}$ M in 1.5 s. This quantity must absorb $\geq 8\%$ of the incident light minus the limit of our detection, 0.5%. Thus, $\epsilon_x c_x/(\epsilon_x c_x + \epsilon_1 c_1) \geq 0.075$ and $\epsilon_x c_x \geq 0.081(\epsilon_1 c_1)$. $\epsilon_x \gg 0.081(\epsilon_1 c_1)/(9.8 \times 10^{-8}$ M) = 1.5×10^6 M^{-1} cm^{-1}.

(24) (a) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; pp 170–172. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(25) (a) The most plausible scenario for the scheme of eq 8 and 9 is that the hypothetical species X is a complex such as RhP$_2$ClH$_2$(cyclooctene) which can either give product upon irradiation or thermally back-react. (A thermal back reaction of species such as RhP$_2$ClH$_2$ or RhP$_2$Cl(cyclooctene) seems less likely in view of the fact that the quantum yields are independent of [cyclooctene] and [H$_2$].) The thermal decay (of any plausible species X) would likely be first-order or at least pseudo-first-order since the concentration of species such as CO, H$_2$, and cyclooctene remains constant during the decay. If, for whatever reason, the decay were greater than first-order, then by analogous reasoning the observed behavior would support the same conclusions even more strongly. (b) If the maximum steady-state concentration of X, c_x, is 4.4×10^{-7} M, then following the procedure of ref 23 we find $\epsilon_x c_x/(\epsilon_x c_x + \epsilon_1 c_1) \geq 0.08$ and therefore $\epsilon_x c_x \geq 0.087(\epsilon_1 c_1)$ $\epsilon_x > 0.087(\epsilon_1 c_1)/(4.4 \times 10^{-7}$ M) = 3.6×10^5 M^{-1} cm^{-1}.
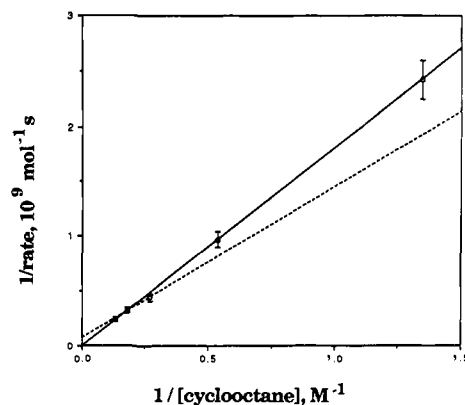

Figure 5. Dependence of rate of reaction 2 ($\lambda > 300$ nm; 50 °C) on cyclooctane concentration; [RhP$_2$(CO)Cl] = 2.0 mM; P_{H_2} = P_{CO} = 400 Torr. Dashed line is theoretical, based on eq 11 and parameters obtained from Figure 4.

irradiation would require a half-life (in the dark) of ≤ 0.4 s, i.e., $k_{-8} \geq 1.7$ s^{-1}. Thus, the maximum possible steady-state concentration of X (assuming a quantum yield of 1.0 for the formation of X) by this argument is 4.4×10^{-7} M. To absorb 8% of the incident light in competition with **1** would in this case still require for X an unreasonably high[24] extinction coefficient of 3.6×10^5 M^{-1} cm^{-1}.[25b]

These observations conclusively demonstrate that complex **1** is the only important photoactive species in the dehydrogenation reaction of cyclooctane with 366-nm irradiation. (Note that if we extrapolate from flash photolysis results with **1** and cyclohexane or benzene[11d] we would expect a slight bleaching effect upon irradiation, barely detectable with our system. This would imply the same conclusion, that there is no photoactive intermediate.)

Kinetics and Mechanism of Reaction 2. The quantum yield (λ = 366 nm) or rate[26] ($\lambda > 300$ nm) of reaction 2 (50 °C, [**1**] = 2.0 mM) is found to be independent of H$_2$ partial pressure[27] and cyclooctene concentration over the ranges 0–2400 Torr of H$_2$ (400 Torr of CO), and 0–0.4 M cyclooctene (400 Torr of H$_2$, 400 Torr of CO). Although the enthalpies of the alkane dehydrogenation reactions are highly positive it has been claimed[28] that they proceed through a photochemically initiated thermochemical cycle. However, our observation that reaction 2 proceeds under hydrogen (which would give under 1 atm at equilibrium,[16] [cyclooctene] = 6×10^{-10} M) is completely inconsistent with this proposal.

The quantum yield (λ = 366 nm, 50 °C, P_{H_2} = 400 Torr) of the cyclooctane dehydrogenation shows a Stern–Volmer dependence on the partial pressure of carbon monoxide (i.e., a plot of $1/\Phi_{obs}$ versus P_{CO} is linear) over the range P_{CO} = 0–3400 Torr (see Figure 4).[29] With broad-band irradiation of constant intensity, the same effect of CO is observed on the rate of the reaction under a variety of temperatures.

Although an excess of trimethylphosphine reacts with **1**, we found that addition of less than ca. 1 equiv of PMe$_3$ has no significant effect on either the infrared or UV–visible spectra of a solution of **1**. The presence of up to 1 equiv (2 mM) of trimethylphosphine was found to have no effect on the quantum yield of reaction 2. (More than about 1 equiv resulted in the formation of a precipitate, presumably either P$_3$RhCl or [P$_4$Rh]Cl.)

(26) For some experiments, broad-band irradiation was used, therefore not allowing quantum yields to be measured. However, on the basis of actinometry measurements at single wavelengths (366, 314 nm), we know that lamp intensity varies by less than ±3%, and therefore reaction rates can be compared to determine the effects of variables.

(27) Although varying initial P_{H_2} was found to have no significant effect on the measured quantum yields for cyclooctane dehydrogenation, we maintained a hydrogen partial pressure of 400 Torr during photokinetic runs for the sake of maintaining constant and reproducible conditions.

(28) Kothiro, N.; Kumagai, H.; Saito, Y. *Shokubai* **1988**, *30*, 204–207.

(29) The reciprocal quantum yield for reaction 2 with cyclooctane in the absence of CO (ϕ = 0.097; $1/\phi$ = 10.3) deviates slightly from the calculated intercept, 9.4. This deviation, which is more pronounced in broad-band irradiation experiments, may be attributed to the formation of Rh$_2$P$_4$Cl$_2$ due to loss of CO under these conditions.

These kinetic data are consistent with two variations of class II mechanisms described in Figures 2 and 3, for which the quantum yield is expressed in eq 11 (where ϕ is the primary

$$\Phi_{obs} = (\phi k_2[C_8H_{16}]k_3k_4)/$$
$$(k_{-1}[CO](k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4) + k_2k_3k_4[C_8H_{16}]) \quad (11)$$

quantum yield for the formation of free RhP_2Cl).[30] The results from Ford's flash photolysis studies[11] are supportive of the mechanism of Figure 2. In particular, a rapid second-order reaction of $RhP_2Cl(C_8H_{14})$ with CO is well precedented; $(PPh_3)_2RhCl(C_2H_4)$ was found to react with CO at the remarkably high rate of 10^8 M^{-1} s^{-1}.[11]

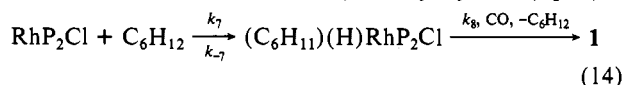$$(PPh_3)_2RhCl(C_2H_4) + CO \xrightarrow{\Delta} (PPh_3)_2RhCl(CO) + C_2H_4 \quad (12)$$
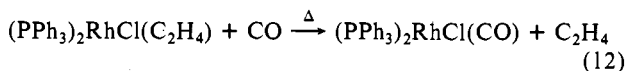
On the other hand, the reaction of CO with $(PPh_3)_2RhClH_2$ was found to proceed slowly and with first-order kinetics ($k = 2.6$ s^{-1}) presumably via loss of H_2.

$$(PPh_3)_2RhClH_2 \xrightarrow{-H_2} [(PPh_3)_2RhCl] \xrightarrow{CO} (PPh_3)_2RhCl(CO) \quad (13)$$
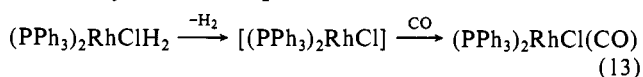
If the trimethylphosphine analogue were to react similarly with CO, this would involve the regeneration of RhP_2Cl, describing a thermochemical cycle that is incompatible with the direction of the reaction. However, in view of the expectedly large differences between PMe_3 and PPh_3 analogues with respect to the relative favorabilities of associative and dissociative attacks, it would only be speculative at this point to choose between the two variations of Figures 2 and 3.

To determine the dependence of the reaction rate on cyclooctane concentration, a series of experiments was performed in which 1 was irradiated in solvent mixtures of varying cyclooctane/cyclohexane ratios. The rate of cyclooctene formation was found to depend on $[C_8H_{16}]$ but to follow eq 11 only approximately (see Figure 5). This is not surprising since cyclohexane is not expected to be chemically inert. Any reaction of RhP_2Cl with cyclohexane which was to result in the regeneration of 1 could explain the observed deviation. The most obvious example of such a reaction is the attack of CO on a rhodium cyclohexyl hydride (eq 14);[31]

$$RhP_2Cl + C_6H_{12} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} (C_6H_{11})(H)RhP_2Cl \xrightarrow{k_8, \, CO, \, -C_6H_{12}} 1 \quad (14)$$

a kinetically indistiguishable possibility is attack of CO on an agostic complex $(C_6H_{12})RhP_2Cl$. (If reaction 14 is added to the scheme of Figure 3, then a plot of $1/\Phi_{obs}$ versus $1/[RH]$ is still expected to be linear but with an intercept less than that found for a plot of $1/\Phi_{obs}$ versus [CO], in accord with observations.[32]

See Figure 5.) Our inability to find a solvent that is genuinely chemically inert and has bulk properties closely resembling cyclooctane prevents us from testing the [cyclooctane] dependence of reaction 2 with any greater precision. Note that the susceptibility of the rhodium cyclohexyl hydride to undergo attack by CO (eq 14) can also explain the observed enhancement of cyclooctane/cyclohexane selectivity of dehydrogenation under CO atmosphere.[33]

The various rate constants in eq 11, and in particular k_4, are of course expected to be strongly dependent on the particular alkane substrate. However, ϕ, the primary quantum yield for CO loss, is not expected to vary greatly with different alkanes. We therefore briefly examined the quantitative behavior of cyclohexane, a substrate found to be much less reactive than cyclooctane in competition experiments as described above. In the absence of added CO, the quantum yield for cyclohexane dehydrogenation (argon atmosphere) is identical with that found for cyclooctane ($\Phi_{obs} = 0.97$).[29,34] A plot of $1/rate$ versus P_{CO} (0–2400 Torr) for cyclohexane dehydrogenation is found to be linear with a slope much greater than that found for cyclooctane, as expected.[34] These results are strongly supportive of our interpretation of such plots, in particular that the limiting value is equal to the rate (or quantum yield) of the primary photoprocess, photoextrusion of CO.

The proposed mechanism of reaction 2 (Figures 2 and 3) includes no reactions of free olefin, reflecting the observed lack of dependence of the reaction rate (or Φ_{obs}) on olefin concentration. This is consistent with the fact that the dehydrogenation system did not catalyze the isomerization of the methylcyclohexene isomers produced by reaction 3, in contrast with the tendency of known transfer hydrogenation systems.[3-5] Whereas the transfer hydrogenation systems by necessity involve intermediates that react with olefins, the system of reaction 2 has no such requirement; any such reactions could only inhibit the rate of dehydrogenation.

Conclusion

trans-$Rh(PMe_3)_2(CO)Cl$, 1, has been found to be an efficient alkane photodehydrogenation catalyst with unusual selectivity. The selectivity, as well as a large isotope effect, can be rationalized with a mechanism involving a reversible C–H bond oxidative addition followed by a β-hydride elimination. Our mechanistic study demonstrates a photochemical cycle in which the energy needed to drive the thermodynamically unfavorable reaction is obtained only from Rh–CO bond photolysis. Combined, these two features of the mechanism allow us to construct a framework for the entire catalytic cycle. To the best of our knowledge, this is the first system in which photoextrusion of an ancillary ligand has been shown to be part of a catalytic cycle and does not serve merely to open a vacant coordination site and provide entry into the cycle. We are currently attempting to develop a more fully detailed understanding of this mechanism, and to extend the chemistry of the 16-electron alkyl hydride intermediate to the catalysis of other alkane reactions.

(30) A plot of $1/\Phi_{obs}$ versus [CO] yields an intercept of 9.4, which according to eq 11 is the reciprocal of the primary quantum yield for Rh–CO bond cleavage. Preliminary attempts to obtain a reliable independent measurement of the primary quantum yield have so far been hindered by the thermal substitution lability of 1 and its thermal reactivity toward halocarbons; however a primary quantum yield greater than $1/9.4$ is indicated by preliminary experiments with halocarbons. Various "quenching" processes could give a Stern–Volmer plot with an intercept greater than $1/\phi$. For example, if Figure 2 is modified to include cyclometallation followed by a reaction with CO to regenerate 1, $RhP_2Cl \xrightarrow{k_9} Rh(\eta^2-PMe_2CH_2)(H)PCl \xrightarrow{CO} 1$, the resulting quantum yield expression becomes $\Phi_{obs} = \phi k_2k_3k_4[C_8H_{16}]/\{k_{-1}[CO](k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4) + k_2k_3k_4[(C_8H_{16}] + k_9\}$. Thus, the Stern–Volmer intercept is $1/\phi + k_9/\phi k_2k_3k_4[C_8H_{16}]$. However, the agreement between the quantum yields for cyclohexane and cyclooctane dehydrogenation (vide infra) indicates that the halocarbon results are not indicative of the true value of ϕ.

(31) Cyclohexane dehydrogenation, if it proceeds in analogy to the mechanism of Figure 2, would also inhibit the rate of cyclooctane dehydrogenation in a cyclooctane/cyclohexane solvent mixture by converting RhP_2Cl to 1. However, the relative rate of cyclohexane dehydrogenation is much too small to significantly affect the rate of cyclooctane dehydrogenation.

(32) The quantum yield for cyclooctane dehydrogenation if we modify the scheme of Figure 2 to account for reaction 14 is found to be equal to $(\phi k_2k_3k_4[C_8H_{16}])/(k_{-1}[CO](k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4) + k_2k_3k_4[C_8H_{16}] + k_7-[C_6H_{12}]k_{-7}/(k_{-7} + k_8[CO]))$. The concentrations of neat cyclohexane and cyclooctane are 9.26 and 7.43 M, respectively. Assuming ideal solution behavior, $[C_6H_{12}] = 9.26$ M $- (9.26/7.43)[C_8H_{16}]$. We find that $1/\Phi_{obs} = 1/\phi + k_{-1}[CO](K_{-2}k_{-3} + k_{-2}k_4 + k_3k_4)/\phi k_2k_3k_4[C_8H_{16}] + k_7(9.26 \text{ M})k_{-7}/(k_{-7} + k_8[CO])_2k_3k_4[C_8H_{16}] - k_7(9.26/7.43)k_{-7}/(k_{-7} + k_8[CO])_2k_3k_4$.

(33) If attack of the corresponding alkyl hydride is greater for cyclohexane than for cyclooctane, we would expect the cyclooctane/cyclohexane selectivity of reaction 2 to be increased under CO atmosphere as is observed. If we modify the scheme of Figure 2 to account for the reaction of CO with the rhodium cyclooctyl hydride (analogous to eq 14), we obtain for the predicted quantum yield of reaction 2 (neat cyclooctane) $1/\Phi_{obs} = 1/\phi + k_{-1}[CO](k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4)/\phi k_2k_3k_4[C_8H_{16}] + k_2k_6[CO](k_{-3} + k_4)/\phi k_2k_3k_4[C_8H_{16}] + k_{-1}k_6[CO]^2 (k_{-3} + k_4)/\phi k_2k_3k_4[C_8H_{16}]$. The fact that a plot of $1/\Phi_{obs}$ versus [CO] is linear within experimental error is consistent with the suggestion that the reaction of the cyclooctyl hydride with CO is not a significant process (relative to reductive elimination and β-hydride elimination). Alternatively, a rapid cyclooctane addition/elimination equilibrium would yield the observed linearity even if β-elimination is slow relative to the reaction of CO with the cyclooctyl hydride.

(34) Because the cyclohexane dehydrogenations *under CO atmosphere* were very slow, broad-band irradiation was used and quantum yields were not measured. Additionally, a 500-W Hg-arc lamp was used instead of the 200-W Hg/Xe-arc lamp used for the cyclooctane dehydrogenation and therefore the $1/rate$ versus P_{CO} slopes obtained with the two substrates may not be quantitatively comparable.

Photochemical Dehydrogenation of Alkanes

J. Am. Chem. Soc., Vol. 111, No. 18, 1989 7093

Experimental Section

Samples of **1** were prepared by the addition of trimethylphosphine to $Rh_2(C_2H_4)_4Cl_2$[35] and were characterized by infrared, ^1H NMR, ^{31}P NMR spectroscopies and elemental analysis.[36,37] The following chemicals were obtained commercially: trimethylphosphine, cyclohexane, cyclooctane, methylcyclohexane, ethylcyclohexane, isopropylcyclohexane, cyclohexene, cyclooctene, 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, methylenecyclohexane, vinylcyclohexane, 1-ethylcyclohexene, 3-ethylcyclohexene, 4-ethylcyclohexene, 1-isopropyl-cyclohexene, 3-isopropylcyclohexene, 4-isopropylcyclohexene. Ethylidenecyclohexane[38] and isopropylidenecyclohexane[39] were prepared by literature methods.

All solvents were purified using accepted procedures[40] to remove unsaturated hydrocarbon impurities and then dried over $CaCl_2$ and distilled from CaH_2 or NaH under argon. All gases were used as supplied by Linde Corporation except argon, which was passed through 4 A sieves and a manganese oxygen scrubber.

Gas chromatographic analyses for experiments with cyclooctane and cyclohexane were performed with a temperature-programmed Varian 3400 using a 50-m HP-1 (cross-linked methylsilicone gum phase) capillary column and a flame ionization detector. Calibration curves were prepared using authentic samples. The identity of cyclohexene and cyclooctene was additionally confirmed by comparison with authentic samples using Carbowax and OV-17 packed columns. C_6D_{10}/C_6H_{10} ratios were determined by capillary GC. Base-line separation of the isotopomers was achieved; the identity of C_6D_{10} was confirmed by comparison with authentic C_6D_{10} generated from dedeuterogenation of C_6D_{12}.

The alkylcyclohexene isomers were identified by comparison of their GC retention times with those of authentic samples. Two columns were used: the HP-1 capillary column and a 2-m silver nitrate/tetraethylene glycol packed column made according to the procedure of Cope et al.[41] Additionally, after each run, the mixture was brominated by the method of Crabtree et al.[42] and compared by GC (HP-1) with the dibromides made from the authentic olefins.

^1H NMR spectra were obtained with a Varian 200-MHz instrument. Full spectrum UV–visible analyses were recorded on a Perkin-Elmer Lambda 3B spectrophotometer. Single-wavelength UV–visible measurements were carried out by using a Gilford 240 spectrophotometer with a constant-temperature chamber. The spectrophotometer was fitted with shutters to allow sample irradiation from an external light source and subsequent absorption measurement within 1.5 s.

All irradiations were with Oriel focused beam lamp systems. A 200-W Hg/Xe-arc lamp was used for all cyclooctane dehydrogenation experiments. For the alkylcycloalkane and cyclohexane dehydrogenations, either a 200-W or a 500-W Hg-arc lamp was used. Irradiations were carried out in a photolysis apparatus which consisted of a 1-cm Pyrex cuvette fused to a 100-mL gas ballast tube fitted with a Kontes high-vacuum valve to allow the addition and removal of gases. Typically, 1.6 mL of a stock solution (maintained in a nitrogen atmosphere glovebox) was added to the photolysis apparatus containing a Teflon stirbar. After several freeze–pump–thaw cycles, the desired atmosphere was added. Samples for GC analysis were periodically withdrawn through an Adjustable Electrode Ace-Thred Adapter just above the cuvette. During irradiation, all samples were maintained at 50 °C in thermostatically controlled mineral oil baths constructed from Pyrex plate glass.

All quantum yield measurements were made by irradiating with 366-nm light (Corning 7-83 filter) and then analyzing the sample by GC. Actinometry was carried out with Aberchrome 540,[43] a commercially available and standardized actinometer. The light sources are quite stable (±0.2% rms with 10% line voltage fluctuation) and were left continuously running in order to further maximize the stability of the output. Actinometry measurements at 366 nm showed a ±3% variation of intensity. The rate of cyclooctane dehydrogenation with broad-band ($\lambda \geq 300$ nm) irradiation under 800 Torr of CO/H_2 (1:1) was found to be reproducible to ±5%, even when runs were carried out weeks apart. Thus, comparison of rates (relative quantum yields) for broad-band irradiation experiments are considered to be valid even without actinometry measurements.

Unless stated otherwise, all experiments were carried out with a 2 mM concentration of **1** in a solution of the alkane substrate. The cyclooctane dehydrogenations were generally allowed to proceed to 0.2–0.5% conversion to cyclooctene. The standard atmosphere for the cyclooctane experiments was 800 Torr of a 50:50 mixture of carbon monoxide and hydrogen. For experiments in which CO or H_2 partial pressure was varied, the gas not being varied was maintained at 400 Torr; when the total CO/H_2 pressure was less than 800 Torr, argon was added to bring the total to 800 Torr. For the alkylcyclohexane and cyclohexane selectivity experiments, an atmosphere of 50 Torr of carbon monoxide and 750 Torr of argon was used unless noted otherwise.

(35) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattry, A. J.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

(36) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 513–518.

(37) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. (A)* **1966**, 597–602.

(38) Wittig, G.; Schoellkopf, U. In *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, pp 751–754.

(39) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411.

(40) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; pp 429–437.

(41) Cope, A. C.; Ambros, D.; Ciganek, C. F.; Howell, C. F.; Jacura, Z. *J. Am. Chem. Soc.* **1959**, *89*, 1750–1753.

(42) Burk, M. J.; Crabtree, R. H.; McGrath, D. *Anal. Chem.* **1986**, *58*, 977–978.

(43) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A.* **1956**, *235*, 518. (b) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341.