# Photochemical Carbonylation of Benzene by Iridium(I) and Rhodium(I) Square-Planar Complexes

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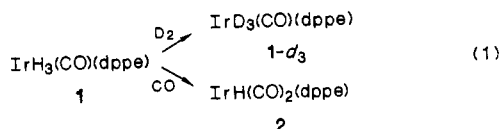
The photochemical carbonylation of unfunctionalized arene C–H bonds is catalyzed by various $d^8$ complexes under low CO pressure at ambient temperature. The carbonylation of benzene to benzaldehyde is achieved by using $IrH(CO)_2(dppe)$, $IrH_3(CO)(dppe)$, or $IrBr(CO)(dppe)$ as the catalyst, and the photoactive species in each case appears to be $IrX(CO)(dppe)$ (X = H or Br). The monodentate phosphine complexes $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) exhibit similar photochemical activity leading to benzene carbonylation. In all cases the amount of benzaldehyde formed is limited by thermodynamics with $\Delta G_{298}° = +1.7$ kcal. When $RhCl(CO)(PPh_3)_2$ is placed under $^{13}CO$ with PhCHO, photochemical decarbonylation is achieved along with significant $^{13}CO$ incorporation into the aldehyde, confirming the occurrence of both carbonylation and decarbonylation. Both processes are thought to involve the same initial photochemical step of ligand dissociation to generate a 14e intermediate.

## Introduction

The activation of carbon–hydrogen bonds by transition-metal complexes is an area of widespread current research which has led to the characterization of several stable aryl and alkyl hydride complexes.[1] However, cleavage of the carbon–hydrogen bond and formation of a metal–carbon bond comprise only the first of a sequence of steps leading to the production of derivatized hydrocarbons. While there now exist a number of examples of C–H bond oxidative addition to metal centers, functionalization of the C–H bond is still a relatively rare phenomenon.[2–4]

In a previous study,[5] we reported the preparation and characterization of the complex $IrH_3(CO)(dppe)$ (1, dppe = 1,2-bis(diphenylphosphino)ethane) including its reactivity with $D_2$ and CO to give $IrD_3(CO)(dppe)$ and $IrH(CO)_2(dppe)$ (2), respectively, as shown in eq 1. While

these exchange reactions were found to occur either thermally or photochemically, the trihydride 1 was seen to catalyze an exchange between $D_2$ and benzene *only* upon photolysis. A photochemical C–H activation step (eq 2),

$$IrH_3(CO)(dppe) \xrightarrow[h\nu]{\Delta} [IrH(CO)(dppe)] \xrightarrow[h\nu]{Ph–H} [IrH_2Ph(CO)(dppe)] \quad (2)$$

was proposed to account for this since no H/D exchange involving benzene was seen to occur thermally. In further probing the photochemical behavior of 1, we discovered that irradiation of a benzene solution of $IrH_3(CO)(dppe)$ under CO produced a small amount of benzaldehyde. Thus a system was found which not only activated arene C–H bonds but also inserted CO to give a functionalized product.

In these experiments, the amount of benzaldehyde produced was always small, which is consistent with thermodynamic considerations. The carbonylation of benzene (eq 3) is unfavorable, with a calculated value of $\Delta G° = +1.7$ kcal/mol.[6] In fact, it is usually the thermodynamically favorable decarbonylation reaction which is studied in terms of catalysis.[7]

The mechanism proposed by us for benzene carbonylation invoked the four-coordinate complex $IrH(CO)(dppe)$ (3) as the photochemically active species, based on the observation that carbonylation only occurs photochemically while loss of $H_2$ from the trihydride 1 can occur thermally. In this mechanism, light was thought to cause ligand dissociation (eq 4) to form a 14e intermediate which would allow coordination of benzene. After subsequent activation of the arene C–H bond by oxidative addition, CO insertion was thought to occur, followed by reductive elimination of benzaldehyde.

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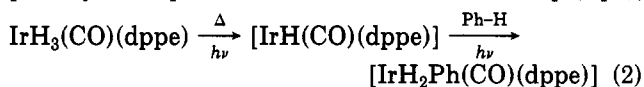
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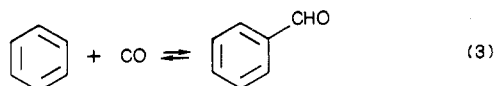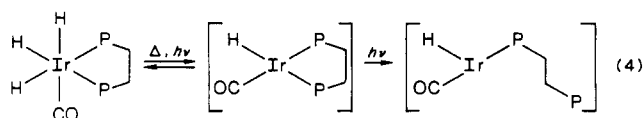
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The present study, part of which has appeared in preliminary form,[8] was undertaken to provide mechanistic insight into the carbonylation of benzene, to examine the effectiveness of related complexes in promoting this functionalization, and to probe the thermodynamic limitations of the carbonylation reaction. During the course of this work, we have found that a variety of $d^8$ square-planar complexes of Rh(I) and Ir(I) containing only the monodentate phosphine ligand PPh$_3$ promote arene carbonylation photochemically.[8]
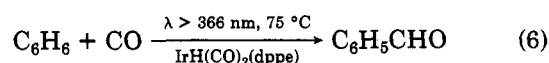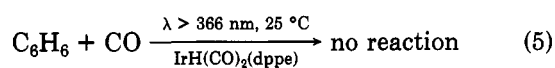
Recently, Tanaka has reported using the closely related complex RhCl(CO)(PMe$_3$)$_2$ to achieve photochemically promoted carbonylation of benzene with similar turnover numbers.[9] His claim of substantially greater reactivity, however, may be exaggerated. For example, Tanaka reported the yield of benzaldehyde under 1 atm of CO as 5729%/Rh, which corresponds to 57 turnovers, while our previous results, which showed that benzene carbonylation was thermodynamically limited, yielded 2 turnovers.[8] However, the lower turnover number we obtained relative to Tanaka's can be attributed in part to a difference in the Rh catalyst concentration which does not affect the position of the equilibrium. Tanaka's system also yields benzyl alcohol as a secondary product in accord with our earlier observations.[5] The most exciting and notable feature of Tanaka's work is an extension of the photochemically promoted functionalization to alkane substrates including n-pentane and cyclohexane.[9b]

In another study from our laboratory, photochemically promoted carbonylation using Ru complexes has recently been described.[10]

## Results and Discussion

The starting point for the present study derives from the mechanistic proposal made previously in the report on benzene carbonylation using either IrH$_3$(CO)(dppe) (1) or IrH(CO)$_2$(dppe) (2) as the photocatalyst complex.[5] These coordinatively saturated complexes undergo the exchange reaction shown as eq 1 thermally or photochemically, presumably through the intermediacy of the four-coordinate species IrH(CO)(dppe) (3). Since benzene carbonylation was only observed upon photolysis, it was proposed that 3 was the photochemically active species for the system. A test of this proposal was performed on the basis of the assumption that 3, as a four-coordinate, 16e species, would be yellow or orange and therefore absorb light at longer wavelengths than the two precursor complexes 1 and 2.

Two samples containing 6 mM solutions of IrH(CO)$_2$-(dppe) (2) in benzene under 600 torr of CO were photolyzed through a 366-nm cutoff filter. Under these conditions, 2 is the only complex in solution observable by $^1$H NMR spectroscopy, but it exhibits no significant absorptions at λ greater than 320 nm. The first sample, which was maintained at room temperature, showed no benzaldehyde formation after 48 h of photolysis (eq 5). The second sample was heated during photolysis to 75 °C at which temperature dissociation of CO from 2 is known to

$$C_6H_6 + CO \xrightarrow[\text{IrH(CO)}_2\text{(dppe)}]{\lambda > 366 \text{ nm, 25 °C}} \text{no reaction} \qquad (5)$$

$$C_6H_6 + CO \xrightarrow[\text{IrH(CO)}_2\text{(dppe)}]{\lambda > 366 \text{ nm, 75 °C}} C_6H_5CHO \qquad (6)$$

**Table I. PhCHO Formation for (Diphosphine)iridium Complexes**

| complex | [M], mM | $P_{CO}$, mm | time, h | [PhCHO], mM |
|---|---|---|---|---|
| IrH(CO)$_2$(dppp) | 4.5 | 670 | 22 | 5.1 |
| IrH(CO)$_2$(dppe) | 4.0 | 670 | 22 | 5.3 |
| IrBr(CO)(dppp) | 4.0 | 600 | 13 | 0.55 |
| IrBr(CO)(dppe) | 4.0 | 600 | 12 | 0.60 |
| IrH$_3$(CO)(dppp) | 3.6 | 680 | 24 | 4.8 |
| IrH$_3$(CO)(dppe) | 3.5 | 680 | 25 | 4.7 |
| IrH$_3$(CO)(dppe) | 3.5 | 420 | 25 | 3.9 |

occur.[5] After 6 h of photolysis, the second sample was analyzed by gas chromatography and found to contain 1.1 × 10$^{-3}$ mmol (1.8 mM) of benzaldehyde (eq 6). This result provides strong support that 3 is the photochemically active species in the previously reported benzene carbonylation system.[5]

The complex IrBr(CO)(dppe) (4) is a reasonable model for 3 and was also found to be effective in promoting the photochemical carbonylation of benzene. Complex 4 under CO exists in equilibrium with the dicarbonyl species IrBr(CO)$_2$(dppe) (eq 7) as evidenced by the change in color from orange to pale yellow and two $\nu_{CO}$ at 2040 and 1940 cm$^{-1}$.[11] After irradiation of a 6.0 mM benzene solution of 4 under 600 mm of CO for 12 h, benzaldehyde is detected by both gas chromatography and $^1$H NMR spectroscopy.

$$\text{IrBr(CO)(dppe)} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \text{IrBr(CO)}_2\text{(dppe)} \qquad (7)$$
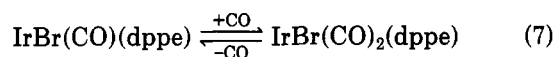
**Variation of the Phosphine Ligands.** A test for the photochemically induced phosphine dissociation step shown in eq 4 involved varying the length of the diphosphine ligand, thereby changing the chelate ring size and the proximity of the proposed dangling end of the diphosphine ligand from the metal center. This test was carried out in one case by using the chelating ligand dppp (1,3-bis(diphenylphosphino)propane) in place of dppe to prepare the complexes IrH$_3$(CO)(dppp) (5), IrH(CO)$_2$-(dppp) (6), and IrBr(CO)(dppp) (7) by procedures analogous to those published.[5,11] These dppp complexes were found to undergo the same thermal and photochemical exchange reactions with CO and H$_2$ as their dppe analogues.

Side-by-side experiments involving analogous Ir(dppe) and Ir(dppp) complexes under the same CO pressure were carried out in a carousel apparatus so the reactions could be compared directly. Experimental conditions and quantification of benzaldehyde are given in Table I. Little difference in the extent or rate of carbonylation is observed between the dppe and dppp complexes. While the similar reactivity found for these pairs of complexes does not support our working hypothesis of photopromoted phosphine dissociation, it is possible that the addition of only one carbon to the chelate ring is not enough of a change to lead to an observable difference in rates. Unfortunately, attempts to prepare monomeric complexes with the larger dppb ligand (dppb = 1,4-bis(diphenylphosphino)butane) were unsuccessful.[12]

The observation that benzene carbonylation could occur under photochemical conditions with four-coordinate complexes of the general formula MX(CO)P$_2$ (X = H, Br) prompted us to consider whether a bidentate phosphine or even a cis disposition of phosphine ligands was necessary for the carbonylation chemistry. In this regard, we have

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**Table II. Benzaldehyde Formation for Complexes Containing Triphenylphosphine**

| complex | [M], mM | $P_{CO}$,[a] mm | time, h | [PhCHO], mM |
|---|---|---|---|---|
| RhCl(CO)(PPh$_3$)$_2$ | 7.2 | 150 | 40 | 15.0 |
| IrCl(CO)(PPh$_3$)$_2$ | 6.4 | 150 | 40 | 0.25 |
| RhH(CO)(PPh$_3$)$_3$ | 6.4 | 150 | 40 | 0.20 |

[a] This value corresponds to the pressure above a frozen solution maintained at 77 K and is therefore less than the actual value at 298 K.

**Table III. Benzaldehyde Formation vs Time as Function of CO Pressure[a]**

| time, h | concn of benzaldehyde, mM | | |
|---|---|---|---|
| | $P_{CO}$ = 30 mm | $P_{CO}$ = 60 mm | $P_{CO}$ = 600 mm |
| 1.00 | 0.90 | | |
| 1.75 | 1.38 | 0.60 | |
| 4.00 | 2.04 | 1.26 | 0.90 |
| 6.00 | 2.48 | 2.10 | 1.30 |
| 7.00 | 2.71 | 2.40 | 1.64 |
| 8.00 | 2.76 | 2.82 | 1.72 |
| 8.75 | 2.78 | 3.16 | 1.90 |
| 9.75 | 2.82 | 3.40 | 2.34 |
| 11.00 | 2.88 | 3.60 | 2.60 |
| 13.00 | 3.04 | 3.70 | 2.91 |
| 15.00 | 3.02 | 3.89 | 3.24 |
| 21.00 | | | 5.00 |

[a] All samples were prepared identically with 7.2 mM RhCl-(CO)(PPh$_3$)$_2$ as catalyst and photolyzed simultaneously in a carousel apparatus.

found that the square-planar complexes RhCl(CO)(PPh$_3$)$_2$ (8) and IrCl(CO)(PPh$_3$)$_2$ (9) and Wilkinson's hydroformylation catalyst RhH(CO)(PPh$_3$)$_3$ (10) also promote benzaldehyde formation upon long-term irradiation in benzene under CO.[8] Experimental conditions and quantification of benzaldehyde are given in Table II.

The low activity of the Ir complex 9 relative to its rhodium analogue 8 toward the promotion of PhCHO formation under the same CO pressure can be rationalized in terms of the relative propensity of these complexes to form five-coordinate carbonyl adducts. When each iridium diphosphine complex IrBr(CO)(P⌢P) is placed under CO, there is a distinct lightening in the solution color, and two carbonyl stretches are observed in the IR spectrum indicating the occurrence of eq 7. The bis(phosphine) 9 behaves similarly (eq 8) and exhibits two carbonyl stretches

$$MCl(CO)(PPh_3)_2 + CO \rightleftharpoons MCl(CO)_2(PPh_3)_2 \quad (8)$$
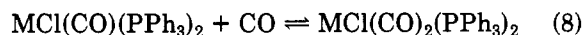
at 1959 and 1918 cm$^{-1}$ when placed under CO. When the rhodium complex 8 is placed under CO, no color change is observed, and there remains only one infrared carbonyl stretch at 1962 cm$^{-1}$. While the documented CO exchange reactions of 8 implicate a dicarbonyl adduct, the equilibrium in eq 8 for M = Rh lies far in the direction of the starting monocarbonyl complex. The relative inefficiency of the Ir system 9 may thus lie in the notion that it requires at least two photons for carbonylation to occur, one to dissociate CO and one to dissociate a ligand, whereas the rhodium system requires only one photon.

**The Effect of CO Pressure on the Rate of Carbonylation.** There is a marked dependence of CO pressure on the rate of benzene carbonylation and on the total amount of benzaldehyde formed. Three samples were prepared employing the same concentration of RhCl-(CO)(PPh$_3$)$_2$, and each was placed under a different pressure of CO (30, 60, and 600 mm of CO). The three samples were irradiated together in a carousel arrangement. The data for these photolyses, which are shown in Table III and Figure 1, indicate that the initial rate of
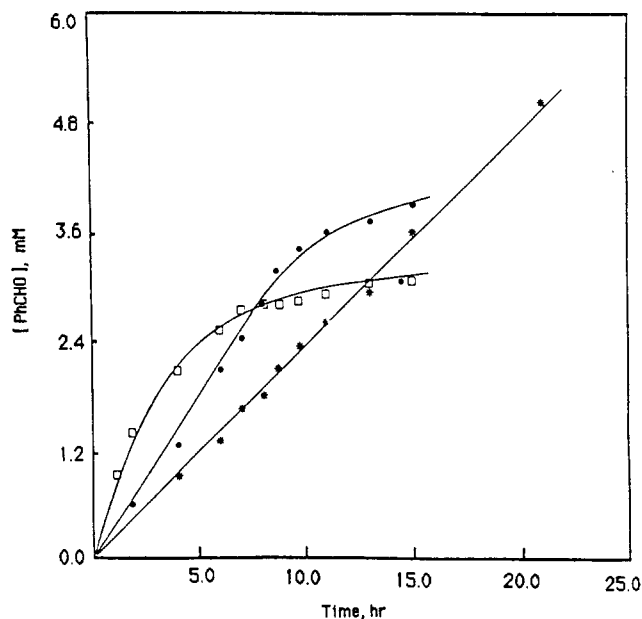


**Figure 1.** [PhCHO] vs time for different $P_{CO}$: □, 30 mm; ●, 60 mm; *, 600 mm.

formation of benzaldehyde is enhanced under lower CO pressure. However, the production of PhCHO levels off or reaches an apparent equilibrium, earlier under low CO pressure, limiting the overall amount of PhCHO formed. As the concentration of CO increases, the rate of PhCHO formation is slower, reaching equilibrium later with greater amounts of benzaldehyde produced. Thus the photochemically promoted carbonylation of benzene is favored kinetically at low concentrations of CO but leads to greater amounts of product under higher pressures of CO.

**Thermodynamic Considerations.** The data in Table III and Figure 1 suggest that an equilibrium is reached when the pressure of added CO is low. We have therefore demonstrated that the low yields of benzaldehyde produced in the carbonylation experiments (Table I and II) are the result of thermodynamic limitations of the reaction and not kinetic inactivity of the system. With RhCl-(CO)(PPh$_3$)$_2$ as the catalyst, we see that the complex remains intact through at least 60 h of photolysis, as determined by $^{31}$P NMR spectroscopy. After equilibrium is reached, the Rh(I) complex continues to promote carbonylation and decarbonylation. For example, when a 7.2 mM benzene solution of 8 containing 20 μmol of PhCHO under 150 mm of CO is photolyzed for 24 h, $^1$H NMR and GC analyses reveal only a slight decrease in the amount of benzaldehyde to 12 μmol and an increase in the amount of benzene present.

To show that the low yields of benzaldehyde produced in the carbonylation experiments with 8 were the result of thermodynamic limitations of the reaction, an experiment involving $^{13}$CO incorporation into benzaldehyde was carried out. A benzene-$d_6$ solution of 8 containing 5 equiv of PhCHO (36 mM) was placed under 1.2 atm of $^{13}$CO and irradiated at 22 °C through a Pyrex filter. The aldehyde resonance in the $^1$H NMR spectrum ($\delta$ 9.63 ($J_{C-H}$ = 173 Hz)) was monitored and revealed significant incorporation of $^{13}$CO into benzaldehyde (eq 9). Figure 2 shows the $^{13}$C

$$PhCHO \xrightarrow[h\nu]{^{13}CO} Ph^{13}CHO \quad (9)$$
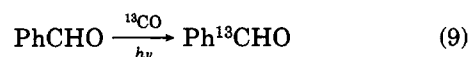
satellites of the aldehyde proton increasing in intensity over 10 days. During this period, the PhCHO concentration decreased from 5 to 2.9 equiv and an increase in the benzene $^1$H NMR resonance was observed. These obser-
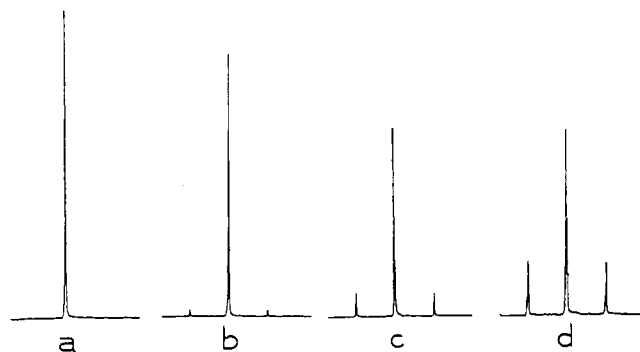
$$\text{PhCHO} \xrightarrow[\Delta]{^{13}\text{CO}} \text{PhCHO} \qquad (10)$$



**Figure 2.** Benzaldehyde proton resonance at $\delta$ 9.73 for RhCl-(CO)(PPh$_3$)$_2$ + $^{13}$CO + PhCHO in C$_6$D$_6$ showing incorporation of $^{13}$C isotope. $J(^{13}\text{C-H})$ = 173 Hz. Irradiation times are (a) $t$ = 0, (b) $t$ = 1 day, (c) $t$ = 5 days, and (d) $t$ = 10 days.
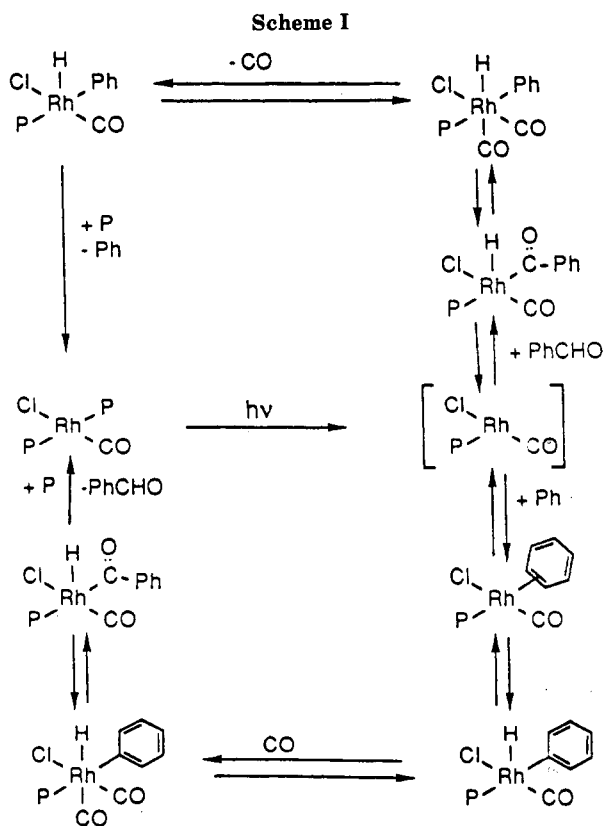
**Scheme I**



vations confirm the occurrence of carbonylation/decarbonylation sequences as shown in Scheme I. The photoactive step in the scheme is not unambiguously established and is discussed further below.

The extent of $^{13}$CO incorporation into PhCHO amounted to 38% over the 10-day period of the experiment. The rate of CO exchange reflects the rate of equilibration between $^{12}$CO, from both the metal complex and the original PhCHO, and $^{13}$CO, both in solution and in the gas phase. Since the partitioning of added $^{13}$CO between solution and gas phase according to Henry's law is achieved early in the experiment, the slow incorporation of $^{13}$CO into the aldehyde reflects the slowness of isotopic equilibration. The key feature of this experiment, however, is that there is continuous incorporation of $^{13}$CO into PhCHO, showing that the system is kinetically active.

A control experiment (eq 10) was performed to rule out thermal incorporation of $^{13}$CO into benzaldehyde since thermal decarbonylation of PhCHO of benzaldehyde is well-known.[7] A sample identical with the one described above (7.2 mM RhCl(CO)(PPh$_3$)$_2$ in benzene with 5 equiv
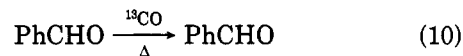
of PhCHO under 1.2 atm of $^{13}$CO) was prepared and heated at 110 °C for 5 days. $^1$H NMR analysis revealed a decrease in the aldehyde resonance and an increase in the benzene resonance, confirming that decarbonylation had occurred. However, there was no observable change in the $^{13}$C satellites of the aldehyde proton, indicating no $^{13}$CO incorporation into the aldehyde.

While the $^{13}$CO exchange experiments demonstrate the reversibility of photochemical carbonylation, they raise the question of whether the pathways leading to carbonylation and decarbonylation involve the same intermediate or if they arise from two independent photoreactions. Intimately related to this question is whether the carbonylation system is at thermal equilibrium or at a photostationary state. To test this, three identical samples were prepared (7.5 mM in 8, 12 mM PhCHO, and 1.0 atm of CO) and irradiated through a Pyrex filter for 3 days. One tube was opened, and GC analysis revealed that the PhCHO concentration had decreased to 10.5 mM. The other two samples were then placed at distances 4 and 16 cm from the light source, and each was irradiated for another day with no change in incident beam focusing. Analysis of these two samples showed each to be 10.1 mM in PhCHO, indicating that the systems had indeed reached thermal equilibrium. We therefore conclude that carbonylation and decarbonylation proceed through a common intermediate and result eventually in an equilibrium mixture of PhCHO, CO, and benzene.

**Mechanistic Considerations.** In order to account for the photochemical exchange of CO under photolysis, equivalence of $^{12}$CO and $^{13}$CO is required at some point in the catalysis. This may be achieved as free CO in solution or as two carbonyls on a metal complex intermediate. On the basis of the necessity of light to promote the catalysis, we propose that the pathways leading to carbonylation and decarbonylation involve the same initial step, loss of a ligand to generate a 14e intermediate. In flash experiments, Ford and Wink have demonstrated efficient photochemical dissociation of CO from RhCl-(CO)(PPh$_3$)$_2$ leading to two observable transients, RhCl-(PPh$_3$)$_2$ and the dimeric species [RhCl(PPh$_3$)$_2$]$_2$.[13,14] However, when these flash experiments are carried out under CO pressures up to 1 atm, another minor product is observed as a small transient bleaching which also decays back to RhCl(CO)(PPh$_3$)$_2$.[14] This minor transient could arise from a process which is much less efficient than CO photodissociation, or it could be assigned to one of the oxidative addition products shown in Scheme I. Since no net chemistry is observed in these flash photolysis experiments, the carbonylation of benzene achieved under long-term irradiation most likely occurs via a pathway which is relatively inefficient. We therefore suggest that PhCHO formation results either from a relatively inefficient thermal reaction of photogenerated RhCl(PPh$_3$)$_2$ with C$_6$D$_6$ leading to arene activation and carbonylation or from a second photochemical process which is much less efficient than CO photodissociation such as PPh$_3$ dissociation to generate RhCl(CO)(PPh$_3$).

The results for toluene and bromobenzene (vide infra) in which functionalization occurs mainly at the meta and para positions are consistent with $\eta^2$-arene coordination in the carbonylation scheme. The absence of ortho

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(14) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436.

functionalization is due to steric hindrance to $\eta^2$ binding. Jones and Feher have shown this feature of arene coordination in their elegant studies.[1k,n]

**Carbonylation of Other Arenes.** The photochemical carbonylation of arenes has been extended to toluene and bromobenzene as substrates. After 36 h of photolysis of a 6.0 mM solution of $RhCl(CO)(PPh_3)_2$ (8) in toluene under CO, three carbonylated products are obtained in a total concentration of 9.0 mM as determined by gas chromatography. The principle products are the meta- and para-substituted tolualdehydes, in a 2:1 ratio, confirmed by both GC and $^1H$ NMR analyses. The absence of o-tolualdehyde suggests that a steric interaction may prevent coordination near and activation at the ortho position. The third product arising from toluene activation (eq 11) is a



$$ (11) $$

$$ 2 \quad : \quad 1 \quad : \quad 0.03 $$
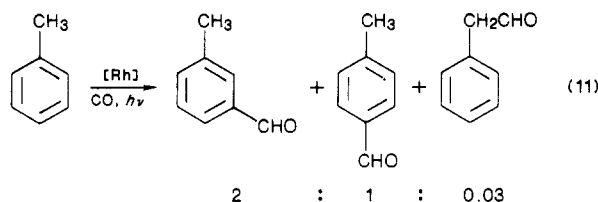
small amount (1% of the product distribution) of phenylacetaldehyde, resulting from activation of the methyl group of the substrate. Confirmation of the identity of each aldehyde product was made by gas chromatography through coinjection of the experimental sample with the authentic samples of the individual aldehydes. While phenylacetaldehyde demonstrates that benzylic C–H bond activation occurs in this system, it is clearly less favorable than arene activation.

The carbonylation of bromobenzene was achieved by irradiation of a solution of $RhCl(CO)(PPh_3)_2$ under CO in a 20/80 mixture of $C_6D_6/C_6H_5Br$. The reaction was monitored by $^1H$ NMR spectroscopy using a peak suppression program which allowed a clear examination of the aldehyde proton region (8.5–11.0 ppm). After 2 days of irradiation, two aldehyde proton resonances were observed which were due to m- and p-bromobenzaldehydes ($\delta$ 9.31 and 9.34, respectively). The resonance for o-bromobenzaldehyde, which comes farther downfield at 9.68 ppm, was not observed in this experiment. While quantification of the aldehydes was not possible by $^1H$ NMR integration, it is apparent that the carbonylated products are the m- and p-bromobenzaldehydes.

**Driving the Equilibrium Past Its Thermodynamic Limit.** The low yields of functionalized products obtained thus far have been accounted for by the unfavorable thermodynamics associated with eq 3. Results of the $^{13}CO$ incorporation experiment show that the system is kinetically active, exchanging $^{12}CO$ with $^{13}CO$, while the amount of benzaldehyde remains constant. In order to make the functionalization reaction catalytically useful, it is necessary to overcome the thermodynamic limitations of the system described. Attempts were made to drive the benzaldehyde equilibrium (eq 3) by funneling benzaldehyde into a second, favorable reaction. Efforts toward this end have focused primarily on the reduction of benzaldehyde to benzyl alcohol[18] (eq 12), which has a calculated value of $\Delta G_{298}° = -3.1$ kcal/mol.[12]



$$ (12) $$
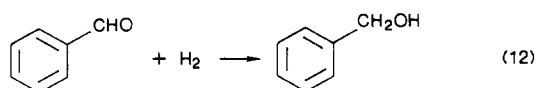
When $RhCl(CO)(PPh_3)_2$ was employed as the catalyst for both carbonylation and hydrogenation, the higher pressures of $H_2$ required for hydrogenation hinder the

carbonylation step. As described earlier, carbonylation is favored under lower CO pressures to facilitate ligand loss. Since hydrogen can also act as a ligand via oxidative addition, its presence may make ligand loss required for carbonylation more difficult. The best results were obtained when the ratio of $H_2$:CO was approximately 5:1. After 24 h of photolysis of a 6.1 mM solution of 8 under 500 mm of $H_2$ and 100 mm of CO, the concentrations of PhCHO and $PhCH_2OH$ were 4.8 and 3.1 mM, respectively, as determind by $^1H$ NMR and GC analyses.

An alternative approach involved using a two-catalyst system, one to promote carbonylation and the other to promote hydrogenation. For the latter, the ruthenium species $Ru(CO)_3(PPh_3)_2$ (11) was found to be an effective photochemical hydrogenation catalyst.[15] However, when the two complexes 8 and 11 were placed together in benzene under CO and $H_2$, the presence of $H_2$ still interfered with the carbonylation process. To overcome this, the two complexes were placed in a resealable NMR tube under 150 mm of CO and photolyzed for 24 h.[16] Carbon monoxide was then removed and replaced with 600 mm of $H_2$, and the sample was photolyzed for another 24 h. The gas atmosphere was sequentially replaced by 150 mm of CO and 600 mm of $H_2$, allowing for 24 h of photolysis under each gas. After three cycles (6 days), the concentrations of benzaldehyde and benzyl alcohol were 10.5 and 27.0 mM, respectively, amounting to approximately six turnovers.

## Conclusions

These studies have demonstrated new photochemical reaction chemistry for a class of $d^8$ transition-metal complexes involving the productive activation of arene C–H bonds in the conversion of benzene to benzaldehyde. In spite of the unfavorable thermodynamics associated with eq 3, the reaction is able to proceed under fairly mild conditions: a soluble metal catalyst at ambient temperature under low pressures of CO.

In probing the mechanism of carbonylation, a combination of known thermal chemistry and selective wavelength photolyses of several iridium di(phosphine) complexes revealed that the photoactive species is a four-coordinate 16e species, $IrX(CO)(P\frown P)$ (X = H, Br). The monodentate phosphine complexes $MCl(CO)(PPh_3)_2$ (M = Rh, Ir), which are electronically analogous to the photoactive species, exhibit similar photochemical activity leading to arene carbonylation.

The photochemical carbonylation of benzene has been shown to be reversible, and both carbonylation and decarbonylation are thought to involve the same initial photochemical step of ligand loss to generate a 14e intermediate. Labeling studies using $^{13}CO$ have demonstrated that arene carbonylation is limited by thermodynamics and, at least for $RhCl(CO)(PPh_3)_2$, not by kinetic inactivity of the catalyst system. The photochemical carbonylation of arenes has also been extended to toluene and bromobenzene. In each case the functionalized arene products are the meta- and para-substituted aldehydes.

## Experimental Section

**Materials.** Solvents were degassed by three freeze–pump–thaw cycles on a high vacuum line and were purified prior to use. Benzene solvents ($C_6H_6$ and $C_6D_6$) were distilled from dark purple solutions of sodium benzophenone ketyl under vacuum. Toluene was distilled from $CaH_2$ under vacuum. Bromobenzene was passed

(15) Gordon, E. M.; Eisenberg, R., unpublished results.

(16) Resealable 5-mm NMR tubes were purchased from Brunfeldt Company, PO Box 2066, Bartlesville, OK 74005.

through a column of alumina prior to refluxing with and distilling from sodium. CO and $H_2$ were both used as received, each from Air Products C.P., 99.3%. $^{13}CO$ was used as received from Monsanto Research Corp., Mound Facility.

Photolyses were carried out by using a 200-W MP Hg/Xe arc lamp with focusing lens from Oriel Corp. $^1H$ NMR spectra were recorded on a Bruker WH-400 spectrometer at 400.13 MHz, and gas chromatography was performed on a Hewlett-Packard 5730A gas chromatograph (FID) equipped with an HP 3380A automatic integrator.

**Preparation of Complexes.** The complexes $IrH_3(CO)(dppe)$,[5] $IrH(CO)_2(dppe)$,[5] and $IrBr(CO)(dppe)$[11] were prepared by procedures reported in the literature, and the dppp complexes $IrH_3(CO)(dppp)$, $IrH(CO)_2(dppp)$ and $IrBr(CO)(dppp)$ were prepared analogously.[5,11] The complexes $RhCl(CO)(PPh_3)_2$,[17] $IrCl(CO)(PPh_3)_2$,[18] and $RhH(CO)(PPh_3)_3$[19] were prepared by the published methods.

**General Procedure for Carbonylation Sample Preparation.** The metal complex is loaded into an NMR tube which is sealed onto a 14/20 ground glass joint adaptable to a high vacuum line. Benzene solvent is distilled into the NMR tube. The desired pressure of CO is added, and the tube is flame sealed. Alternatively, for several samples prepared at once, a stock solution of metal complex in benzene is prepared in the drybox, and 0.5 mL of the stock solution is added to each NMR tube. The desired pressure of CO is added on a high vacuum line, and the tubes are flame-sealed.

**Purification of Benzaldehyde.** For use in decarbonylation experiments, benzaldehyde was purified by washing with 10% $Na_2CO_3$ and then with $Na_2SO_3$ and water. After drying over $CaCl_2$, it was distilled under nitrogen at reduced pressure.

**General Procedure for Decarbonylation Sample Preparation.** The metal complex is loaded into an NMR tube which is sealed onto a 14/20 ground glass joint adaptable to a high vacuum line and which is equipped with a short, septum-capped side arm. Benzene solvent is distilled into the NMR tube, and

the desired pressure of CO is added. Benzaldehyde is then added by syringe through the side arm, and the tube is flame-sealed. For preparation of several samples at once, a stock solution of metal complex and benzaldehyde in benzene is prepared in the drybox, and 0.5 mL of this solution is added to each NMR tube. The desired pressure of CO is added on a high vacuum line, and the tubes are flame-sealed.

**Comparison of Experimental Samples.** For samples which were directly compared, photolyses were carried out simultaneously in a carousel to avoid uneven light flux.

**Identification of Products by Gas Chromatography.** Benzaldehyde, m- and p-tolualdehydes, phenylacetaldehyde, and benzyl alcohol were detected and quantified on a 10-ft column of 15% Apiezon L on Chromosorb W. Conditions for benzaldehyde and benzyl alcohol were as follows: oven, 150 °C; injector, 200 °C; FID detector, 200 °C; a He carrier gas flow, 30 mL/min. Retention times: benzene, 1.5 min; benzaldehyde, 4.5 min; benzyl alcohol, 6.2 min. Conditions for tolualdehydes were as follows: oven, 160 °C; injector, 200 °C; FID detector, 250 °C; He flow, 30 mL/min. Retention times: toluene, 2.1 min; m-tolualdehyde, 7.4 min; p-tolualdehyde, 7.9 min; phenylacetaldehyde, 5.9 min.

Solutions of each aldehyde and benzyl alcohol were prepared in concentrations of 0.25–25 mM, and a calibration curve ([aldehyde] vs area) for each was prepared. Experimental concentrations of aldehydes and benzyl alcohol were determined by comparison to these calibration curves.

(17) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

(18) Collman, J. P.; Sears, C. T.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

(19) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660.