# On the mechanism and regioselectivity of alkane photocarbonylation catalyzed by Rh(PMe₃)₂(CO)Cl

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## Abstract

Photochemical carbonylation of hexane catalyzed by $Rh(PMe_3)_2(CO)Cl$ (**1**) is found to proceed via at least two different mechanisms. One requires a secondary photochemical reaction and gives primarily (ca. 98%) linear aldehyde, while the other is radical-based, much less regioselective, and apparently involves only one photochemical step. In accord with this mechanistic understanding, it has proven possible to find conditions leading simultaneously to high photoefficiency and regioselectivity, and greatly increased chemical yields. The presumed photointermediate in the two-photoprocess pathway has been photochemically generated at low temperature and characterized by NMR spectroscopy.

*Keywords:* Rhodium; Alkane activation; Carbonylation; Photochemistry

## 1. Introduction

In 1983 Eisenberg reported that *trans*-$Rh(PPh_3)_2(CO)Cl$ photochemically catalyzed the carbonylation of benzene (Eq. (1), R = Ph) [1].

$$RH + CO \xrightarrow{h\nu} RC(O)H \qquad (1)$$
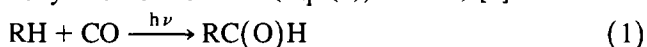
Tanaka subsequently found that the $PMe_3$ analog, *trans*-$Rh(PMe_3)_2(CO)Cl$ (**1**), catalyzed carbonylation of alkanes as well as arenes [2]; the regioselectivity of the alkane carbonylations was later found to be extremely wavelength dependent [3]. Unfortunately, in all cases photoefficiency and/or chemical yields were quite modest. The highest regioselectivity and photoefficiency were obtained using short wavelength irradiation; however, in this case yields were severely limited by secondary photolysis of the aldehyde product to give olefin and other radical derived (Norrish Type II) products [3,4].

Shortly thereafter, several other hydrocarbon functionalizations were found to be catalyzed by **1** [5,6]. In particular alkane photo- and thermochemical dehydrogenation were found to be much more efficient than the carbonylation reactions [7–10]. For example, the quantum yield for photodehydrogenation ($\lambda = 366$ nm) is 0.1 vs. ca. $10^{-5}$ for benzene photocarbonylation; photodehydrogenation was also the first of the **1**-catalyzed functionalizations to be subject to detailed mechanistic investigation [9]. We have proposed that the sole photoprocess of the dehydrogenation cycle is loss of CO, to give the three-coordinate fragment $Rh(PMe_3)_2Cl$ which oxidatively adds an alkane C–H bond. The resulting 16-electron alkyl hydride then undergoes $\beta$-H-elimination and loss of alkene to give $Rh(PMe_3)_2ClH_2$; CO then displaces $H_2$ to regenerate **1** [9]. The proposed photochemical and hydrocarbon-activating steps are thus relatively straightforward and have been observed independently, with benzene, in flash-photolysis work by Ford et al. [11].

In view of the good agreement between the results of the flash photolysis and continuous wave photokinetic studies, as well as numerous indications of the high reactivity of three-coordinate Rh(I) or Ir(I) fragments, the reactivity of $Rh(PMe_3)_2Cl$ may have appeared to be the key to **1**-catalyzed hydrocarbon functionalization in general. Our mechanistic investigations of the carbonylation reactions, however, have not supported this view and have instead indicated a surprising diversity of pathways.

**1**-catalyzed alkane photocarbonylation was found to be greatly promoted by the presence of added aromatic aldehyde [12]. This phenomenon was shown to be due

Table 1
Varying irradiation wavelength effect (T = 35°C) [a]

| $\lambda$ (nm) | d[RCHO]/dt (mM h$^{-1}$) | L [b] % [d] | B [c] | Time (h) | L conc. (mM) | B | pentene |
|---|---|---|---|---|---|---|---|
| > 270 | 52.2 | 97 | 3 | 0.5 | 25.55 | 0.79 | 4.29 |
| > 310 | 7.5 | 93 | 7 | 1.5 | 10.08 | 0.68 | 1.07 |
| > 350 | 0.3 | 73 | 27 | 10 | 1.98 | 0.90 | – |

[a] Conditions: hexane solution; [1] = 2 mM; $P_{CO}$ = 1600 torr; 500 W Hg-arc lamp; solution volume = 1.5 ml; all product concentrations determined by gc, compared with authentic samples.
[b] Linear aldehyde (1-heptanal).
[c] Branched aldehyde (2-methylhexanal and 2-ethylpentanal).
[d] Relative values of linear and (total) branched hexanal product.

to photoexcitation of the aldehyde, which then abstracts hydrogen from alkane; thus in this case 1 does not play a role in the actual C–H activation step. The resulting radical adds to 1 and is carbonylated to ultimately give aldehyde [12].

To examine hydrocarbon carbonylation without the likely involvement of radical pathways, we subsequently focussed on 1-catalyzed benzene photocarbonylation. As might be expected based on the strength of the phenyl–H bond, this catalysis does proceed via an entirely different, non-radical, pathway. Photokinetics demonstrate that the catalytic cycle involves two photochemical reactions (i.e. it is a "two-photon" process) [13]. By irradiating 1 in benzene at low temperature Field has generated the benzene C–H oxidative addition product, Rh(PMe$_3$)$_2$(CO)ClHPh, 2-Ph [14]. Kinetic studies of its decomposition [14] are in excellent agreement with photokinetic studies in our laboratory of the catalytic carbonylation. In particular, using pulsed irradiation the carbonylation quantum yield is dependent on the time between pulses so as to imply a photoactive intermediate that obeys the decomposition kinetics observed by Field for 2-Ph [13]. Unlike alkane dehydrogenation, the photoefficiency of benzene carbonylation is extremely wavelength dependent. With shorter wavelength irradiation, the reaction is much more efficient and apparently proceeds via addition of benzene to an intact (four-coordinate) excited state of 1 to give 2-Ph directly [13].

Returning to alkane substrates, in this paper we report preliminary results of mechanistic studies on 1-catalyzed photocarbonylation in the absence of added aldehyde. We find that at least two very different pathways are operative. One of these is a one-photon radical process yielding branched aldehyde while the other, like benzene carbonylation, proceeds via a two-photon non-radical pathway to give primarily linear product.

## 2. Results and discussion

As noted above, it has previously been reported that total aldehyde yield and regioselectivity of reaction 1 are remarkably wavelength-dependent [3]. This is in agreement with data in Table 1, although it is important to note that such experiments, using broadband irradiation sources and cut-off filters, involve varying total photon flux as well as wavelength. For a given wavelength range, we find that the relative quantum yields of reaction 1 for linear aldehyde product are also highly dependent on irradiation intensity, a result arguing strongly for the involvement of a two-photon process [15]. Intensity-dependence data are shown in Tables 2 and 3. It may be noted that the intensity dependence is greatest under the conditions which lead to the lowest rates of aldehyde production (long wavelength, low intensity, high temperature), while under the most effec-

Table 2
Varying temperature and irradiation intensity. $\lambda$ > 270 nm [a]

| T (°C) | I [b] % | d[RCHO]/dt (mM h$^{-1}$) | $\varnothing_{rel}$ [c] | L % | B | Time (h) | L (mM) | B | pentene |
|---|---|---|---|---|---|---|---|---|---|
| 35 | 100 | 51.6 | 1.0 | 97 | 3 | 0.3 | 14.77 | 0.49 | 2.86 |
| 35 | 40 | 15.5 | 0.75 | 97 | 3 | 1.12 | 16.15 | 0.57 | 4.53 |
| 35 | 14 | 3.5 | 0.48 | 95 | 5 | 1.44 | 4.91 | 0.26 | 0.84 |
| 35 | 5.6 | 0.6 | 0.21 | 91 | 9 | 4.0 | 2.26 | 0.24 | 0.53 |
| 0 | 100 | 46.7 | 0.91 | 96 | 4 | 0.3 | 12.12 | 0.56 | 1.02 |
| 0 | 14 | 9.3 | 1.3 | 97 | 3 | 2.16 | 18.38 | 0.61 | 1.87 |
| 0 | 5.6 | 4.7 | 1.6 | 98 | 2 | 8.0 | 38.68 | 1.05 | 4.46 |

[a] See footnotes, Table 1.
[b] Relative irradiation intensity, varied by using neutral density filters.
[c] Relative quantum yield.

$$1 + RH \underset{k_{-1}}{\overset{k_{h\nu 1}}{\rightleftharpoons}} X \xrightarrow{k_{h\nu 2}} \text{aldehyde}$$
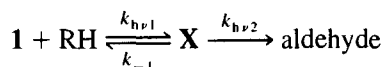
Scheme 1.

tive conditions there is a much less pronounced intensity dependence.

These observations are consistent with conditions ranging between two limits, which can be discussed in terms of Scheme 1. $k_{h\nu 1}$ is the rate of the primary photoprocess. This would be equal to $\int I_n \phi_p A_1 / V$ (integrated over all wavelengths $\lambda_n$) where $I_n$ is the irradiation intensity in einstein s$^{-1}$ at $\lambda_n$, $V$ is the solution volume, $\phi_p$ is the primary quantum yield at $\lambda_n$, and $A_1$ is the fraction of light absorbed by 1 at $\lambda_n$. $A_1$ would be nearly equal to unity for wavelengths $\lambda <$ ca. 400 nm under the experimental conditions, making $k_{h\nu 1}$ approximately equivalent to a thermochemical zero-order reaction rate constant. $k_{h\nu 2}$ is the rate of the secondary photoprocess and is defined analogously; however $A_2$, the fraction of light absorbed by intermediate X, is much less than unity and would be dependent on the concentration of X. Thus $k_{h\nu 2}$ is roughly equivalent to a thermochemical first-order rate constant. For this general case, if the steady state approximation for the concentration of X is valid, the overall reaction rate is $k_{h\nu 1} \times k_{h\nu 2} / (k_{h\nu 2} + k_{-1})$ and $\emptyset_{rel}$, the overall relative quantum yield is therefore

$$\emptyset_{rel} = \left[ k_{h\nu 1} \times k_{h\nu 2} / (k_{h\nu 2} + k_{-1}) \right] / I_{rel} \qquad (2)$$

In the limit where $k_{h\nu 2} \ll k_{-1}$, increased irradiation intensity will result in increased $\emptyset_{rel}$, since both $k_{h\nu 1}$ and $k_{h\nu 2}$ are proportional to intensity. In the limit $k_{h\nu 2} \gg k_{-1}$, however, $\emptyset_{rel} \propto k_{h\nu 1} / I_{rel}$, and the intensity term in $k_{h\nu 1}$ will be cancelled out.

For alkane dehydrogenation the observed quantum yield has been found to increase with increasing temperature [9]; this is at least partly attributable to a positive

temperature dependence of the primary quantum yield for CO loss. However, quantum yields for individual photoreactions are generally much less temperature-dependent than thermochemical reaction kinetics. Therefore, according to Eq. (2), the overall carbonylation quantum yield $\emptyset_{rel}$ would be expected to increase with decreasing temperature owing to a decrease in $k_{-1}$. Indeed the temperature dependence is found to be extraordinarily inverse in some cases. For example, in runs 1 and 3, Table 3, a 50-fold increase in relative quantum yield is found upon a decrease in temperature from 35°C to 0°C ($\lambda > 350$ nm; cut-off values refer to 5% transmittance). Also in agreement with Scheme 1 is the lack of an inverse temperature dependence toward the limit where, presumably, $k_{h\nu 2} \gg k_{-1}$. Thus with high intensity irradiation and a cutoff of $\lambda > 270$ nm (i.e. large $k_{h\nu 2}$ value), there is no significant change (in fact, a slight decrease) in quantum yield resulting from the same temperature change of 35°C to 0°C. However, with the same wavelength cutoff and under the same conditions, but with a neutral density filter allowing only ca. 5.6% transmittance, the temperature dependence is again strongly inverse, presumably because $k_{h\nu 2}$ is decreased so that it is no longer much greater than $k_{-1}$.

The dependence of total (mostly linear) aldehyde yield on temperature and irradiation intensity is thus explainable in terms of Scheme 1. Qualitatively, the wavelength effect observed for the yield of total aldehyde would also follow from Scheme 1 assuming that intermediate X absorbs light more strongly at short wavelengths; $A_2$ and therefore $k_{h\nu 2}$ would be greater at short wavelengths. Since we propose (vide infra) that intermediate X is the d$^6$-octahedral species **2-alkyl**, it is entirely reasonable that this should be the case [16].

The dependence of branched aldehyde yields on intensity, wavelength and temperature is much less pronounced than linear aldehyde yields. Therefore regio-

Table 3
Varying temperature and irradiation intensity, $\lambda > 350$ nm [a]

| T (°C) | I % | d[RCHO]/dt (mM h$^{-1}$) | $\emptyset_{rel}$ | L % | B | Time (h) | L (mM) | B | pentene |
|---|---|---|---|---|---|---|---|---|---|
| 35 | 40 | 0.03 | 0.25 | 65 | 35 | 10 | 0.33 | 0.18 | – |
| 35 | 100 | 0.3 | 1.0 | 73 | 27 | 10 | 1.98 | 0.90 | – |
| 0 | 100 | 15 | 50 | 97 | 3 | 10 | 155 | 2.39 | 0.13 |

[a] See footnotes, Table 1 and 2.

Table 4
Varying temperature, $\lambda > 310$ nm [a]

| T (°C) | d[RCHO]/dt (mM h$^{-1}$) | $\emptyset_{rel}$ | L % | B | Time (h) | L (mM) | B | pentene |
|---|---|---|---|---|---|---|---|---|
| 65 | 0.6 | 0.09 | 89 | 11 | 2.5 | 1.31 | 0.16 | 0.21 |
| 35 | 6.5 | 1.0 | 93 | 7 | 2.5 | 13.8 | 1.02 | 1.52 |
| 0 | 29.6 | 4.6 | 97 | 3 | 1.0 | 30.2 | 0.93 | 0.94 |

[a] See footnotes, Table 1 and Table 2.

selectivity for linear aldehyde formation increases with increasing intensity, decreasing temperature, and shorter wavelengths. It has been considered that the wavelength dependence is due to the photoisomerization of an alkyl hydride intermediate (from secondary alkyl to linear) [3]. While such a photoisomerization could, in principle, explain the wavelength dependence and also the intensity dependence of the regioselectivity, it cannot easily explain the fact that total aldehyde yield is strongly dependent on those two parameters and inversely temperature-dependent (Table 4). If it were assumed that the only secondary photoprocess is isomerization, then the relative quantum yield of total aldehyde should be unaffected by intensity, for example, and the quantum yield for branched aldehyde would actually decrease with increasing intensity. Thus at a minimum it would be necessary to propose additional, unrelated, secondary (or tertiary) photoprocesses, as well as the (unprecedented) photoisomerization, in order to accommodate the photokinetic data to a photoisomerization-based explanation.

Experiments in the presence of the radical-trap 9,10-dihydroanthracene (DHA) help provide an explanation for the variations in regioselectivity. Under conditions which give low total yield and high percentage of branched product, the addition of DHA dramatically suppresses the production of branched, but not linear, aldehyde (Table 5; runs 1–4). This would imply that branched aldehyde is largely formed via a radical pathway. It may be noted in this context that (i) secondary alkyl radicals are thermodynamically more stable than primary; thus it is reasonable that a radical pathway would favor branched aldehyde; and (ii) it has already been demonstrated that formation of alkyl radicals in the presence of 1 leads to efficient thermochemical carbonylation [12]. The increasing percentage of branched aldehyde with decreasing irradiation intensity implies that branched aldehyde is not formed primarily via a two-photon process. Similarly, the increasing percentage of branched aldehyde with increased temperature or increased wavelength (i.e. wavelengths not necessarily absorbed by a photoactive intermediate) is con-

$$1 + RH \underset{k_{-1}}{\overset{k_{h\nu1}}{\rightleftharpoons}} X \overset{\Delta}{\underset{k_{h\nu2}}{<}} \quad \overset{R \cdot \xrightarrow{1 CO}}{\longrightarrow} \text{branched aldehyde}$$
$$\longrightarrow \text{linear aldehyde}$$
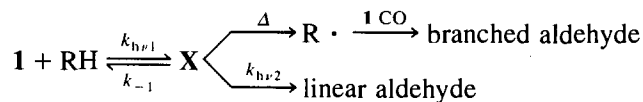
Scheme 2.

sistent with a one-photon process. We propose a mechanism of the type outlined in Scheme 2.

A single intermediate **X**, or a mixture of species, would be consistent with the above results. We propose that photolysis of **2-(1-hexyl)** leads to linear aldehyde whereas the significant percentage yields of branched aldehyde results from thermolysis of the respective secondary rhodium-alkyl isomers.

At low temperature, upon irradiation of high intensity and short wavelength ($\lambda > 270$ nm), i.e. under conditions most favorable for the two-photon process, the effect of varying temperature and intensity on regioselectivity is much less pronounced. Similarly, the presence of added DHA is much less dramatic or even negligible under these conditions (Table 5; runs 5 and 6). These results imply that a relatively constant percentage of the aldehyde produced via the non-radical two-photon pathway is branched; although the percentage is small (ca. 2%) when the total aldehyde produced via the two-photon pathway is very large relative to the radical pathway, then the two-photon route is the major source of branched aldehyde.

Fairly high photoefficiency and regioselectivity for reaction 1 were previously achieved only by using short wavelength irradiation [3]. Such irradiation, however, is also absorbed by the aldehyde product, resulting in decomposition and severely limiting aldehyde yields. Indeed, with short wavelength light ($\lambda > 310$ nm) it was reported that the major product after 16.5 h irradiation of alkane solutions of 1 was the $C_{n-1}$ 1-alkene (e.g. 20.0 mM 1-nonene, 10.2 mM undecanal and 0.29 mM 1-methyldecanal was obtained from n-decane) [4]. With long wavelength light ($\lambda > 350$ nm; and presumably without temperature control), 1-nonene was not observed but the regioselectivity for linear aldehyde was extremely low: 6% of a total aldehyde yield of 3.9 mM,

Table 5
Effect of added dihydroanthracene (DHA) [a]

| $\lambda$ (nm) | [DHA] (mM) | T (°C) | d[RCHO]/dt (mM h$^{-1}$) | L % | B | Time (h) | L (mM) | B | pentene |
|---|---|---|---|---|---|---|---|---|---|
| > 350 | 0 | 35 | | 0.5379 | 21 | 7.5 | 3.14 | 0.84 | – |
| > 350 | 100 | 35 | 0.30 | 96 | 4 | 15 | 4.51 | 0.19 | – |
| > 342 | 0 | 35 | 0.39 | 74 | 26 | 7.5 | 2.18 | 0.75 | – |
| > 342 | 200 | 35 | 0.87 | ≥ 99 | ≤ 1 | 7.5 | 4.61 | ≤ 0.05 | – |
| > 310 | 0 | 35 | 29.6 | 97 | 3 | 1.05 | 30.2 | 0.93 | 0.94 |
| > 310 | 200 | 35 | 10.2 | 98 | 2 | 1.5 | 15.5 | 0.35 | 0.63 |
| > 310 | 0 | 65 | 0.59 | 89 | 11 | 2.5 | 1.31 | 0.16 | 0.21 |
| > 310 | 200 | 65 | 0.38 | ≥ 95 | ≤ 5 | 2.5 | 0.94 | ≤ 0.05 | – |

[a] See footnotes, Table 1.

after 16.5 h irradiation [3] (both the irradiation source and solution volumes were similar to those used in this work). As indicated in Scheme 2, however, lowering the reaction temperature should result in higher yields as well as higher photoefficiency and higher regioselectivity. This is found to be the case to a remarkable degree: for example, after 24 h of $\lambda > 350$ nm irradiation of **1** in hexane at 0°C, 270 mM 1-heptanal was formed along with only 4 mM branched aldehyde and 0.6 mM 1-pentene (similarly, see run 3, Table 3).

An efficient thermochemical alkane carbonylation system (coupled with a secondary reaction to favor the thermodynamics) would have great technological potential, but it would seem unlikely that such a photochemical system could ever find practical applications. However, the significant enhancement of efficiency and regioselectivity of reaction 1 described herein may offer promise in terms of organic synthesis. The selective carbonylation (indeed any functionalization) of unactivated methyl groups is at present not a synthetically feasible reaction. The primary/secondary selectivity of the present system is presumably based on a high sensitivity to steric effects. Particularly if this sensitivity could be exploited to discriminate between different methyl groups in a molecule, we believe that the system of reaction 1 could find specialized applications, possibly even if high chemical yields could not be achieved. In this context it is worth noting that 1-catalyzed alkane reactions have already been found to be tolerant of several functional groups [9].

## 2.1. Nature of the photoactive intermediate

By analogy with photokinetic [13,14] and flash photolysis studies [11] on the 1-catalyzed benzene carbonylation, the intermediate indicated as **X** in Scheme 2 should be a mixture of isomers $Rh(PMe_3)_2(CO)ClH(alkyl)$, **2-alkyl**. Given the generally much lower stability of alkyl versus aryl hydrides, however, such species might be expected to be too short-lived to absorb light under the reaction conditions or to permit observation at lower temperatures. It is thus somewhat surprising to find that **2-alkyl** can be rather easily observed and generated at temperatures only slightly lower than those required for **2-phenyl**.

Irradiation of **1** in hexane at −50°C results in the appearance of a single major product as revealed in the $^{31}P$ NMR spectrum. $\delta$ (relative to $H_3PO_4$) and $J_{Rh-P}$ values are −3.1 ppm and 107.0 Hz, similar to those of **2-phenyl** [14], −6.6 ppm and 100.4 Hz, respectively. Proton-decoupling selective for the alkyl region revealed that the complex contained a single hydride; varying the decoupling frequency range allowed us to estimate the hydride chemical shift resonance as ca. (−8)–(−10) ppm. This hydride $\delta$ value would indicate that the hydride is trans to CO based on analogy

with **2-phenyl** for which isomers are observed with H trans to CO ($\delta$ −8.1) as well as H trans to Cl ($\delta$ −14.8) [14]. Irradiation of **1** in pentane followed by removal of pentane at −78°C and addition (vacuum-line transfer) of acetone-$d_6$ permitted us to obtain a $^1H$ NMR spectrum which revealed a small single hydride resonance with $\delta$ −8.74, $J_{P-H} \sim J_{Rh-H} \sim 14$ Hz (cf. the anlogous isomer of 2-phenyl for which $J_{P-H} \sim J_{Rh-H} = 13.2$ Hz [14]). Unfortunately, the very low solubility of **1** in pentane at −50°C (ca. 1 mM), coupled with some loss of **2** during the change of solvent, allowed only very small concentrations to be obtained by this process. As a result it was not possible to characterize the presumed pentyl group (for which the $\alpha$-protons should give a very complex pattern if observable). The presence of a single stable isomer, however, argues strongly for its identity as the n-alkyl species for two reasons: (i) n-alkyl hydrides are more stable than secondary in all cases of which we are aware; (ii) if for some reason the secondary alkyls were more stable than the primary in this case, one would expect a mixture of the 2-alkyl and 3-alkyl secondary isomers.

Whereas thermochemical reaction intermediates are often present in extremely low concentrations, any photoactive intermediate must be sufficiently long-lived, under the actual reaction conditions, to build up in the quantities necessary to significantly absorb light. The observed decomposition half-life of **2-hexyl** at −35°C is found to be approximately 90 min. Assuming that $\Delta S^{\neq}$ for decomposition is approximately zero, this corresponds to $\Delta H^{\neq} = 18$ kcal mol$^{-1}$, and estimated half-lives of 35 s and 0.7 s at 0°C and 35 °C respectively. Alternatively, using Field's value for $\Delta S^{\neq}$ for the decomposition of **2-phenyl**, −13.4 eu [14], the respective estimated half-lives are 84 s and 3.3 s. Thus assuming any reasonable entropy value, these half-lives, albeit very rough estimates, seem entirely consistent with a species which would be long-lived enough to undergo secondary photolysis at the experimental temperatures and intensities. In particular the lifetime could permit secondary photolysis to occur with high efficiency at 0°C and a short-wavelength cut-off, in accord with the lack of an inverse intensity-dependence under these conditions (Table 2, runs 5–7). These estimated activation parameters will be the subject of kinetic studies.

Thus the observation that **2**, and no other species, is generated in high yields, at temperatures not very far below the catalytic reaction temperatures, is consistent with and strongly supportive of its proposed role as an intermediate in Eq. (1).

## 2.2. Conclusion

The pronounced dependence on wavelength, irradiation intensity, and temperature observed for the yields

and regioselectivity of reaction 1 can be explained based on the operation of two pathways. One requires a secondary photochemical reaction and gives primarily (ca. 97%) linear aldehyde, while the other is radical-based, much less regioselective and apparently involves only one photochemical step. The presumed major photointermediate in the two-photon pathway has been photochemically generated, and is found to be fairly stable in accord with the need to build up in quantities sufficient to absorb a significant percentage of irradiation under the catalytic reaction conditions. The exact nature of the photochemical reaction steps and the potential applicability of the reaction inorganic synthesis remain to be determined; these issues among others are the subject of further investigation.

## 3. Experimental section

### 3.1. General procedures

All samples were handled under an argon atmosphere in a Vacuum Atmospheres Dry-Lab glovebox. Deuterated solvents were distilled under vacuum from NaK alloy. $n$-Hexane was purified prior to drying by a standard procedure to remove alkene impurities [17], and then distilled from dark purple solutions of sodium benzophenone ketyl prior to use. $Rh(PMe_3)_2(CO)Cl$ was prepared as described previously [13].

NMR spectra were recorded on a Varian XL-400 NMR spectrometer. Organic product concentrations were determined using a Varian 3400 gas chromatograph. GC-MS was performed using a Hewlett Packard 5980 Series II gas chromatograph with a 5971 mass spectrometer. Irradiations were conducted using a 500 W Hg-arc Oriel lamp. Wavelength was varied using filters obtained from FJ Gray, and irradiation intensity was varied using neutral density filters obtained from Oriel (measured, rather than nominal, optical densities were used for all calculations).

### 3.2. Typical photolysis conditions

In general, 1.5-ml samples of 2 mM 1 in $n$-hexane were placed under 1600 torr CO in an optical glass cuvette ($\lambda > 290$ nm cutoff) sealed to a ballast used to maintain constant partial gas pressures and equipped with ports for attachment to a vacuum line and for removal of microliter samples for GC analysis. Samples were stirred magnetically while suspended in a constant temperature bath equipped with appropriate filters. The samples were then analyzed at varying time intervals by GC for the determination of the products. The products were independently calibrated using authentic samples.

In order to study the effect of 9,10-dihydroanthracene, a stock solution of 2 mM 1 in $n$-hexane with 200

mM DHA was prepared. The solutions were then irradiated and analyzed as above.

### 3.3. Observation of 2-hexyl by low temperature photolysis

A sample of 2 mM 1 in $n$-hexane was placed in a resealable (J. Young) NMR tube, along with a capillary containing acetone-$d_6$ for locking and $PPh_3$ as a standard. The sample was then irradiated at $-50°C$ in a hexane/dry ice bath (the temperature was maintained at $-50°C$ by the occasional addition of crushed dry ice to the bath). The sample was then monitored by $^{31}P$ NMR spectroscopy at $-80°C$. A new product was seen to grow in at $\delta -3.1$ ppm with $J_{Rh-P} = 107.0$ Hz. Selective $^1H$ decoupling of the methyl resonances revealed a single P–H coupling, $J_{P-H} = 14$ Hz, confirming the presence of one hydride ligand. The chemical shift of the hydride ligand could be approximated as being $-8$ to $-10$ ppm by varying the power and frequency range of the decoupler.

### 3.4. Irradiation of 1 in n-pentane

A sample of 4.0 mM 1 in $n$-pentane was placed in a resealable NMR tube, along with a capillary containing acetone-$d_6$ for locking and $PPh_3$ as a standard. The sample was then irradiated at $-50°C$ in a hexane/dry ice bath, followed by the slow removal of $n$-pentane in vacuo at $-78°C$. Acetone-$d_6$ was then added by vacuum-line transfer at $-78°C$, and the sample was then monitored by $^1H$ NMR spectroscopy at $-80°C$. A hydride resonance was observed at $-8.74$ ppm, but the alkyl region was obscured by residual $n$-pentane.

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