

Dynamics of reactive intermediates as probed by flash photolysis: the rhodium(I) complexes $\text{RhCl}(\text{CO})\text{L}_2$ [$\text{L} = \text{PPh}_3, \text{P}(p\text{-tolyl})_3, \text{or PMe}_3$]

Peter C. Ford^a, Thomas L. Netzel^b, Cris Tina Spillett^a and D. B. Pourreau^b

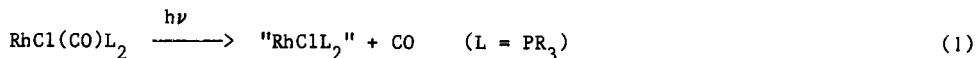
a. Chemistry Dept., University of California, Santa Barbara, CA 93106, USA

b. Amoco Technology Co., Amoco Research Center, Naperville, IL 60566, USA

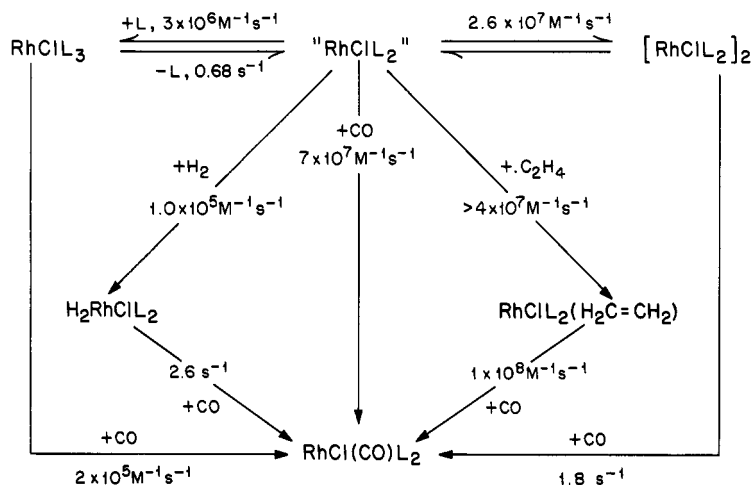
Abstract - Flash photolysis of the title compounds in each case leads to formation of a "tricoordinate" intermediate RhClL_2 (**A**) (more likely the solvated species RhClL_2S) which is capable of various competitive reactions with substrates in solution. Picosecond techniques indicate complexity even in the formation of this intermediate. Subsequent reactions of **A** are strongly dependent on the nature of L as well as of the medium. For $\text{L} = \text{PPh}_3$, rapid recapture of **A** by CO and competitive dimerization are the observable reactions regardless of solvent. However, for $\text{L} = \text{PMe}_3$, activation of solvent benzene and cyclohexane by reversible C-H oxidative addition appears predominant in the absence other substrates. The PTol_3 ($\text{Tol} = p\text{-tolyl}$) complex shows intermediate behavior by activating benzene but not cyclohexane.

INTRODUCTION

Several years ago we demonstrated (ref. 1) that photolysis of the rhodium(I) complex $\text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$ (**I**) results in CO dissociation to give a highly reactive "tricoordinate" intermediate **A** (eq. 1, $\text{L} = \text{PPh}_3$) (ref. 1). This conclusion was based on the kinetics behavior of **A**. Our interest in this system was based partially on the proposal of the same transient as an intermediate in alkene hydrogenation catalysis by $\text{RhCl}(\text{PPh}_3)_3$ ("Wilkinson's catalyst") (ref. 2). By using flash photolysis techniques, we succeeded in characterizing certain reaction kinetics of this intermediate as summarized in Scheme 1. Subsequently, it has been shown by several groups (ref. 3) that, under continuous photolysis, activation of hydrocarbon solvents (carbonylation and/or dehydrogenation) (e.g., eq. 2) occurs for various $\text{RhCl}(\text{CO})\text{L}_2$, apparently a result of RhClL_2 oxidative addition to solvent C-H bonds (ref. 4).



Summarized here are laser and conventional flash lamp kinetic flash photolysis studies of such complexes under various conditions relevant to photocatalytic hydrocarbon activation.

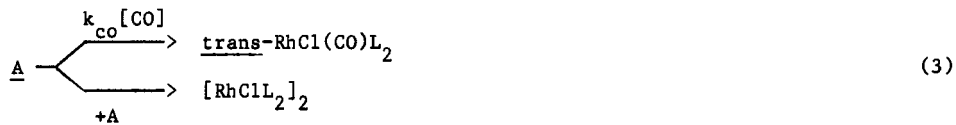


Scheme 1 Reactions of $\text{RhCl}(\text{PPh}_3)_2$ and other species formed subsequent to the flash photolysis of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$.

The present investigations are concerned with the reaction dynamics of photoinduced transients from the $\text{RhCl}(\text{CO})\text{L}_2$ systems in two overlapping time regimes. At the University of California, photolyses were carried out using a "conventional" xenon flash lamp apparatus with a dead-time about 25 μs and excitation wavelength selected by solution filters which pass a broad band of frequencies below a certain cutoff energy (ref. 1). Owing to the configuration of the photolysis cells (10 cm pathlength), reaction solutions were required to be dilute, an advantage in alkane solutions where solubilities are low. Experiments were carried out in benzene, tetrahydrofuran and cyclohexane solutions. At Amoco, transient absorption studies were carried out using the third harmonic of a Nd/YAG pulsed laser (355 nm) for excitation (ref. 5). The dead-time of this apparatus was about 30 ps. For these experiments, the high intensities of the excitation pulses required a flowing solution in a cell with a shorter pathlength (1 cm) and precluded the use of benzene, which displayed multiple photon solvent photochemistry.

COMPARISON OF THE FLASH (μs) PHOTOLYSIS BEHAVIOR FOR $\text{L} = \text{PMe}_3$ OR PTol_3

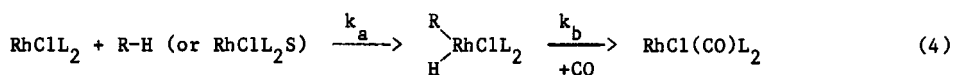
Flash lamp photolysis ($\lambda > 330$ nm) of trans- $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ (II) in deaerated benzene under argon led to formation within 25 μs of a transient A' with increased absorption in the spectral region 390-450 nm ($\Delta\text{Abs}(\text{max})$ at ~ 415 nm) similar to that of the transient A observed from the analogous treatment of trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (ref. 1)). However, unlike A, which under the same conditions decays via competitive second-order paths (eq. 3, $\text{L} = \text{PPh}_3$), A' decays exponentially (rate constant $k_a = 2.8 \pm 0.7 \times 10^3 \text{ s}^{-1}$, 23°C, ref 6) to a second transient B' with a lower absorbance than II in the same spectral region ($\Delta\text{Abs}(\text{max})$ at ~ 400 nm). Subsequently, the bleached transient B' underwent slower, first order decay ($k_b = 0.038 \pm 0.006 \text{ s}^{-1}$) to give the initial spectrum of II. Under the same conditions, analogous temporal spectral changes were observed for the flash photolysis of trans- $\text{RhCl}(\text{CO})(\text{PTol}_3)_2$ (III) in benzene. However, the initially formed absorbing intermediate A'' ($\Delta\text{Abs}(\text{max})$ at ~ 425 nm) decayed to the bleached intermediate B'' ($\Delta\text{Abs}(\text{max})$ at ~ 400 nm) with a rate constant k_a an order of magnitude smaller than that for the trimethyl phosphine species while k_b for the subsequent decay of B'' was two orders of magnitude larger.



However, the behaviors of II and III differed markedly from one another when each was flashed in deaerated cyclohexane. For II sequential formation of absorbing and bleached transients with spectral changes and rates similar to those observed in benzene was again seen. In contrast, the behaviour of III in cyclohexane was parallel to that described above for I in benzene, i.e., A'' decayed by second order kinetics to give a new long-lived, transient C which is absorbing, not bleached relative to III over the range 400 - 500 nm. The spectral and reactivity properties of this species, which undergoes slow first order decay to regenerate III, are consistent with those of a dimer such as that indicated in eq. 3. The flash photolysis of III in THF solution was similar to that seen in cyclohexane, i.e. the absorbing transient A'' ($\Delta\text{Abs}(\text{max})$ at 440-450 nm) decayed to give the apparent dimer.

The similarity of spectral properties of the absorbing transients A' and A'' to those of A suggest that the μs flash photolysis of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ and $\text{RhCl}(\text{CO})(\text{PTol}_3)_2$ in each case results in CO dissociation (eq. 1) as previously noted for I. This view is reinforced by the observation that when II was flashed in benzene under 1% CO (the balance being argon), the disappearance of A' was markedly accelerated, but the concentration of B' formed was only about 35% that seen in the absence of CO. In contrast, the decay rate of B' back to II was unaffected. Similarly, for III in benzene, added CO accelerated the disappearance of A'' and suppressed formation of B''. In contrast, adding comparable concentrations of PTol_3 had little effect. Although the intermediate A was referred to as "tricoordinate" above, it is probable, especially in the context of recent experimental studies demonstrating significant solvation of unsaturated metal carbonyls such as $\text{Cr}(\text{CO})_5$ by alkanes and other solvents (ref. 7), that the absorbing transients A, A' and A'' are better formulated as having the composition $\text{RhCl}(\text{PR}_3)_2\text{S}$. The modest solvent dependent shifts in the $\Delta\text{Abs}(\text{max})$ of the difference spectra of A and A'' would be consistent with this view.

The spectral properties of the bleached transients B' and B'' are similar to those of the dihydride $\text{H}_2\text{RhCl}(\text{PPh}_3)_2$ formed from the reaction of A with H_2 in benzene. Thus, the first order kinetics behavior for forming these transients suggest that in benzene the intermediates A' and A'' are both sufficiently reactive to undergo oxidative addition of benzene to form $\text{Rh}(\text{III})$ phenyl hydride species (eq. 4), logical intermediates in the observed photocatalytic functionalization of this solvent.



It is not surprising that, when L is the more basic phosphine PMe_3 , this type of reactivity extends to cyclohexane, but not when $\text{L} = \text{PTol}_3$. Notably, the different behaviors of $\underline{\text{A}}'$ in the two solvents supports the view that the intermediates $\underline{\text{B}}'$ and $\underline{\text{B}}''$ are formed from reactions with solvent rather than from intramolecular processes such as orthometalation of the phosphine ligands. It is perhaps less predictable that the relatively subtle differences between the properties of PTol_3 and PPh_3 would result in the dominant reaction for $\underline{\text{A}}'$ being C-H activation of benzene while such a process for $\underline{\text{A}}$ was not detectable in the flash experiment in the absence of added CO. (However, it should be noted that low efficiency benzene carbonylation is the result of long term continuous photolysis of $\underline{\text{I}}$ in benzene under CO (ref. 3)).

LASER (ps) FLASH PHOTOLYSIS STUDIES

Figure 1 displays the temporal absorbance changes monitored at 420 nm as the result of ps laser excitation (355 nm) of $\underline{\text{III}}$ in THF solution. Within the laser pulse, a strongly absorbing species $\underline{\text{Y}}'$ is immediately formed. This undergoes exponential decay with a lifetime ~ 560 ps to give a second, much longer lived transient, which is also absorbing relative to $\underline{\text{III}}$ at 420 nm. The difference spectrum of the second transient shown in Figure 2 is qualitatively the same as that determined for $\underline{\text{A}}'$ via the conventional flash photolysis studies in THF described above. The laser flash photolysis behavior of $\underline{\text{I}}$ in THF solution is closely analogous. The difference spectrum of the initial transient $\underline{\text{Y}}$ displays a significantly greater absorbance than the starting complex over the range 380 to > 550 nm with a $\Delta\text{Abs}(\text{max})$ at ~ 410 nm. This decays exponentially with a lifetime of ~ 260 ps to give a second absorbing transient with a lifetime and spectrum consistent with the formation of the transient $\underline{\text{A}}$, e.g., eq. 5.

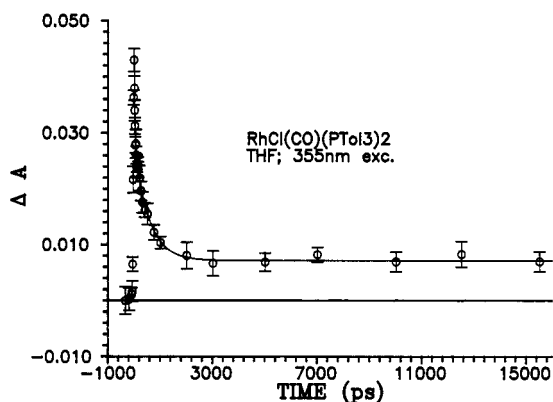
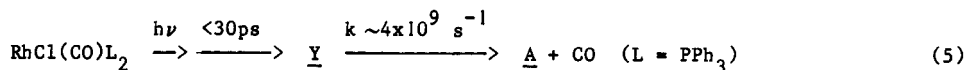


Figure 1: Temporal absorbance changes at 420 nm resulting from pulse laser excitation at 355 nm of $\text{trans-RhCl(CO)(PTol}_3)_2$ in THF.

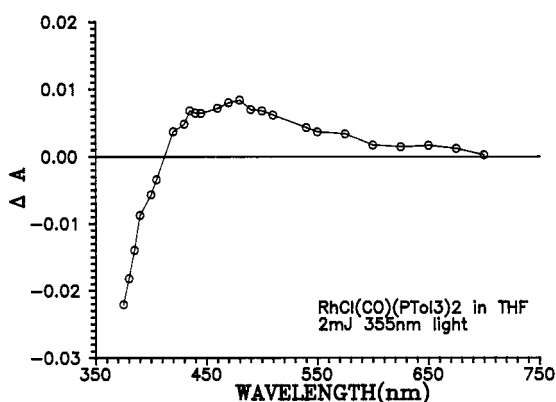


Figure 2: Difference spectrum (15.5 ns) for the longer lived transient observed in Figure 1.

One is tempted to attribute the species $\underline{\text{Y}}$ and $\underline{\text{Y}}'$ to the reactive excited states of $\underline{\text{I}}$ and $\underline{\text{III}}$, respectively, and the subsequent sub-nanosecond decays to the dissociation of CO to give $\underline{\text{A}}$ and $\underline{\text{A}}'$, respectively. Several Rh(I) tetracoordinate phosphine complexes are known to be luminescent in ambient temperature fluid solutions as are a number of metal carbonyl complexes (ref. 8). However, the present authors do not know of any cases where the lifetime has been measured for a reactive excited state for which the principal deactivation pathway is CO dissociation. It has been recently demonstrated that CO dissociation from excited Cr(CO)_6 may occur in < 1 ps, so that it is possible that $\underline{\text{Y}}$ and $\underline{\text{Y}}'$ are the actual "naked" tricoordinate RhClL_2 species and the decay processes seen involve coordination of solvent to these. Again the experience from the chemistry of Cr(CO)_5 (ref. 9) would suggest that formation of the solvated intermediate might occur at a faster rate, however, the systems are so different that it is not clear that the chromium carbonyl serves as a realistic model for either the excited state reactivity or the solvation kinetics.

Figure 3 displays traces for ps flash photolysis of II in THF. Clearly evident is that the absorbance changes enroute to A' follow a path more complicated than noted above for I and III. Excitation leads to the initial large absorbance increases characterizing the intermediate Y' (Figure 4), but, this decays rapidly ($\tau = 55$ ps) to another transient which further decays over some ns to a spectrum approximating that of A' described above. Numerical analysis of the absorbance vs time curves suggest that the latter process is not a simple exponential but may involve several steps. Multiphoton absorptions are a possibility; however, variation of pulse energies did not indicate nonlinear processes. The behavior in cyclohexane is no simpler (even another transient appears to be present), so these complexities cannot be attributed to the several potential coordination sites of THF (the O plus two different C-H's). We have no definitive explanation for the greater complexity of the sub-microsecond dynamics from the ps flash photolysis of II; although one speculative possibility is that the smaller PMe_3 allows formation of both cis and trans isomers for both the naked $\text{RhCl}(\text{PMe}_3)_2$ and its solvated analog thereby increasing the number of intermediates and dynamic processes.

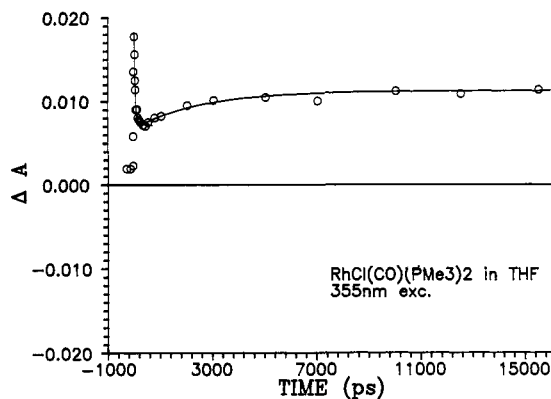


Figure 3: Temporal Absorbance Changes at 420 nm resulting from pulse laser excitation at 355 nm of trans- $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ in THF

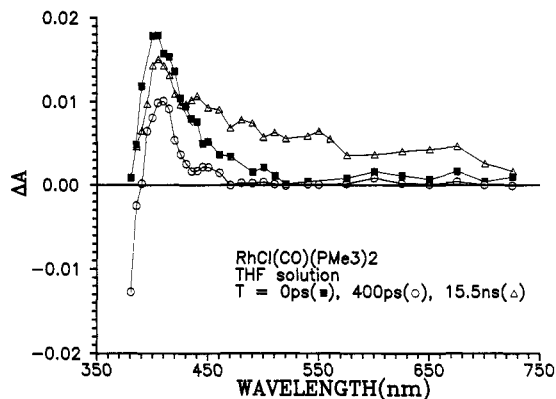


Figure 4: Difference spectra recorded of initial transient Y' (0 ps, squares) and at delays of 400 ps and 15.5 ns

SUMMARY

The flash photolysis of trans- $\text{RhCl}(\text{CO})\text{L}_2$ leads to CO loss to give RhClL_2 , or, more likely, the solvated species RhClL_2S . For $\text{L} = \text{PMe}_3$, this intermediate reacts with solvent cyclohexane or solvent benzene via C-H activation at rates sufficient to compete with second order dimerization or trapping by the CO generated by the flash. For $\text{L} = \text{PTol}_3$, similar, but slower, reversible C-H activation is also predominant in benzene but not in cyclohexane. Notably, PTol_3 is sufficiently more basic than PPh_3 for this pathway to be favored for III, but not for I, in benzene. Despite apparent differences in the sub- μs dynamics, ps studies show immediate formation of analogous short lived transients Y, Y' and Y'' which decay by "simple" or complicated pathways to A, A' and A'', respectively, the apparent key players in the photocatalytic activation of various hydrocarbons.

Acknowledgements Studies at UCSB were supported by a grant to PCF (DE-FG03-85ER13317) from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy and by a grant to R. G. Pearson from the ACS-PRF from which a fellowship to CTS was awarded.

REFERENCES

1. D. A. Wink, P. C. Ford, *J. Am. Chem. Soc.* **109**, 436-442 (1987)
2. J. Halpern, *Inorg. Chim. Acta* **50**, 11-19 (1981)
3. a) A. J. Kunin and R. Eisenberg, *J. Amer. Chem. Soc.* **108**, 535-536 (1986); b) T. Sakakura and M. Tanaka, *Chem. Let.* 249-252, 1113-1116 (1987); *JCS Chem. Comm.* 758-759 (1987); c) K. Nomura and Y. Saito, *JCS. Chem. Comm.* 161-162 (1988)
4. C. T. Spillett and P. C. Ford, *J. Am. Chem. Soc.*, **111**, 1932-1933 (1989)
5. T. L. Netzel, to be published
6. In ref. 4, a k value about twice this was reported. The difference may be attributed to a mathematical error in the original calculations.
7. G. K. Yang, V. Vaida and K. S. Peters, *Polyhedron* **7**, 1619-1622 (1988)
8. A. J. Lees, *Chem. Rev.* **87**, 711-743 (1987)
9. a) L. Wang, X. Zhu and K. G. Spears, *J. Phys. Chem.* **93**, 2-4 (1989)
b) A. G. Joly and K. A. Nelson, *J. Phys. Chem.*, **93**, 2876-2878 (1989)