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Study of the Mechanism of Photochemical Carbonylation of Benzene Catalyzed by $Rh(PMe_3)_2(CO)Cl$

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Abstract: Although near-UV irradiation of $Rh(PMe_3)_2(CO)Cl$ (**1**) has been shown to lead to efficient carbon–hydrogen bond activation, the title reaction is promoted with much greater efficiency by shorter wavelength ($\lambda <$ ca. 320 nm) irradiation: for example, the carbonylation quantum yield at 314 nm is found to be 1.5×10^{-3} vs 2.0×10^{-5} at 366 nm. A comprehensive mechanistic study reveals that the shorter wavelength irradiation is required for two separate steps in the catalytic cycle. Photoextrusion of CO, which occurs upon near-UV irradiation and leads to efficient C–H bond activation, is not a major step toward carbonylation under the reaction conditions of the present study nor, apparently, is any other dissociative photoreaction. It is proposed that the first reaction step is the oxidative addition of a benzene C–H bond to an intact photoexcited state of **1**. Independently, Field and co-workers have generated and characterized the resulting six-coordinate phenyl hydrido complexes, $Rh(PMe_3)_2(Ph)(CO)HCl$ (**2**) under low-temperature conditions. Kinetic studies of the catalytic reaction indicate the involvement of a photoactive intermediate, the decay rate of which is in good agreement with the activation parameters determined by Field et al. for the low-temperature decay of the phenyl hydrido complexes, **2**. Short wavelength light is required for the efficient photoreaction of **2**, possibly because longer wavelength light is not significantly absorbed, particularly in competition with **1**. The carbonylation efficiency increases with CO pressure; this is attributable to the reaction of CO with the unsaturated benzoyl complex, $Rh(PMe_3)_2(COPh)HCl$, which results from CO insertion into the Rh–phenyl bond of **2**. Reversible loss of benzoyl chloride from the CO addition product, $Rh(PMe_3)_2(COPh)(CO)HCl$, is shown to lead to the formation of C_6H_5CDO and C_6D_5CHO when the reaction is conducted in C_6H_6/C_6D_6 mixtures.

Introduction

The selective functionalization of hydrocarbons remains one of the most important goals of catalysis.[1] Carbonylation is one such reaction of particular potential value since aldehydes, particularly linear isomers, are presently produced in large quantities via multistep processes such as cracking, oligomerization, and hydroformylation. Thus it was of considerable interest when, in 1983, Eisenberg reported that $Rh(PPh_3)_2(CO)Cl$ and several related complexes catalyzed the photochemical carbonylation of benzene.[2] Subsequently, Tanaka reported that the trimethylphosphine analogue, $Rh(PMe_3)_2(CO)Cl$ (**1**), effected the first example of catalytic alkane carbonylation: photochemical conversion to aldehydes with high selectivity for the terminal position in the case of *n*-pentane.[3]

We have reported that **1**-catalyzed alkane photocarbonylation is greatly accelerated by the presence of added aldehyde or ketone and have shown that this system operates via a radical-based pathway.[4] However, in the absence of added organic carbonyl, catalysis by both **1** and $Rh(PPh_3)_2(CO)Cl$ appears to involve a non-radical mechanism. This is most strongly indicated by the observation that both catalysts exhibit a high selectivity for benzene, a substrate resistant to radical-based pathways.[2,3] (For example, the **1**-catalyzed carbonylation of benzene is not accelerated by the presence of aldehyde or ketone[4].) In order to investigate non-radical-based **1**-catalyzed hydrocarbon carbonylation pathways, we initiated a mechanistic study, choosing benzene as a substrate. (Benzene offers the additional advantage of its inability to undergo dehydrogenation, which can be catalyzed by **1** much more efficiently than carbonylation in the case of alkanes.) Herein we report the results of this study which, in conjunction with an independent study by Field, reveals a catalytic mechanism and relevant chemistry that have several unusual aspects.[5]

Results and Discussion

Irradiation of benzene solutions of $Rh(PMe_3)_2(CO)Cl$ (**1**; typically 7–10 mM) under CO atmosphere (0.1–4.0 atm) at 50 °C results in the formation of benzaldehyde, eq 1. Other organic

$$C_6H_6 + CO \xrightarrow{\mathbf{1},\, h\nu} C_6H_5C(O)H \qquad (1)$$

products are also formed, but initially in much smaller quantities than benzaldehyde. In a typical run (10 mM **1** in benzene; 2.5 h of irradiation, 500 W Hg-arc lamp, $\lambda > 290$ nm, 50 °C, 800 Torr of CO, 2 mL) product yields were the following: benzaldehyde, 44.1 mM; benzyl alcohol 1.6 mM; benzophenone, 1.0 mM; biphenyl, 0.5 mM. In an otherwise similar but more extended run (24 h of irradiation, 7 mM **1**), yields were the following: benzaldehyde, 0.37 M (corresponding to 52 catalytic turnovers); benzyl alcohol 0.19 M; benzophenone, 0.13 M; biphenyl, 0.019 M.

Yields of Benzaldehyde. Benzene carbonylation catalyzed by $Rh(PPh_3)_2(CO)Cl$ upon irradiation was reported by Eisenberg et al. to yield benzaldehyde concentrations equal to the corresponding thermal equilibrium values under several different CO pressures.[2] When a benzene solution with a benzaldehyde concentration greater than the equilibrium value was irradiated,

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[1] For lead references see: (a) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation*; VCH Publishers, Inc.: New York, 1990. (b) Hill, C., Ed. *Activation and Functionalization of Alkanes*; John Wiley & Sons: New York, 1989.

[2] (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.

[3] (a) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758–759. (b) Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 249–252. (c) Sakakura, T.; Sasaki, K.; Tokunaga, M.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 155–158. (d) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221–7229.

[4] Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 350–351.

[5] Boyd, S. E.; Field, L. D.; Partridge, M. G. *J. Am. Chem. Soc.* Preceding paper in this issue.

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Table 1. Results from Benzaldehyde Crossover Experiments[a]

entry	P_{CO}/ Torr	[1]/ mM	C_6H_5-CHO	C_6H_5-CDO	C_6D_5-CHO	C_6D_5-CDO	% crossover[b]
1	800	7.0	34.8	17.2	17.5	30.5	69.4
2	800	7.0	66.2	0.0	3.4	30.4	
3	100	7.0	38.2	13.0	16.6	32.2	59.2
4	1600	7.0	40.7	18.0	20.3	21.0	76.6
5	800	2.0	42.0	15.8	18.7	23.5	69.0

[a] Conditions: 50 °C, 1:1 C_6H_6:C_6D_6 except entry 2 (neat C_6D_6 with 4 mM added C_6H_5CHO). [b] Calculated by taking the sum of the percentages of C_6H_5CDO and C_6H_5CHO and doubling to allow for randomly produced C_6H_5CHO and C_6D_5CDO.

net *decarbonylation* resulted until equilibrium was achieved. These results strongly indicated that the actual catalytic cycle was *nonphotochemical*; the role of light was only to generate a thermochemical catalyst, presumably via ligand photoextrusion. In the case of **1**-catalyzed carbonylation, however, we find that benzaldehyde concentrations significantly above equilibrium values (ca. 0.002 M/atm of CO at 50 °C[2]) can be obtained. For example, in addition to obtaining 0.37 M benzaldehyde under 1 atm as noted above, 0.080 M benzaldehyde was obtained under similar conditions with a CO pressure of only 50 Torr. In addition, 4 mM benzaldehyde added to a C_6D_6 solution does not show any deuterium incorporation during the reaction (Table 1), thus suggesting the irreversibility of the elimination of benzaldehyde in the catalytic cycle. These results are not altogether surprising given the ability of **1** to catalyze *alkane* carbonylation which would yield only undetectable quantities of aldehyde upon reaching thermal equilibrium ($<10^{-6}$ M at 298 K),[6] in contrast with the significant yields reported by Tanaka.[3] Thus, in the case of **1**, light drives the catalysis beyond the thermal equilibrium aldehyde concentration for both alkanes and benzene—and therefore at least one of the steps within the catalytic cycle must be photochemical.

CO Pressure Dependence. Flash photolysis studies conducted by Ford have revealed that loss of CO is the dominant photoreaction of **1** (at wavelengths >330 nm) and that the resulting $Rh(PMe_3)_2Cl$ fragment oxidatively adds a benzene C–H bond.[7] CO loss was also found to be the dominant photoreaction of $Rh(PPh_3)_2(CO)Cl$ ($\lambda > 315$ nm).[8] In accord with these findings, the rate of benzene carbonylation catalyzed by $Rh(PPh_3)_2(CO)Cl$ has been found to vary *inversely* with CO pressure.[2] Likewise, alkane dehydrogenation catalyzed by **1** is strongly inhibited by CO atmosphere.[9] It is thus somewhat surprising that the rate of benzene carbonylation catalyzed by **1** (7.0 mM, 50 °C, 500-W Hg-arc lamp, $\lambda > 290$ nm) is found to be approximately *proportional* to the CO pressure at less than 1 atm and appears to approach saturation at higher pressures (see Figure 1). This finding is difficult (but not impossible) to reconcile with a mechanism in which CO loss is the primary photoprocess.

Wavelength Dependence. The quantum yield of reaction 1 was determined at 366 nm to be 2.0×10^{-5} ($I = 3.3 \times 10^{-7}$ einstein/s). At 314 nm ($I = 2.8 \times 10^{-8}$ einstein/s) the quantum yield was found to be 75 times greater, 1.5×10^{-3}. This pronounced wavelength effect has significant implications concerning the primary photoprocess of the reaction. The primary quantum yield for CO loss from **1** has been independently determined to be 0.1 at 366 nm.[9] Therefore, loss of CO from **1** to generate the 14-electron $Rh(PMe_3)_2Cl$ fragment cannot be the only photochemical process occurring, as this would require an impossibly high quantum yield for CO loss from **1** at 314 nm (7.5, i.e., 75 × 0.1). Significantly, this conclusion is consistent with the above noted (positive) CO pressure dependence of the rate of reaction 1 (Figure 1). These findings leave open three possible roles of irradiation (ca. 314 nm) in reaction 1: (i) the catalytic cycle may involve a single photoprocess, one that is not CO extrusion; (ii) CO photoextrusion may be involved, along with a second photoprocess responsible for the marked wavelength dependence; or (iii) the catalytic cycle may contain two (or more) photoprocesses, neither of which is CO extrusion.

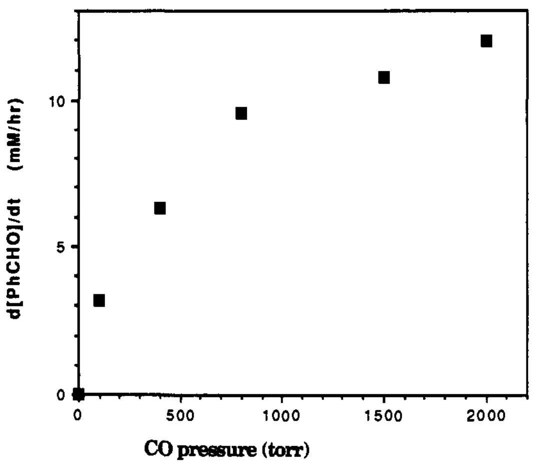

Figure 1. Rate of benzaldehyde formation as a function of CO pressure.

Irradiation Intensity Dependence. In an attempt to determine if the catalytic cycle of reaction 1 involved more than one photochemical step, we examined the dependence of the quantum yield on the intensity of irradiation. Using broadband irradiation (7 mM **1**, 800 Torr of CO, 50 °C, $\lambda > 290$ nm, 500-W Hg-arc lamp) we found that the rate of benzaldehyde formation was linearly proportional to the light intensity (i.e. the quantum yield was intensity independent) over a 300-fold intensity range (obtained with the use of 200- and 500-W lamps and with neutral density filters). While this result is consistent with a one-photon (single-photoprocess) cycle, it does not preclude a two-photon cycle if the second photochemical step occurs with high efficiency relative to any thermochemical processes of the photoactive intermediate under these reaction conditions.

If the second photochemical step of the cycle is occurring with high efficiency under $\lambda > 290$ nm irradiation, then any increase in the rate of the first photoprocess should be reflected in a proportional increase in the overall rate of benzaldehyde formation. In this context we conducted a "dual-beam" experiment in which the sample was irradiated with two sources simultaneously, a 200-W Hg/Xe-arc lamp with a >290 nm cutoff filter and a much more intense (ca. 5–10 fold) 500-W Hg-arc lamp with a >340 nm cutoff filter. Individually, the 500-W lamp effected a benzaldehyde production rate of 0.068 mM/min as compared with 0.24 mM/min from the 200-W lamp. With the two lamps irradiating simultaneously, the resulting rate was 0.31 mM/min, approximately equal to the sum of the single-lamp rates. The 500-W lamp, however, would necessarily greatly increase the extent of CO photoextrusion from **1**. We can thus conclude that, *even if a two-photon mechanism is operable, the predominant catalytically significant initial photoreaction is not CO loss.* This conclusion is of course consistent with the promoting effect of increased CO pressure noted above (Figure 1), as well as the wavelength dependence which, by itself, eliminates the possibility of CO loss as the photoprocess of a *one*-photon mechanism. The photocatalysis thus originates from an excited state of **1** different from the one obtained upon low-energy irradiation. In this context it is probably significant that the above noted wavelength dependence (e.g. 314 vs 366 nm) involves irradiation into different

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(6) Calculated according to the following values for ΔH°_f (kcal/mol) and S° (cal/mol·deg·K) respectively: hexane(l) (–47.52, 70.76); CO(g) (–26.42, 47.04); heptanal(l) (–74.5, 83.3) [obtained from: Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Robert E. Kreiger Publishing: Malabar, FL, 1987].

(7) (a) Spillet, C. T.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1932–1933. (b) Ford, P. C.; Netzel, T. L.; Spillet, C. T.; Porreau, D. B. *Pure Appl. Chem.* **1990**, *62*, 1091–1094.

(8) (a) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5566–5567. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, 1794–1796. (c) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442.

(9) (a) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088–7093. (b) Maguire, J. A.; Boese, W. T.; Goldman, M. E.; Goldman, A. S. *Coord. Chem. Rev.* **1990**, *97*, 179–192.

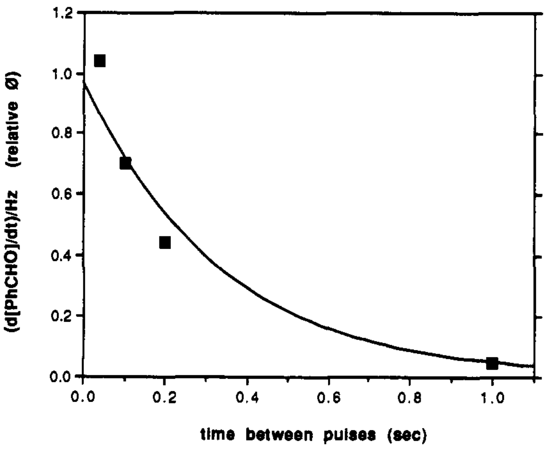

Figure 2. Benzaldehyde formation per laser pulse (308 nm excimer laser) vs time delay between pulses.

bands of the electronic absorption spectrum of **1** (λ_{max} = 280 and 360 nm, respectively).

During the course of this work, Tanaka reported that the rate of reaction 1, using a 308 nm excimer laser, was not proportional to the frequency of pulses: when a sample was irradiated with 10 pulse/s (Hz), the rate of reaction 1 was reportedly more than ten times greater than that resulting from 1 Hz irradiation.[10] We have quantified this experiment (see Figure 2). It is important to note that for a simple one-photon catalytic cycle *a horizontal line would be expected for the function graphed in Figure 2* (i.e. quantum yield should be independent of the pulsing frequency); the results shown in Figure 2, therefore, argue very strongly against a one-photon mechanism. (We assume that there are two photochemical steps although we cannot rule out the possibility of more than two.) Figure 2 reveals that a plot of the relative quantum yield increases with delay between pulses in a very roughly first-order exponential manner with a decay rate constant of ca. 3.0 s^{-1}. This result is strongly supportive of a catalytic cycle involving a photoactive intermediate, generated by the initial laser pulse, which undergoes thermal decay with a rate constant equal to the exponential term, ca. 3.0 s^{-1}. Thus with increasing delay between pulses, a decreasing concentration of the photoactive intermediate is present. Since the decay process is thermal, these results are complemented by the observation that in experiments using a constant output Hg-arc source ($\lambda > 290$ nm), a pronounced *inverse* temperature dependence is found for the rate of eq 1. The rates of benzaldehyde formation in a 7 mM benzene solution of **1** were as follows: 26 °C, 0.58 mM/min; 50 °C, 0.32 mM/min; 77 °C, 0.09 mM/min.

Wavelength Effect on the Second Photoprocess. As noted above, using the excimer laser source, a dependence on pulsing frequency (in effect, irradiation intensity) was noted for the rate of reaction 1, in contrast to the intensity-independence found for the broadband irradiation conditions. Thus under the conditions of the laser experiment thermal decay of the photoactive intermediate is significantly competitive with its photoreaction. Using the excimer laser (308 nm, 10 pulse/s), another "dual-beam" experiment was conducted, by simultaneously irradiating the sample with a >360 nm light source (200-W Hg-arc lamp). The combination of short (308 nm) and long wavelength (>360 nm) light resulted in no significant increase in benzaldehyde production above that resulting from laser irradiation alone (7.1 mM/h). This observation further supports the conclusion that the primary photoprocess is not CO photoextrusion which would be accelerated by the added long wavelength light source. Furthermore, since under the conditions of this dual-beam experiment the second photochemical step was *not* occurring with complete efficiency (as demonstrated by the pulse-frequency dependence), the failure of the long wavelength light to enhance the rate demonstrates that *short wavelength light is required for efficient promotion of the second, as well as the first, photochemical step.* The requirement of short wavelength light for the irradiation of the photoactive intermediate may simply result from failure of the intermediate to appreciably absorb longer wavelength light, especially in competition with **1**. This is especially consistent with the intermediacy of a six-coordinate d^6 intermediate (*vide infra*) since such species are generally bleached in comparison with their d^8 four-coordinate precursors.[11]

The Primary Photoprocess Is Not Dissociative. As noted above, both **1**-catalyzed alkane photodehydrogenation[9] and $Rh(PPh_3)_2(CO)Cl$-catalyzed benzene photocarbonylation[2] are inhibited by the presence of even low pressure CO atmospheres. In contrast, the rate of **1**-catalyzed benzene photocarbonylation (eq 1; $\lambda >$ 290 nm) is *promoted* by increased CO pressure under ca. 1 atm, above which it is independent of CO pressure (Figure 1). These results argue against CO photoextrusion as a primary photoprocess, in accord with the conclusion that short wavelength light is required for the primary (as well as the secondary) photoreaction. This conclusion may appear somewhat surprising in view of Ford's finding that CO loss is a major photoprocess of **1** ($\lambda >$ 330 nm) and that the resulting $Rh(PMe_3)_2Cl$ fragment oxidatively adds the benzene C–H bond.[7] However, Ford's flash photolysis studies reveal why CO loss is *not* a viable primary photoprocess for carbonylation in the CO pressure range of the present work. In the flash photolysis studies, a CO pressure of 7.6 Torr was found to result in a 65% decrease in the formation of the benzene C–H addition product, attributable to a very rapid reaction of $Rh(PMe_3)_2Cl$ with CO.[7] Extrapolation leads to the conclusion that, under 800 Torr of CO, C–H addition would be inhibited 195-fold. Even if in the absence of added CO $Rh(PMe_3)_2Cl$ undergoes C–H addition with complete efficiency, under 800 Torr of CO the quantum yield for the C–H addition step (314 nm) is predicted to be less than 5×10^{-4}.[12] Since this value is lower than our value for the *overall* quantum yield of benzaldehyde formation (1.5×10^{-3}) under 800 Torr, CO extrusion cannot make a dominant contribution to the catalysis under 1 atm or greater CO pressure. Further confirmation of this conclusion is obtained from experiments using a high-pressure vessel equipped with quartz windows: under 46 atm of CO the rate of benzaldehyde formation (2.87 mM/h) is approximately equal to that under 1.0 atm (2.70 mM/h), and therefore the carbonylation quantum yield (314 nm) is approximately 1.5×10^{-3} even under 46 atm. Under such pressure, however, the quantum yield for C–H addition to the three-coordinate species observed by Ford, extrapolated as above, should be no greater than 1.2×10^{-5}.[12]

Any three-coordinate species resulting from ligand loss from **1**—not only $Rh(PMe_3)_2Cl$—would be expected to readily add CO to give a relatively unreactive four-coordinate complex. Thus, on a less quantitative level, the failure of even 46 atm of CO to inhibit reaction 1 argues not only against CO loss as the primary photoprocess but also against loss of either of the other two ligands as well. This conclusion is further supported by the observation that reaction 1 is uninhibited by the presence of any of the following

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(10) Moriyama, H.; Sakakura, T.; Yabe, A.; Tanaka, M. *J. Mol. Catal.* **1990**, *60*, L9–L12.

(11) See for example: (a) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679–680. (b) Sacco, A.; Ugo, R.; Moles, A. *J. Chem. Soc. A* **1966**, 1670.

(12) Since the ratio of CO addition (k_{CO}) to C–H addition (k_{CH}) is 65:35 = 1.86 under 7.6 Torr of CO, the ratio under 800 Torr (assuming Henry's law) should be $(800/7.6) \times 1.86 = 195$. Similarly under 46 atm the ratio should be $(46(760)/7.6) \times 1.86 = 8540$. An estimate for the primary quantum yield for CO photoextrusion can be obtained from a determination of the quantum yield ($\lambda = 308$ nm) for catalytic cyclooctane dehydrogenation obtained in the absence of CO atmosphere, which is 0.1 when $\lambda = 308$ nm (approximately equal to that for $\lambda = 366$ nm): Maguire, J. M.; Goldman, A. S. Unpublished results. This value (0.1) is used to calculate the quantum yield for C–H addition to $Rh(PMe_3)_2Cl$: under 46 atm, for example, the value would be $0.1/8540 = 1.2 \times 10^{-5}$. Note that even if the quantum efficiency of CO photoextrusion is assumed to be 100%, the calculated quantum yield for C–H addition, 1.2×10^{-4}, is significantly below the overall carbonylation quantum yield, 1.5×10^{-3}.

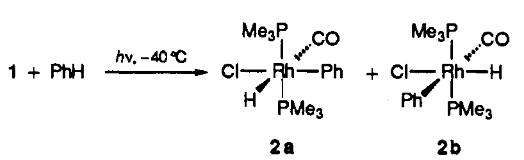
species in solution: PMe_3 (7 mM; higher concentration results in formation of $Rh(PMe_3)_3Cl$), Me_3PO (20 mM), and CH_3CN (0.5 M).

In view of the observation that increased CO pressure promotes reaction 1, and that added PMe_3 or other ligands do not inhibit the reaction, it would appear unlikely that loss of PMe_3 from **1** could be the primary photoprocess. We nevertheless investigated this possibility further by attempting to catalyze reaction 1 using $Rh(PMe_3)(CO)_2Cl$. CO loss from $Rh(PMe_3)(CO)_2Cl$ would give the same intermediate, $Rh(PMe_3)(CO)Cl$, as obtained upon PMe_3 loss from **1**. Photoextrusion of CO from this dicarbonyl would seem at least as favorable as from **1**; even a quantum yield of only ca. 10^{-4} for CO loss from $Rh(PMe_3)(CO)_2Cl$ should then lead to detectable benzaldehyde formation under the conditions of the experiment.[13] In fact, $Rh(PMe_3)(CO)_2Cl$ was found to be completely photoinactive (benzaldehyde formation was below the limit of detection, ca. 0.3 mM), supporting the conclusion that $Rh(PMe_3)(CO)Cl$ is not an intermediate in the catalytic cycle.

To our knowledge, photochemical halide loss in a nonpolar solvent is an unprecedented process. Further, the chloride-loss product $Rh(PMe_3)_2(CO)^+$ should readily react with CO or the added ligands noted above (particularly 0.5 M CH_3CN) to give metastable cations that should then recombine with Cl^- to regenerate **1**. To further probe this possibility of a chloride-loss intermediate, however, we conducted reaction 1 in the presence of a source of added Cl^-, $[K(18\text{-crown-}6)]Cl^-$ (16 mM). No effect on the rate of reaction 1 was observed.

Although it seems unlikely that a radical-based process would show selectivity for benzene over alkane substrates, we considered another dissociative reaction as a primary photoprocess for reaction 1: homolytic cleavage of the Rh–Cl bond. However, the presence of added 9,10-dihydroanthracene (0.1–0.5 M), a highly effective radical trap, shows no inhibition of reaction 1.[14-16] Additionally, a negligible isotope effect was found in experiments using C_6H_6 and C_6D_6, $k_H/k_D = 1.2 \pm 0.2$ (both individually and in competition; see Table 1), further arguing against any radical mechanism and entirely consistent with a C–H(D) oxidative addition process.[17]

An Associative Primary Photoprocess: Formation of a Phenyl Hydrido Complex. The above observations strongly argue against a primary photoprocess involving ligand dissociation from **1**. We therefore propose an associative mechanism. It does not seem plausible that photoinduced CO addition, leading to an 18e complex, could lead to benzene carbonylation. We thus propose that the primary photoprocess of reaction 1 is the photoinduced addition of benzene to an electronically excited state of **1**, yielding an 18e phenyl hydrido complex. Such a process is to our knowledge unprecedented; however, independent low-temperature studies by Field et al. during the course of this work are consistent with the same conclusion of photoinduced, associative, benzene addition to **1**: irradiation ($\lambda > 290$ nm, –40 °C) of **1** in a C_6H_6/THF (1:4) solution yields two isomers of $Rh(PMe_3)_2(CO)Cl(Ph)H$, **2a** and **2b**, as determined by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. Both isomers have a cis phenyl–hydride arrangement, consistent with oxidative addition to the four-coordinate complex.[5]



(2)

Significantly, reaction 2 is not significantly inhibited by the presence of 1 atm of CO (0–1 atm).[18] This implies that if formation of **2** were to proceed primarily via CO loss, then the rate of benzene addition to $Rh(PMe_3)_2Cl$ must be much faster than CO addition, even under 1 atm of CO (a hypothesis inconsistent with the flash photolysis work discussed above).[7,8] In such a case the reaction rate should be independent of benzene concentration. However, we simultaneously irradiated ($\lambda > 330$ nm) at –40 °C two THF solutions of **1**, containing 5% and 20% benzene, respectively, under 1 atm of CO. After 5 h, the formation of both **2a** and **2b** was found to be 4-fold greater in the 20% benzene solution (0.42 and 0.26 mM, respectively) than in the 5% solution (0.08 and 0.04 mM).[19] Thus the reaction rate is apparently proportional to the benzene concentration; this result in tandem with the CO pressure *independence* of eq 2 (reproduced under the same conditions as the present benzene-dependence experiment)[20] rules out the possibility that photoextrusion of CO is a major pathway for reaction 2 under these conditions.

Further evidence against the intermediacy of $Rh(PMe_3)_2Cl$ in the short wavelength irradiations was obtained by conducting separate short and long wavelength irradiations of **1** (–78 °C). The resulting distribution of $Rh(PMe_3)_2Cl(Ph)(H)(CO)$ isomers was found to be significantly wavelength dependent: the ratio of **2a**:**2b** was 4.5 vs 1.9 at short ($\lambda > 330$ nm) and long ($\lambda > 360$ nm) wavelengths, respectively. This result rules out the intermediacy of ground-state $Rh(PMe_3)_2Cl$ in the short wavelength irradiations, assuming in accord with Ford's work[7,8] that the *long wavelength* irradiations proceed via formation of $Rh(PMe_3)_2Cl$ and subsequent addition of benzene to give $Rh(PMe_3)_2Cl(Ph)(H)$. Further, this result can be used to exclude *any mechanism* proceeding via $Rh(PMe_3)_2Cl(Ph)(H)$. For example, a pathway involving irradiation of **1** to give *excited state* $Rh(PMe_3)_2Cl$, which, hypothetically, would undergo thermal decay or reaction with benzene much faster than CO addition, would afford kinetics identical to those for our proposed mechanism involving an undissociated excited state.[21] However, since it shares a common intermediate ($Rh(PMe_3)_2Cl(Ph)(H)$) with the long wavelength irradiation pathway, a hypothetical *excited state* $Rh(PMe_3)_2Cl$ pathway should give the same distribution of isomers of **2**, in contrast with the observed results.[22]

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[13] Our limit of detection for benzaldehyde formation is ca. 0.3 mM. In order to achieve detectable benzaldehyde levels (after 24 h of irradiation) the rate of benzaldehyde formation would need to be greater than ca. 6×10^{-4} times that resulting from **1**-catalyzed carbonylation. If **1**-catalyzed carbonylation proceeded via PMe_3 loss, assuming an upper limit of 0.1 for the primary quantum yield for PMe_3 loss (a process not detected in Ford's flash photolysis work), then the quantum yield for CO loss from $Rh(CO)(PMe_3)_2Cl$ required for benzaldehyde detection would be $0.1 \times 6 \times 10^{-4}$.

[14] 9,10-Dihydroanthracene would be subject to hydrogen abstraction by free phenyl radicals, yielding benzene and anthracene. The rate constant for this reaction is presumably significantly greater than that for the reaction of phenyl radical with diphenylmethane[15] which can be estimated[16] as ca. 1×10^7 M^{-1} s^{-1}. Note that unlike benzaldehyde formation, however, formation of biphenyl is severely inhibited by added 9,10-dihydroanthracene, and the amount of anthracene formed is equal to the amount of biphenyl formed in the absence of added 9,10-dihydroanthracene. This implies that the biphenyl that is formed during the reaction results from a radical pathway.

[15] Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1968**, *46*, 2661–2665.

[16] Fischer, H., Ed. *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: Berlin-Heidelberg, 1984; Vol. 13, Subvolume b, pp 26, 28, 213.

[17] Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91 and references cited therein.

[18] Field, L., personal communication.

[19] The merry-go-round type apparatus used resulted in a very low effective light intensity, resulting in low conversions even after 5 h of irradiation. Irradiating individual samples introduces some comparative error due to variations in focussing the light beam on the 5 mm NMR tube and possible fluctuations in temperature; however, much higher conversions were obtained (leading to the same conclusion of benzene concentration dependence). Specifically, after 2.5 h of irradiation (–40 °C) a 5% benzene solution afforded 1.83 mM **2a** and 1.03 mM **2b** while a 20% benzene solution gave 11.85 mM **2a** and 7.67 mM **2b**.

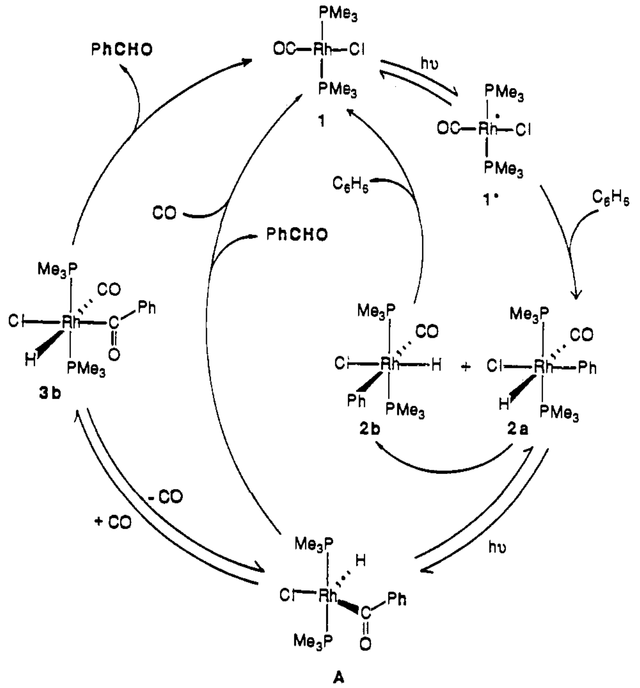
[20] Simultaneous irradiation of a third sample, with 20% benzene under N_2 atmosphere, resulted in the formation of 0.47 mM **2a** and 0.37 mM **2b** (vs 0.42 and 0.26 mM, respectively, under 1.0 atm of CO). Thus (assuming this difference is not simply due to experimental error) it represents only a 12% increase in the rate of formation of the catalytically relevant complex, **2a**. This increase, which likely results from a concomitant pathway involving CO loss and benzene addition to $Rh(PMe_3)_2Cl$, would be expected to be considerably less significant (virtually undetectable) under even low CO pressures (see ref 11), which are of course necessary for catalytic carbonylation.

[21] We thank a referee for suggesting the intriguing possibility of an excited-state $Rh(PMe_3)_2Cl$ intermediate.

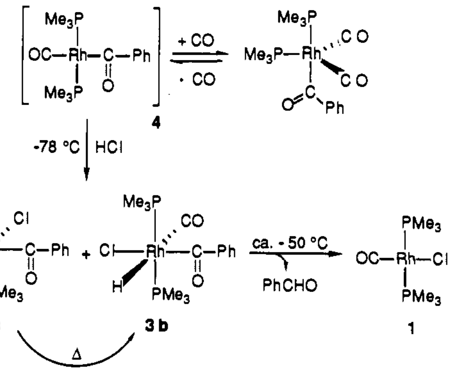
Bimolecular reactions of organometallic excited state species are rare, and unprecedented in the case of C–H oxidative additions. However, in retrospect it seems reasonable that the present reaction should be exceptional in this respect for several reasons: (i) Complex **1** is a 16e complex so it is at least formally capable of direct oxidative addition. (ii) Oxidative addition of H_2 (electronically related to C–H addition) is well-known for the (ground state) iridium analogues[23] of **1** and for related tris-phosphine–rhodium halide complexes,[24] and it has recently been shown to occur for **1** itself to give a labile intermediate.[25] (iii) The barrier to oxidative addition to the related complex, *trans*-Ir(PH_3)$_2$(CO)Cl, has been shown by *ab initio* calculations (in the case of H_2) to be largely due to repulsion between the electron pairs of the substrate and the d_{z^2} orbital.[26] Thus any transition that removes an electron from the d_{z^2} orbital (the HOMO of both the Ir complex and **1**)[27] might greatly facilitate addition.[28] (iv) The significant kinetic barrier to reductive elimination reactions of octahedral d^6 complexes[29] should serve to stabilize the addition product (which in this case enables both its observation and its subsequent photolysis). In cases where the kinetic barrier is small, even if photoinduced addition can occur, the adduct may be too short-lived to observe if elimination is thermodynamically favorable. Alternatively, if addition is thermodynamically favorable, a small kinetic barrier would enable the corresponding thermal addition to obscure the photoreaction. (v) The occurrence of associative reactions of organometallic excited states is minimized by their generally short lifetimes. In a case such as this however, a reaction with a solvent molecule, the time required to encounter the substrate is obviously very short. (vi) On the basis of the above criteria, a relatively small class of organometallic compounds would appear favorable for photoassociative reactions; of these the best studied are complexes of the form ML_3X and ML_2(CO)X (where M is Rh or Ir, L is generally a phosphine, and X is a formally anionic ligand). Since steric factors generally play an important role in associative reactions, it is noteworthy that complex **1** is clearly one of the least sterically hindered of this class of compounds.

Of the two Rh(PMe_3)$_2$(CO)Cl(Ph)H isomers, only **2a** is in the correct geometry to undergo a migratory insertion to form a benzoyl group. Therefore it is **2a** that may be considered to be the metastable photoactive intermediate, with the quantum yield for reaction 1 dependent upon a competition between thermal decay of **2a** and its photochemical processes. The rate constant for thermal decay of the photoactive intermediate, obtained from the laser pulse experiment described above, is roughly 3.0 s^{-1} (50 °C). This value is, within experimental error, in full agreement with the rate constant for the thermal rearrangement of **2a** to **2b** (1.7 s^{-1} at 50 °C), independently obtained from low-temperature NMR spectroscopy and extrapolated to 50 °C,[5] in strong support of **2a** as the identity of the photoactive intermediate.

Scheme 1. Proposed Mechanism of **1**-Catalyzed Benzene Photocarbonylation (Short Wavelength Irradiation)



Scheme 2. Independent Synthesis of Acyl Hydrido Intermediates (and Elimination of Benzaldehyde)



Reaction Steps Subsequent to the Formation of 2a. As an octahedral Rh(III) complex, a photoactive intermediate **2a** would undoubtedly absorb long wavelength (λ > ca. 330 nm) light much less strongly than **1**,[11] in accord with the conclusion that the second photoprocess is greatly favored by short wavelengths. Presumably, the catalytically significant photochemical reaction of **2a** results in migratory insertion to yield a 16e benzoyl hydrido complex (**A** in Scheme 1). A subsequent competition between CO addition and migratory deinsertion would explain the observed CO pressure dependence of the rate of reaction 1. Addition of CO to **A** could produce up to three trans-phosphine isomers of Rh(PMe_3)$_2$(CO)(Cl)(COPh)H (**3**). Reductive elimination of benzaldehyde from either **3a** or **3b** (see Scheme 2) would then complete the catalytic carbonylation cycle (the third possible isomer does not have the correct stereochemistry to reductively eliminate benzaldehyde).

The proposed acyl hydrido carbonyl intermediate, **3**, was generated *in situ*. CO (800 Torr) was added to an acetone-d_8 solution of Rh(PMe_3)$_2$(CO)Ph (**4**)[30] to give a solution of Rh(PMe_3)$_2$(CO)$_2$(COPh). Excess 2,6-di-*tert*-butylpyridine·HCl (a convenient source of HCl) was then added to the solution at −78 °C, and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy (see Scheme 2). The reaction was repeated with ^{13}CO and monitored by ^{13}C NMR spectroscopy. Only two of the three possible trans-phosphine isomers were observed at −65 °C;

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[22] Rh(PMe_3)$_2$Cl(Ph)(H) would be expected to isomerize quickly. Thus even if C–H addition to excited state and ground state Rh(PMe_3)$_2$Cl gave different isomers the resulting CO adducts would be expected to have the same geometry. See, for example: (a) El-Idrissi, I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671–677 and references cited therein. (b) Koga, N.; Morokuma, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 6883–6892. (c) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. To be submitted for publication.

[23] Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335–344.

[24] Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

[25] Duckett, S. B.; Eisenberg, R.; Goldman, A. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1185–1187.

[26] Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. *J. Phys. Chem.* **1993**, *97*, 5890–5896.

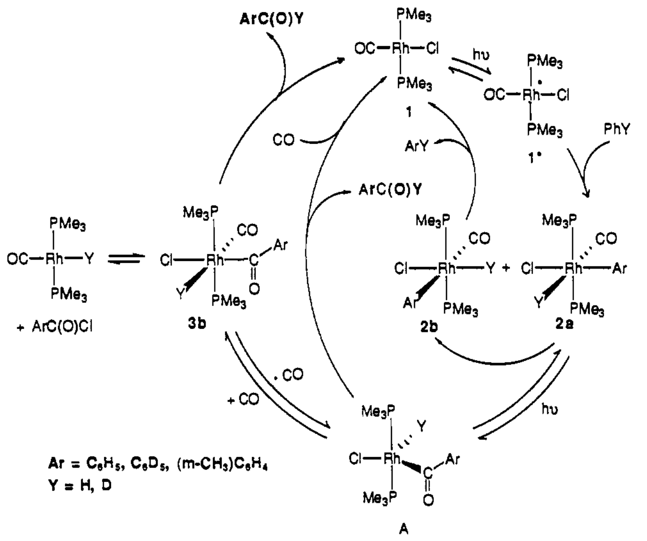
[27] Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485–1488.

[28] The band at ca. 280 nm has not been assigned. It is interesting to note, however, that the lowest energy band has been assigned to a $d_{z^2} \rightarrow b_{1\pi}$ transition;[27] since the $b_{1\pi}$ orbital has largely p_z character this might not significantly reduce the barrier to oxidative addition.

[29] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 324–333.

[30] Boyd, S. E.; Field, L. D.; Hambley, T. W.; Partridge, M. G. *Organometallics* **1993**, *12*, 1720–1724.

Scheme 3. Proposed Mechanism of **1**-Catalyzed Benzene Photocarbonyl (Short Wavelengths) Including Reversible Loss of ArC(O)Cl To Account for the Results of Crossover Experiments and the Effects of Added Aroyl Chlorides



these were spectroscopically determined to be **3a** and **3b** (Scheme 2). At early reaction times the trans HCl addition product, **3a**, was the major (>70%) product, in accord with the known addition of HCl to the related complex **4**.[5] The concentration of **3a** was then seen to slowly diminish with time with the concurrent growth of **3b**. At temperatures above −55 °C, **3a** completely disappears leaving only **3b**, and **1** is observed to begin growing in slowly. **3b** decomposes to give **1** and benzaldehyde (quantitative by GC) rapidly at temperatures above −40 °C. This indicates that reductive elimination of benzaldehyde from **3b** occurs thermally and very rapidly under the conditions of the catalysis (50 °C), consistent with our assignment of the second photoprocess as being a photoreaction of **2a** (and not **3**). The rate of thermal decay of **3a** and **3b** also explains why these intermediates were not observed during Field's experiments which were done at −40 °C, a temperature at which **2a** and **2b** are stable but **3a** and **3b** are not.

In an attempt to directly investigate the photochemistry of the phenyl hydrido complexes, a sample of **1** in THF/C_6D_6 (4:1) was irradiated at −40 °C to initially obtain a good conversion to **2a** and **2b** (some **4** is also formed). The solution was then placed under CO, irradiated at −78 °C, and then monitored by NMR spectroscopy. It was found that small quantities of **3b** (but not **3a**) were observed under these conditions (see Experimental Section).

Formation of Crossover Product. The mechanism indicated in Scheme 1 implies that both the phenyl group and the aldehydic proton of the benzaldehyde product derive from the same molecule of benzene. A series of crossover experiments were conducted in 1:1 C_6H_6:C_6D_6, and the products were analyzed by GC-MS (see Table 1). The results indicate that a substantial amount of crossover is occurring, although the amount is less than that which would be expected from a completely random process.

A priori, the instability of phenyl radicals would seem to make a radical pathway an unlikely explanation for the observation of crossover product, particularly in view of the selectivity observed for benzene vs alkane carbonylation. Empirically, the lack of inhibition by the presence of a high concentration (0.5 M) of 9,10-dihydroanthracene (noted above) would seem to rule out the involvement of phenyl radicals. Finally, it should be noted that the fact that the extent of crossover is less than statistical indicates that, regardless of the source of crossover product, a significant non-radical pathway does exist.

Field et al. have found that irradiation of **1** at low temperatures yields, in addition to **2a** and **2b**, small amounts of $Rh(PMe_3)_2(CO)Ph$ (**4**).[5] This presumably arises from the loss of HCl from either or both of the phenyl hydride complexes **2** (which is most likely a photochemical step since HCl readily adds thermally to both **1** and **4** at the reaction temperature). In the case of C_6H_6/C_6D_6 solutions, reversible loss of HCl/DCl from **2** (or **3**) would result in the formation of crossover product. To address this possibility, experiments were conducted in which either water (to saturation; 10 μL/mL) or *tert*-butyl alcohol (0.21 M) was added to the reaction mixture prior to irradiation. If free HCl/DCl were being formed during photolysis, it would be expected to undergo rapid exchange with both the water and the alcohol, converting free DCl to HCl. This would decrease the amount of benzaldehyde formed with deuterium in the aldehydic position. It was found that both water and *tert*-butyl alcohol had only a marginal effect on the isotopic composition of the benzaldehyde formed, suggesting that most of the **2** and **3** formed do not reversibly lose HCl(DCl) under our reaction conditions.

If the benzaldehyde crossover product observed during the photolysis of **1** resulted from a binuclear HCl/DCl scrambling pathway, then the amount of crossover should be dependent on the concentration of **1**. However, no such concentration dependence was found (see Table 1). Therefore, these experiments (independence of the crossover on the concentration of **1** or on the presence of added water or *tert*-butyl alcohol) eliminate the possibility that the observed crossover is due to a pathway that involves reversible loss of HCl/DCl.

A series of reactions was carried out in order to further investigate the formation of aldehyde crossover product. It was found that neither added PMe_3 nor CO inhibited the degree of crossover, implying that neither of these ligands need to be lost to generate an open coordination site necessary for scrambling to occur. Surprisingly, the degree of crossover was found to *increase* with increasing CO pressure (Table 1). This can be explained by proposing that the scrambling takes place after coordination of CO to **A**, and that at lower CO pressures, direct reductive elimination of isotopically pure benzaldehyde (C_6H_5CHO or C_6D_5CDO) from **A** effectively competes with CO addition to give **3** which can then lead to isotopic scrambling. Consistent with this interpretation, loss of benzaldehyde from **A** has previously been postulated by Milstein.[31]

Since the loss of neither HCl, PMe_3, nor CO was found to be responsible for the majority of the observed crossover, experiments were conducted to determine whether or not the loss of chlorobenzene from **2** or the loss of benzoyl chloride from **3** (in both cases generating the same intermediate, $[Rh(PMe_3)_2(CO)H]$), could be responsible. Added chlorobenzene had no effect on the amount or isotopic distribution of the products. However, addition of (undeuterated) benzoyl chloride to a C_6H_6/C_6D_6 reaction solution resulted in the formation of benzoyl-d_5 chloride and an excess of d_0 and d_1 aldehyde, indicating that reversible benzoyl chloride loss does occur from **3**. Note that loss of benzoyl chloride from $Rh(PPh_3)_2(COPh)(CO)Cl_2$, a complex closely related to **3**, has been reported;[32] and further, we have found that loss of benzoyl chloride from $Rh(PMe_3)_2(COPh)(CO)Cl_2$ occurs and is reversible.[33]

In order to further probe the reversible loss of benzoyl chloride from **3**, experiments were conducted in which *m*-toluoyl chloride was added to solutions of **1** in C_6D_6 prior to irradiation. In addition to benzaldehyde-d_6, benzoyl-d_5 chloride and *m*-tolualdehyde-d_1 were observed. Evidence for the reversibility of the insertion step was also obtained: toluene was formed and the amount decreased with increasing CO pressure (see Experimental Section). This is consistent with Scheme 1 which implies that CO addition to the *m*-toluoyl analogue of **A** should prevent deinsertion. Since arene elimination occurs via the aryl hydride complex **2a**, irradiation of which leads to CO insertion, Scheme 1 also suggests

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[31] Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221–226.

[32] Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514. See also: Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 4093–4100 and references cited therein.

[33] Rosini, G. P.; Goldman, A. S. To be submitted for publication.

that the amount of toluene formed should decrease with increasing irradiation intensity. Experiments were conducted using neutral density optical filters, and the ratio of toluene/*m*-tolualdehyde was monitored by GC. It was found that the amount of toluene was indeed dependent on the intensity (see Experimental Section), supporting the proposal that the insertion step is in fact photochemically induced.

Possible Role of $Rh(PMe_3)_2(CO)Ph$ (4). As noted above, Field et al. have reported that **4** forms during low-temperature irradiation of **1** in benzene/THF (1:4). In addition, these workers have found that **4** is itself a benzene photocarbonylation catalyst. The question thus arises as to how much (if any) of the observed chemistry of **1** is occurring through the participation of **4** under our conditions (50 °C). The participation of **4** could readily explain the formation of benzophenone, as well as the observed benzaldehyde crossover, since the aldehydic proton must derive from a second molecule of benzene. Although there is no detectable **4** observed upon monitoring (by IR) a reaction sample run at 50 °C, the possibilities that small concentrations of **4** strongly absorb short wavelength UV light or that larger concentrations are present during irradiation were considered. An experiment was conducted in order to compare the rates of benzaldehyde formation of **1** and **4**. Under identical conditions (10 mM complex, 800 Torr of CO, 50 °C), a solution of **1** yielded approximately ten times more benzaldehyde than **4** (44.1 and 4.2 mM, respectively) while yielding somewhat less benzophenone (1.0 and 1.5 mM, respectively). This implies that the majority of the chemistry observed during the photolysis of **1** does not involve the participation of **4**. Additionally, even if it is assumed that all of the benzophenone formed during the **1**-catalyzed reaction is due to the participation of **4**, then an upper limit can be placed on the amount of benzaldehyde formed due to concurrent photochemistry of **4**, if it is also assumed that the ratio of benzaldehyde/benzophenone produced by **4** is unaffected by the presence of **1**. This leads to the conclusion that, for example, in a typical run where 44 mM benzaldehyde and 1.0 mM benzophenone are formed during the photolysis of **1**, only 3 mM benzaldehyde may be due to concurrent photochemistry of **4**. (Of course it is entirely possible that some or all of the benzophenone does not arise via a **4**-catalyzed pathway; 3 mM is therefore an upper limit.)

Summary and Conclusions. A mechanism of the full catalytic cycle of the **1**-catalyzed photochemical (short wavelength) carbonylation of benzene is proposed. The most unusual aspect of the cycle is that the primary photoprocess does not involve ligand loss. Photochemical CO loss from **1** is known to lead to C–H addition[7] and, in the case of alkanes, catalytic dehydrogenation.[9] Similarly, loss of a ligand (either PPh_3 or CO) from $Rh(PPh_3)_2(CO)Cl$ leads to benzene carbonylation.[2] In the present case, however, the C–H addition step proceeds predominantly via an unrelated, associative, process. This conclusion is based on studies of the dependence of the catalytic and stoichiometric reaction rates on CO pressure, wavelength, and irradiation intensity, the results of which are anomalous when compared with the behavior of these other systems which operate via addition to three-coordinate rhodium(I). Note that in the case of **1**-catalyzed *alkane* carbonylation, the most effective conditions involve an entirely different mode of breaking the C–H bond (hydrogen abstraction by a photoexcited organic carbonyl), independent of any rhodium complex.[4]

In spite of the different modes of C–H bond activation, the **1**-catalyzed alkane dehydrogenation and the $Rh(PPh_3)_2(CO)Cl$-catalyzed benzene carbonylation systems share with the present system important mechanistic features characteristic of organorhodium-catalyzed chemistry. All three systems (and the radical-based alkane carbonylation system as well) depend upon the ability of rhodium to shuttle between the I and III oxidation states, and all involve both six- and five-coordinate Rh(III) aryl, alkyl, and/or benzoyl hydrido intermediates. In all three cases the ability of the 16e square planar precursor to remain unsaturated, even in the presence of CO or H_2 (conditions which would lead to 18e complexes in the case of iridium analogues), is critical for the catalysis. The small steric bulk of the PMe_3 ligand (in contrast, most notably, with PPh_3) favors the stability of the crowded Rh(III) intermediates; this also applies to the radical-based system[4] and presumably to carbonylation catalyzed by $Rh(PMe_3)_2(CO)Ph$.[5] The combination of all these features, in addition to the well-established ability of Rh–C σ bonds to undergo insertion, should perhaps be viewed as the key to the hydrocarbon-functionalization properties of **1** and related complexes, rather than any particular ability to react with C–H bonds.

Experimental Section

General Procedures. All samples were handled either under a nitrogen atmosphere in a Vacuum Atmospheres Dry-Lab glovebox or under vacuum. Deuterated solvents were distilled under vacuum from NaK alloy (except for acetone which was dried with molecular sieves). All other solvents were distilled from dark purple solutions of benzophenone ketyl and stored in the glovebox. Benzene was purified prior to drying by a standard procedure to remove thiophene and alkene impurities.[34]

NMR spectra were recorded on a Varian XL-400 NMR spectrometer. Concentrations of organic products were quantified by gas chromatography using a Varian 3400 gas chromatograph with a flame ionization detector and a 50-m methyl silicone gum capillary column. GC-MS was performed using either a Hewlett Packard 5890 Series II gas chromatograph/5971 mass spectrometer or a Finnigan-Mat 8230 high resolution magnetic sector mass spectrometer. The irradiations employing constant output sources were carried out in an apparatus described previously.[9] The laser experiments employed a Lambda-Physik pulsed excimer laser charged with XeCl for an output wavelength of 308 nm. Pulsing frequencies were determined with an oscilloscope and the power was determined with a joulemeter. The power remained relatively constant during the course of the experiments at 50 mJ/pulse.

Preparation of $Rh(PMe_3)_2(CO)Cl$ (1). $[Rh(COD)Cl]_2$ (2 g) was dissolved in 75 mL of toluene and stirred in an ice bath. Carbon monoxide was then bubbled through the stirring solution for 30 min. PMe_3 (1.66 mL) was then added dropwise over a 5 min period, at which time the solution turns bright yellow. The solution is then allowed to warm to room temperature over 30 min. The solvent was then removed in vacuo, and the product was recrystallized from hexanes (2.06 g, 80% yield).

Preparation of $Rh(PMe_3)_2(CO)Ph$ (4). $Rh(PMe_3)_2(CO)Me$[30] (80 mg) was dissolved in a mixture of 2 mL of benzene and 8 mL of THF. The solution was then irradiated at 0 °C for 2 h. The solvent was then removed in vacuo, and the crude product was sublimed at 70 °C to give a yellow powder (75 mg, 78% yield).

Typical Conditions for 1-Catalyzed Carbonylation Reactions. In general, 2-mL samples of 7–10 mM **1** in benzene were placed under CO pressure 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/Schlenk line and for removal of microliter samples for GC analysis. Samples were typically irradiated for 2.5 h in a 50 °C water bath with a 500-W Hg-arc lamp while being stirred magnetically. The samples were then analyzed by GC or GC/MS for the determination of the products, calibrated in all cases with the use of commercially obtained authentic samples.

Effect of CO Pressure on the Rate of Aldehyde Formation. A stock solution of 2 mM **1** in benzene was prepared. Samples (2 mL) were then irradiated at 50 °C under varying pressures of CO, and the products were analyzed by GC. The rate of benzaldehyde formation for each run was determined and is shown in Figure 1.

Quantum Yields at 314 and 366 nm. Two 2-mL samples of 2 mM **1** in benzene were placed under 800 Torr of CO and irradiated using either a 314 nm interference filter or a combination of 0-52 and 7-60 filters for 366 nm. Actinometry was done using a 2-mL solution of Aberchrome 540[35] in toluene in a 1 cm quartz cell to determine the intensity (einstein/s) of the light at each wavelength. The amount of benzaldehyde formed was then determined by GC for each experiment, and the quantum yield was determined to be 1.5×10^{-3} at 314 nm and 2.0×10^{-5} at 366 nm.

Intensity Dependence Studies. A stock solution of 7 mM **1** in benzene was prepared, and 2-mL samples under 800 Torr of CO were irradiated at 50 °C. The intensity of the light was changed by using neutral density

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(34) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980; pp 118–119.

(35) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkins Trans. 1* **1981**, 341.

filters and by varying the source using either a 500-W or a 200-W lamp. The rate of benzaldehyde formation was then determined for each sample.

Dual-Beam Experiments. Two milliliters of a 7 mM benzene solution of **1** was placed under 800 Torr of CO and irradiated at 50 °C with two sources, both individually and simultaneously (at 90° to each other). In the first experiment, the sources were a 200-W lamp (>290 nm) and a 500-W lamp (>340 nm), and in the second experiment the sources were a 200-W lamp (>340 nm) and a 308 nm excimer laser (10 pulse/s). The rate of aldehyde formation was determined for each experiment. As in all photochemical experiments, light sources were carefully focussed to irradiate a large area (ca. 0.3–0.8 cm in diameter) centered on the midpoint of the irradiated windows. Note also that the apparently long lifetime of the photoactive intermediate (ca. 0.3 s as obtained from single excimer-source experiments) would allow the vigorous magnetic stirring (ca. 1000 rpm) to ensure a homogeneous distribution of the intermediate.

Effect of Laser Pulse Rate. Samples (2.5 mL) of 0.2 mM **1** in benzene were placed under 800 Torr of CO and irradiated with a 308 nm excimer laser. The pulsing frequency was varied from 25 to 0.5 Hz, and the rate of aldehyde formation and quantum yield was determined for each experiment by GC. The graph in Figure 2 summarizes the data.

Effect of Added Ligands on Photolysis of 1. To each of three samples of 2 mL of 7 mM **1** in benzene was added 7 mM PMe_3, 20 mM Me_3PO, 0.5 M CH_3CN, and 16 mM $[K^{+}18\text{-crown-}6]Cl$. Each sample was then placed under 800 Torr of CO and then irradiated at 50 °C. The rate of benzaldehyde formation was then determined for each sample and compared to a control sample that had no extra ligand added to it. It was found that the rate was unaffected in each of the experiments performed.

Attempted Carbonylation with $Rh(PMe_3)(CO)_2Cl$. $Rh(PMe_3)(CO)_2Cl$ was generated by adding CO atmosphere to a solution of $[Rh(PMe_3)(CO)Cl]_2$ (2 mg/2 mL; ν_{CO} = 1975 cm^{-1}) resulting in a rapid color change and the conversion to $Rh(PMe_3)(CO)_2Cl$ as revealed in the IR spectrum (ν_{CO} = 2001, 2086 cm^{-1}), as has been described previously.[36] The solution was then irradiated at 50 °C for 69 h, and GC analysis showed that there was less than 0.3 mM benzaldehyde formed.[12]

Wavelength Dependence of the Ratio of 2a:2b. A 10 mM stock solution of **1** (12.4 mg) in C_6H_6 (0.8 mL)/THF (2.75 mL)/acetone-d_6 (0.35 mL) was prepared. Samples in NMR tubes were subjected at –78 °C (dry ice/acetone) to irradiation of either $\lambda > 330$ nm (1 cm acetone, which transmits the 334 nm Hg-arc line) or $\lambda > 360$ nm (two Corning 0-52 filters). ^{31}P NMR spectra were obtained at –80 °C. The ratio of **2a**:**2b** was determined on the basis of integration of the peaks at δ –6.5 and –8.5, respectively, and was periodically monitored. The ratio varied only slightly over time; values for the $\lambda > 330$ nm experiment were the following (time, ratio): 10 min, 4.66; 15 min, 4.74; 20 min, 4.79; 40 min, 5.13; 60 min, 5.40. Values for the $\lambda > 360$ nm experiment were the following (time, ratio): 20 min, 2.02; 30 min, 2.08; 40 min, 2.12; 50 min, 2.19; 60 min, 2.23. The values of 4.5 and 1.9 were obtained by extrapolation to time = 0 to discount the effect of any secondary reactions of **2a** or **2b** (although such reactions would in any event be minimal due to the thermal stability of **2**[5] and its presumably weak absorbance at $\lambda > 330$ nm[11]).

Synthesis of $Rh(PMe_3)_2(CO)(COPh)(Cl)H$ (3). A sample of **4** in acetone-d_6 was placed under 800 Torr of CO in a resealable NMR tube. This generated only $Rh(PMe_3)_2(CO)_2(COPh)$ in solution by ^{31}P NMR at –65 °C (the spectrum was broad at room temperature, suggesting reversible CO loss). The CO was then removed in vacuo at –78 °C and then an excess of 2,6-di-*tert*-butylpyridine·HCl was added, followed by a freeze–pump–thaw cycle. The reaction was then monitored by NMR spectroscopy at –65 °C, and two new complexes were seen to grow in. The reaction was repeated with ^{13}CO, and this in conjunction with the previous experiment allowed the two isomers to be unequivocally assigned as **3a** and **3b**. **3a**: ^{1}H NMR (acetone-d_6) 8.938 (m, 1H), 8.317 (m, 2H), 8.093 (m, 2H), 1.683 (br pseudo-triplet, PMe_3), –13.406 (dt, J_{H-Rh} = 28.5 Hz, J_{H-P} = 12.2 Hz). ^{31}P NMR (acetone-d_6): –9.05 (dd, J_{P-H} = 12.0 Hz, J_{P-Rh} = 99.7 Hz); ^{13}C NMR (acetone-d_6) 241.0 (m, *C*(O)Ph), 188.7 (m, *C*O). **3b**: ^{1}H NMR (acetone-d_6) 8.906 (m, 1H), 8.306 (m, 2H), 8.145 (m, 2H), 1.789 (br pseudo-triplet, PMe_3), –7.544 (dt, J_{H-Rh} = J_{H-P} = 12.9 Hz (J_{H-C} = 61 Hz)). ^{31}P NMR (acetone-d_6) –8.40 (dd, J_{P-H} = 12.2 Hz, J_{P-Rh} = 105.4 Hz). ^{13}C NMR (acetone-d_6) 241.9 (dt, J_{P-C} = 7.5 Hz, J_{Rh-C} = 33.0 Hz, J_{H-C} < 5 Hz, *C*(O)Ph), 185.6 (m, *C*O, J_{C-H} = 62.1 Hz, J_{C-Rh} = 44.2 Hz, CO).

Direct Observation of 3 during Photolysis of 1. A 50 mM sample of **1** in THF/benzene (4:1) was irradiated at –40 °C for 2.5 h giving a 65% conversion of **1** to a mixture of products (**5**:**2a**:**2b**:**4** = 13:25:13:12). A second sample was irradiated for 5 h giving a 99% conversion (**5**:**2a**:**2b**:**4** = 12:53:21:13).[37] These samples were then placed under 800 Torr of CO and irradiated at –78 °C in an attempt to detect the formation of **3**. In both samples a small amount of **3b** was observed to grow in (in both cases the amount of **3b**:**2a** was roughly 6.5%).

Crossover Studies. A 7 mM stock solution of **1** in a 1:1 C_6D_6:C_6H_6 solvent mixture was prepared and 2-mL samples were irradiated at 50 °C under the conditions stated below. The isomeric distribution of the benzaldehyde formed was determined by GC/MS. The crossover experiments with varying CO pressure are summarized in Table 1. Two samples were prepared with either 0.3 μL of PMe_3 or nothing added (control) to a 1-mL sample of the stock solution prior to irradiation, and the samples were then placed under 800 Torr of CO and irradiated for 2.5 h at 50 °C. The PMe_3 was found to have had no effect on the total percentage of crossover. Two samples were prepared adding either 10 μL of water or 20 μL of *tert*-butyl alcohol (2.5 h irradiation at 50 °C), and the amount of C_6H_5CDO formed was compared to a control sample in which nothing was added. The results showed minimal change between the control sample and the added water and alcohol (17.1% versus 16.0% and 15.3%, respectively).

Effect of Added Chlorobenzene. To a 1-mL sample of 10 mM **1** in C_6D_6 was added 2 μL of chlorobenzene. The sample was then placed under 800 Torr of CO and irradiated for 2.5 h at 50 °C. Analysis of the sample by GC/MS showed that there was no chlorobenzene-d_5 or benzaldehyde-d_1 formed, indicating that reversible chlorobenzene loss is not occurring.

Effect of Added Benzoyl Chloride. To a 1-mL sample of 10 mM **1** in C_6H_6/C_6D_6 was added 0.3 μL of benzoyl chloride. The sample was then placed under 800 Torr of CO and irradiated for 2.5 h at 50 °C. Analysis of the sample by GC/MS showed that there was 30% benzoyl-d_5 chloride formed along with an excess of benzaldehyde-d_0,d_1 (d_0,d_1:d_5,d_6 = 68:32 compared to 50:50 for the control experiment), indicating that reversible benzoyl chloride loss is in fact occurring.

Effect of CO Pressure on the *m*-Toluoyl Chloride Reaction. Two 2-mL samples of 10 mM **1** in C_6D_6 were prepared, to which were added 2.65 μL of *m*-toluoyl chloride. One sample was then placed under 800 Torr of CO, while the other sample was placed under 50 Torr of CO (the balance being Ar). Each sample was then irradiated for 5 h at 50 °C, and then the *m*-tolualdehyde:toluene ratio was determined by GC. It was found that under 800 Torr of CO the ratio was 2.4, while under 50 Torr of CO the ratio was only 0.5, thus indicating that toluene formation is inhibited by increasing CO pressure.

Effect of Light Intensity on the *m*-Toluoyl Chloride Reaction. Two 1.5-mL samples of 7 mM **1** in C_6D_6 were prepared, to which were added 2.0 μL of *m*-toluoyl chloride. Each sample was then placed under 50 Torr of CO (the balance being Ar) and then irradiated for 5 h at 50 °C. One sample was irradiated at full intensity, while the other sample had an 0.5 optical density filter. The *m*-tolualdehyde:toluene ratio of each sample was then determined by GC. It was found that the ratio for the full intensity sample was 3.7, while the ratio for the 0.5 OD sample was 2.5, thus indicating that aldehyde formation is enhanced by increasing light intensity.

Carbonylation with 4. One milliliter of a 10 mM solution of **4** in benzene was placed under 800 Torr of CO and irradiated at 50 °C for 2.5 h. A second sample of 1 mL of a 10 mM solution of **1** in benzene was also irradiated under identical conditions. It was found that **1** catalyzed carbonylation roughly 10 times faster than **4** under identical conditions. Products for **4**: 4.2 mM benzaldehyde, 0.0 mM benzyl alcohol, 0.2 mM biphenyl, 1.5 mM benzophenone. Products for **1**: 44.1 mM benzaldehyde, 1.6 mM benzyl alcohol, 0.5 mM biphenyl, 1.0 mM benzophenone.

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(37) Product **5**, which has spectroscopic properties similar to **2a**, is tentatively assigned as the analogous THF addition product, $Rh(PMe_3)_2(CO)ClH$-(tetrahydro-2-furyl).