

Time-Resolved Infrared Spectral Studies of Photochemically Induced Oxidative Addition of Benzene to *trans*-RhCl(CO)(PMe₃)₂

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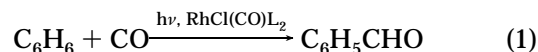
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Summary: Time-resolved infrared and time-resolved optical spectroscopy were used to examine the pathway(s) by which 355 nm photolysis of the rhodium(I) species *trans*-RhCl(CO)(PMe₃)₂ (**1**) in benzene leads to the C–H oxidative-addition product (Ph)(H)RhCl(CO)(PMe₃)₂ (**2**). Two reaction pathways to the formation of **2** were found. One of these was the “prompt” formation (<150 ns) of **2**, the apparent result of a direct reaction of the electronic excited state of the four-coordinate species **1** with the C₆H₆ solvent. The second route was more a convoluted stepwise process, involving CO photodissociation to give the “tricoordinate” intermediate RhCl(PMe₃)₂ followed by benzene oxidative addition then CO addition to give **2**.

Selective catalytic functionalization of hydrocarbons has long been a chemical “holy grail” of substantial economic importance.¹ The key step in any such scheme is the activation of C–H bonds which may be accomplished by free-radical hydrogen-atom abstraction and electrophilic attack or oxidative addition of a low-valent transition metal. Oxidative addition has the potential to provide the highest selectivity, although most examples of C–H activation by this route have not led to catalytic hydrocarbon functionalization. As a consequence, the several reports that Rh(I) complexes of the type *trans*-RhCl(CO)L₂ (where L = a trialkyl or triaryl phosphine R₃P) may serve as precursors to catalytic or photocatalytic species for the functionalization of various hydrocarbons have drawn considerable experimental^{2,3} and some theoretical interest.⁴ Described here are the results of laser flash photolysis studies using both time-resolved infrared (TRIR) and time-resolved optical (TRO) detection to probe the key

C–H activation step in the photocatalytic carbonylation of benzene by RhCl(CO)L₂ (eq 1).



Among the mechanisms proposed for this reaction, two pathways for the C–H activation step appear to be the most credible. One mechanism is the oxidative addition of a benzene C–H bond directly to an electronic excited state [RhCl(CO)L₂]* giving the hexacoordinate Rh(III) transient species in a single step (Scheme 1). Migratory insertion of CO into the resulting Rh–Ph bond followed by reductive elimination of the acyl hydride would give benzaldehyde. Although such excited states have been shown to be short lived (<~250 ps),⁵ this would not be a limitation to a bimolecular reaction since the substrate is the solvent.

The alternative mechanism involves initial photodissociation of CO to give the “tricoordinate” intermediate “RhClL₂” (**3**, Scheme 2). Evidence that such a species is considerably activated toward oxidative-addition reactions comes from the demonstration in this laboratory that H₂ addition to RhCl(PPh₃)₂ occurs ~5 orders of magnitude more rapidly than the analogous H₂ addition to RhCl(PPh₃)₃.⁶ Theoretical studies appear to confirm this point.⁴

Hexacoordinate complexes (Ph)(H)RhCl(CO)(PMe₃)₂ (**2**) have been identified by NMR spectroscopy³ to be stable intermediates formed by photolysis of low-temperature tetrahydrofuran/benzene solutions of *trans*-RhCl(CO)(PMe₃)₂ (**1**). However, it should be noted that both the single-step excited-state oxidative-addition pathway (Scheme 1) and the stepwise mechanism (Scheme 2) lead to the same product. The issue of which scheme is preminent can be addressed by flash photolysis studies of sufficient temporal resolution.

FTIR investigations of low temperature (–60 °C) solutions of **1** in THF/C₆H₆ (5/1 v/v) under conditions analogous to those used for the NMR studies described above demonstrated that photolysis with 355 nm light led to the disappearance of the ν_{CO} band of **1** at 1962 cm^{–1} and appearance of a strong band at 2070 cm^{–1}, which we attribute to the formation of **2**. (Note: No new absorptions were seen in the 2000–2150 cm^{–1} region of the spectrum when the low-*T* photolysis was carried out in neat THF.⁷) The NMR trapping studies

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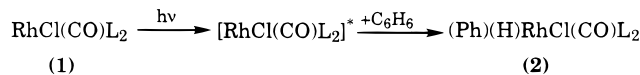
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Scheme 1



Scheme 2

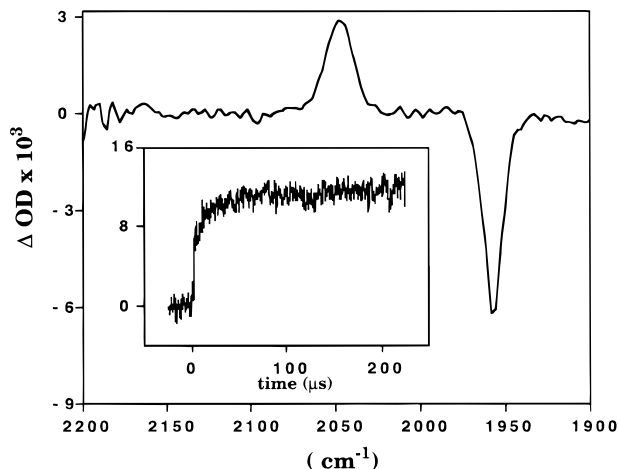
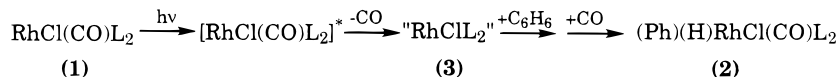


Figure 1. TRIR difference spectrum (recorded by the stepped-scan technique) in the ν_{CO} region of a C_6D_6 solution of *trans*- $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ subsequent (~ 0 – $100 \mu\text{s}$) to 355 nm flash photolysis. The negative peak represents depletion of **1**, while the positive peak represents formation of species attributed to **2**. *Inset:* Temporal IR absorbance change at 2070 cm^{-1} subsequent to 355 nm flash photolysis of a C_6H_6 solution of *trans*- $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, showing the prompt and delayed formation of ν_{CO} absorbance attributed to **2** in this medium (see text). The vertical scale on both the large figure and the inset is $\Delta\text{OD} \times 10^3$.

indicated two isomers of **2**; however, the FTIR spectra displayed only one broad band, which may be due to similar ν_{CO} frequencies for the isomers. Two other new bands, approximately one-fourth the intensity of that at 2070 cm^{-1} , appear at 2130 and 2188 cm^{-1} . These bands are consistent with Rh–H stretching frequencies reported for similar compounds.⁸ Consistent with this assignment is the absence of these bands when the photolysis was carried out in C_6D_6 . The ν_{CO} band appeared at lower frequency (2050 cm^{-1}), perhaps owing to the absence of Fermi coupling to another vibration of comparable frequency.

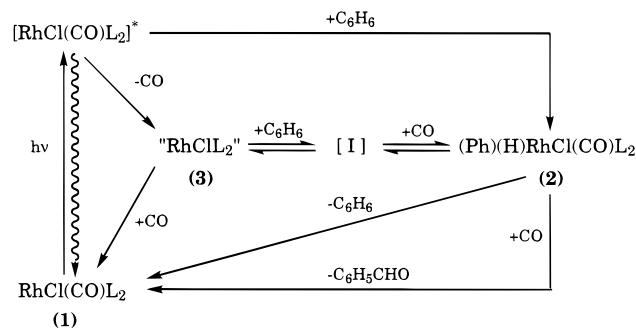
Figure 1 illustrates the result of laser flash photolysis (355 nm) of **1** in benzene- d_6 solution under Ar using a stepped-scan infrared spectrometer for TRIR detection.⁹ The transient difference spectrum displays a bleaching at 1962 cm^{-1} representing the loss of **1** and a new, broad absorbance at 2050 cm^{-1} corresponding to the formation of an intermediate. When temporal absorbance changes in the IR were examined using a tunable single-frequency probe source,¹⁰ formation of the transient shows

(7) It should be noted that after very long term photolysis of **1** in low temperature THF, previous workers did observe some photoproducts but the photolysis times used in those experiments were about 2 orders of magnitude longer than in the present experiments, suggesting that these photoreaction pathways are quite inefficient in THF.

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Scheme 3



a prompt rise (within the 150 ns rise time of the system), consistent with direct reaction with the short-lived excited state as shown in Scheme 1 (Figure 1 inset). However, these data also indicate another process, a “delayed” rise of the absorbance attributed to **2**, which could be fit to a first-order rate law with $k_{\text{obs}} = (8.3 \pm 1) \times 10^4 \text{ s}^{-1}$. The analogous pathway in perprotio-benzene gave $k_{\text{obs}} = (1.0 \pm 0.1) \times 10^5 \text{ s}^{-1}$, indicating, at most, a small deuterium isotope effect ($k^{\text{H}}/k^{\text{D}} \approx 1.3 \pm 0.3$) as is often the case with oxidative-addition processes.¹¹ Under these conditions the ratio of the signals due to prompt and delayed formation of **2** was about 1.2.¹² However, when the analogous experiment was carried under 0.1 atm CO of ($7 \times 10^{-4} \text{ M}$), the temporal response of the absorbance at 2050 cm^{-1} changed; the prompt rise remained, but the slower, first-order rise was quenched.

These observations can be interpreted in terms of Scheme 3 which incorporates key features of both Schemes 1 and 2. Prompt formation of **2** via direct reaction with $[\text{RhCl}(\text{CO})\text{L}_2]^*$ should be independent of $[\text{CO}]$, while CO quenching of the slower stepwise pathway can be attributed to formation of the CO-dissociated intermediate **3**. This intermediate reacts competitively by benzene oxidative addition to give **2** and CO addition to regenerate **1**. Under argon, the first-order oxidative-addition pathway of **3** is quite competi-

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(12) The first-order nature of the slow rise suggests that the rate-limiting step for the formation of complex **2** is the oxidative-addition step and not the second-order reaction of intermediate **I** with carbon monoxide. The quantum yield for the loss of CO was reported to be 0.1 in cyclohexane. By comparing the amount of complex **2** formed via the prompt process versus the stepwise process and assuming the same quantum yield for CO loss in benzene, an upper limit of 0.12 can be placed on the quantum yield for the production of complex **2** via the prompt process. The mixed-order kinetics reinforces that the quantum yield of 0.12 for the formation of complex **2** via the prompt process is an upper limit.

tive with second-order recombination with the labilized CO, but at excess CO concentrations as low as 7×10^{-4} M CO, the latter pathway apparently dominates. The features of Scheme 3 are also evident when a benzene solution of **1** (0.5 mM) was subjected to flash-photolysis excitation (355 nm) using TRO detection. The difference spectrum in the visible region shows a transient absorption from 400 to 550 nm with a λ_{max} at 430 nm. Under Ar, the decay of this peak could be fitted equally well as a first-order decay or as a second-order decay, but under CO, the decay could be fit only to a first-order rate law. (Note: the spectrum did not fully decay to the base line within the TRO detection limits (~ 50 ms), even under higher [CO]). Longer-lived intermediate(s) consistent with the formation of **2** persisted, although comparisons of spectra before and after photolysis using a standard optical spectrometer indicated eventual decay to the base line. The k_{obs} values obtained for the decay of the first transient were found to be first order in [CO]; a plot of k_{obs} vs [CO] is a straight line with a slope (k_{CO}) of $(1.2 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and a non-zero intercept of $\sim 1.5 \times 10^5 \text{ s}^{-1}$.¹³

The observation of a non-zero intercept for this plot would be consistent with partitioning of intermediate **3** between the second-order trapping by CO to reform **1** and other CO-independent pathways, one being an oxidative-addition pathway to give **2**. However, the TRO technique is not as effective as TRIR detection in separating the various processes, owing to the similarity and overlap of the electronic spectra of reactants, products, and intermediates. As a consequence, the intercept (which is prone to sizable experimental uncertainty) is likely to reflect other pathways as well as benzene oxidative addition to give **2**.¹³

In summary, these data indicate that the alternative C–H activation steps described by Schemes 1 and 2 are

not mutually exclusive mechanisms. Under the appropriate conditions both are effective, but under conditions designed to favor hydrocarbon carbonylation (excess CO), the unsaturated species **3** would be trapped by CO at a rate sufficient to minimize its participation in C–H activation. Thus, another mechanism such as direct activation of the hydrocarbon by the four-coordinate excited state^{3b} must be responsible for the low-yield photocatalytic carbonylations of aromatic hydrocarbons reported. Nonetheless, in the absence of CO and other ligands with a high affinity for Rh(I), **3** is likely to play an important role in the activation of various C–H bonds. Studies describing the detailed kinetics of various intermediates of this type will be reported.¹⁴

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(13) This intercept was obtained for flash photolysis studies with a low concentration of **1** (0.1 mM). Higher values of the intercept (but the same value of the slope) were found when higher initial concentrations of **1** were used. This observation suggests that, under such conditions, trapping of the intermediate **3** by excess **1** to form dimers is a significant contributor to the CO-independent decay pathways sampled by the TRO experiment.

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