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Reaction Dynamics of the "Tricoordinate" Intermediates $MCl(PPh_3)_2$ (M = Rh or Ir) as Probed by the Flash Photolysis of the Carbonyls $MCl(CO)(PPh_3)_2$[1]

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Abstract: Reported is a kinetics flash photolysis investigation of the rhodium(I) complex $RhCl(CO)(PPh_3)_2$ in benzene solution. These results are interpreted in terms of the transient formation of the unsaturated species $RhCl(PPh_3)_2$ (A), an intermediate crucial to proposed mechanisms of "Wilkinson's catalyst" reactions such as olefin hydrogenation, but which has not been the subject of previous direct investigation. Kinetics of the dimerization of A and of the reactions of this transient with CO, C_2H_4, PPh_3, and H_2 are also described. The second-order rate constant for the reaction with H_2 is 1.0×10^5 M^{-1} s^{-1} in good agreement with the value $>7 \times 10^4$ M^{-1} s^{-1} estimated by Halpern and Wong (*J. Chem. Soc., Chem. Commun.* **1973**, 629) from kinetics investigations of the hydrogenation of $RhCl(PPh_3)_3$. Furthermore, the equilibrium constant for triphenylphosphine dissociation from $RhCl(PPh_3)_3$ can be calculated as 2.3×10^{-7} M from the ratio of the first-order dissociation rate constant 0.68 s^{-1} determined by those workers and the second-order rate constant 3.0×10^6 M^{-1} s^{-1} for the back reaction determined here. Rates of the subsequent reactions of other adducts formed from A and various ligands with the CO liberated in the flash experiment were also determined. Flash photolysis studies of the iridium(I) analogue $IrCl(CO)(PPh_3)_2$ in benzene demonstrated CO photolabilization in this case as well. The back reaction of the resulting transient species $IrCl(PPh_3)_2$ with CO displayed second-order kinetics with the respective rate constant 2.7×10^8 M^{-1} s^{-1}. These results are discussed in terms of the catalytic mechanisms involving such species.

Investigations in this laboratory have long been concerned with the quantitative photochemistry of inorganic and organometallic complexes. Such investigations must address each of the sequential steps resulting from electronic excitation, i.e., the formation of initial electronic excited states, intersystem crossing/internal conversion to lower energy states, and the dynamics and mechanisms of reactions as well as nonradiative and radiative deactivation from the various states.[2] A key aspect of the photochemistry of metal complexes as well as of other substrates is that the initial product of an excited-state reaction may itself be a high-energy species. A major goal of modern applied photochemistry is to find ways of preserving such species for later use under controlled conditions, i.e., for energy storage. However, these initial products of excited-state reactions more often are very reactive themselves, existing only transiently under the reaction conditions and observable only by pulse photolysis techniques. In this laboratory, one interest in the chemistry of such transients is drawn from the fact that in many cases these are formulated as having compositions identical with species proposed as intermediates in thermal reactions, for example, homogeneous catalytic cycles. Thus, flash photolysis techniques provide an entry to the synthesis and the interrogation of such intermediates. The present article addresses the chemistry of the "tricoordinate" rhodium(I) species $RhCl(PPh_3)_2$ which has been often invoked[3-6] as a key intermediate in homogeneous catalysis cycles involving Wilkinson's catalyst $RhCl(PPh_3)_3$. Similarly addressed is the quantitative chemistry of the iridium(I) analogue $IrCl(PPh_3)_2$.

Experimental Procedures

Materials. Solvents were spectragrade benzene and methylene dichloride (Mallinckrodt) dried over $LiAlH_4$ and then distilled under N_2. Tetrahydrofuran (THF) was distilled from Na/benzophenone under N_2. The gases CO, H_2, D_2, C_2H_4, and Ar (all CP grade) were purchased from Linde. The argon was purified by passing successively through columns of BASF catalyst, molecular sieve, and CrO/silica gel.[7] The other gases were used without further purification.

The complexes $RhCl(CO)(PPh_3)_2$,[8] $RhCl(PPh_3)_3$,[3] $[RhCl(PPh_3)_2]_2$,[3] and $IrCl(CO)(PPh_3)_2$[8] were prepared by literature methods. With the exception of $RhCl(CO)(PPh_3)_2$, all complexes used in these studies are air sensitive in solution and had to be handled accordingly.

Flash Photolysis Procedures. Solutions for flash photolysis experiments were prepared by transferring the solvents via syringe to a vacuum manifold ($<10^{-4}$ Torr), where they were degassed by 4 freeze–thaw–pump cycles and then distilled from a Na/K amalgam to a preevacuated photolysis cell containing the solid complex. Agitation of the solutions under the appropriate gas ensured homogeneity. The photolysis cells (1 cm in diameter and 8 to 20 cm in length) were concentrically jacketted so that aqueous solutions of various compositions could be used as UV cutoff filters as well as IR filters. For an UV cutoff of 320 nm, a 0.1 M solution of $NaNO_3$ was used, while for an UV cutoff of 260 nm, a 0.1 M solution of $Na_2S_2O_3$ was employed. The flash photolysis apparatus was a modified Xenon Corp Model A micropulser system with a "dead time" due to flash lamp decay of about 20 μs. This system has been described previously.[9] Transmittance vs. time data were recorded on a Biomation Model 805 transient digitizer coupled to a Hewlett-Packard Model 86 computer for data analysis. All flash photolysis experiments were carried out at ambient temperature (23 ± 2 °C).

Stopped-Flow Kinetics Experiments. These were carried out on a Durham Model D110 stopped-flow kinetics spectrophotometer. Data were collected with use of the Biomation 805 transient digitizer and Hewlett-Packard 86 computer.[10] All stopped flow experiments were carried out at 25.0 °C. Solutions were prepared on the high-vacuum line as described above and transferred to the reservoir syringes of the stopped-flow spectrometer with care to avoid exposure to air.

Results

A. Flash Photolysis Investigation of $RhCl(CO)(PPh_3)_2$. When benzene solutions of $RhCl(CO)(PPh_3)_2$ ($5\text{-}20 \times 10^{-5}$ M) under argon were subjected to flash photolysis ($\lambda_{irr} > 315$ nm), a transient species A was observed which displayed a stronger absorption, relative to the starting complex, over the wavelength range 390–550 nm (Figure 1). When the temporal spectral changes were monitored at various wavelengths, the observed transient

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(1) Preliminary communications describing aspects of this work are as follows: (a) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1794–1796. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5566–5567.

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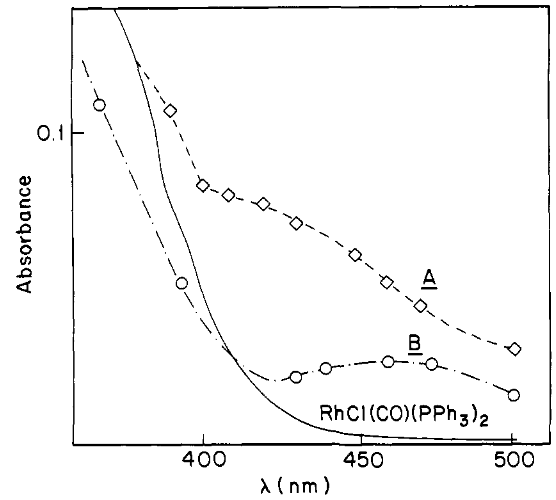

Figure 1. Transient absorption spectra resulting from the flash photolysis of $RhCl(CO)(PPh_3)_2$ in deaerated benzene solution. A: spectrum 100 μs after the flash. B: spectrum 10 ms after the flash.

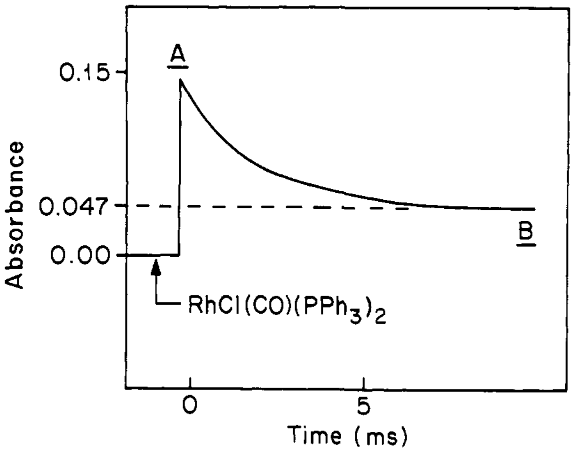

Figure 2. Temporal absorbance changes at 450 nm after the flash photolysis of $RhCl(CO)(PPh_3)_2$ ($\lambda_{irr} > 315$ nm) in deaerated benzene solution.

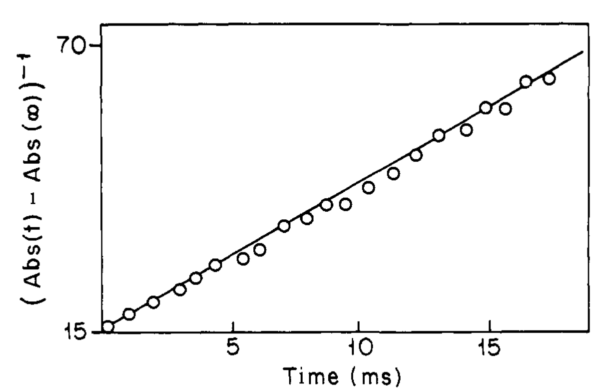

Figure 3. Second-order plot of the decay of transient A formed by the flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene ($\lambda_{mon} = 410$ nm).

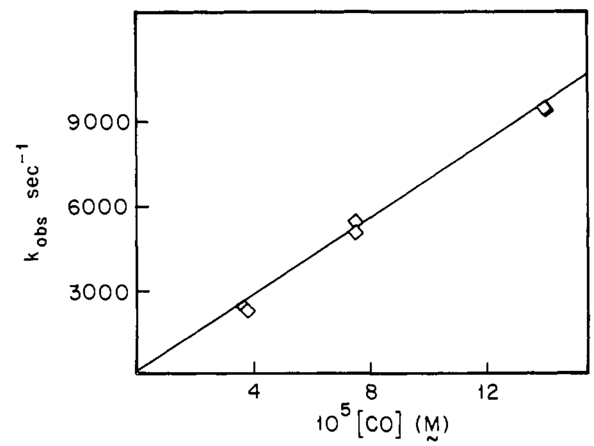

Figure 4. Plot of the first-order rate constant k_{obsd} vs. [CO] measured for the decay of transient A to $RhCl(CO)(PPh_3)_2$ under excess CO.

absorption decayed via second-order kinetics over a period of several milliseconds to give absorbances corresponding to the formation of a second species B (Figures 2 and 3). The spectral features of this second transient are also shown in Figure 1. Over a longer time frame (several seconds), B decayed back to the original base line via first-order kinetics. The overall reversibility of these processes is consistent with the previous report from continuous photolysis studies reporting that this system does not undergo any net photoreaction.[11]

Flash photolysis of similar solutions of $RhCl(CO)(PPh_3)_2$ under excess CO ($0.3-1.5 \times 10^{-4}$ M)[12] led to marked increases in the decay rate for A, and the formation of B was no longer observed. In this case, plots of ln $(A - A_\infty)$ vs. time were linear, indicating a first-order rate law. The k_{obsd} values derived from these plots proved to be directly proportional to [CO] (Figure 4), demonstrating that the rate law for this reaction is

$$d[A]/dt = k_3[A][CO] \qquad (1)$$

with $k_3 = (6.9 \pm 0.2) \times 10^7$ M^{-1} s^{-1}.

When the flash photolysis was carried out in the presence of 0.05 M PPh_3 instead, there was immediate formation of a new transient C, which displayed the same spectrum as does $RhCl(PPh_3)_3$.[13] These observations, plus the kinetics data for the reaction of A with CO, clearly indicate that the initial photoreaction resulting from flash photolysis is the dissociation of CO (eq 2) to give the "tricoordinate" intermediate $RhCl(PPh_3)_2$ noted above as often invoked as key to the reactions of Wilkinson's catalyst. Reaction of A with CO or PPh_3 gives $RhCl(CO)(PPh_3)_2$ or $RhCl(PPh_3)_3$, respectively.

$$RhCl(CO)(PPh_3)_2 \xrightarrow{h\nu} \underset{A}{RhCl(PPh_3)_2} + CO \qquad (2)$$

$$A + CO \xrightarrow{k_3} RhCl(CO)(PPh_3)_2 \qquad (3)$$

$$A + PPh_3 \xrightarrow{k_4} RhCl(PPh_3)_3 \qquad (4)$$

The transient C, formed when the flash photolysis was carried out with excess PPh_3, was also shown to undergo a second-order decay to reform $RhCl(CO)(PPh_3)_2$. This second-order reaction was found to be independent of the concentration of added PPh_3 and presumably reflects the consumption of $RhCl(PPh_3)_3$ by reaction with the stoichiometric concentration of photolabilized CO (eq 5). The second-order rate constant $k_5 = (2.0 \pm 0.4) \times 10^5$ M^{-1} s^{-1} was calculated on the basis of the differences in extinction coefficients of these two complexes at the monitoring wavelength (435 nm, $\Delta\epsilon = 900$ M^{-1} cm^{-1}). These conclusions were confirmed by examining the stopped-flow kinetics for the reaction of $RhCl(PPh_3)_3$ (1.0×10^{-4} M) with excess CO. For the two [CO] values 3.0×10^{-4} and 7.5×10^{-4} M, first-order rate constants of 50 ± 5 and 168 ± 8 s^{-1}, respectively, were measured. From these were calculated the value $k_5 = (1.95 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, in good agreement with that derived from the flash photolysis experiments.

$$RhCl(PPh_3)_3 + CO \xrightarrow{k_5} RhCl(CO)(PPh_3)_2 + PPh_3 \qquad (5)$$

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[11] Geoffroy, G. L.; Denton, D. A.; Keeney, M. E.; Bucks, R. R. *Inorg. Chem.* **1976**, *15*, 2382–2385.

[12] Braker, W.; Mossman, A. L. *The Matheson Unabridged Gas Databook: A Compilation of Physical and Thermodynamic Properties of Gases*; Matheson Gas Products: East Rutherford, NJ, 1974; Vol. 1, p 11. Concentrations of gases dissolved in the benzene solutions were calculated from the solubility data presented in this source: CO, 6.9×10^{-3} mol L^{-1} atm^{-1}; H_2, 2.8×10^{-3} mol L^{-1} atm^{-1}; C_2H_4, 0.14 mol L^{-1} atm^{-1} (25 °C).

[13] Geoffroy, G. L.; Keeney, M. E. *Inorg. Chem.* **1977**, *16*, 205–207.

The question remains regarding the nature of the second transient B. The spectrum of this longer lived transient is close to that of the known dimer $[RhCl(PPh_3)_2]_2$ described previously[13] and discussed in the mechanistic schemes for Wilkinson's catalyst.[6] The spectral differences are due to the fact that the transient spectrum after several milliseconds represents a mixture of the dimer plus $RhCl(CO)(PPh_3)_2$. Presumably, B is formed by the dimerization of $RhCl(PPh_3)_2$ (eq 6), in competition with trapping of A by CO and decays by reaction with CO to reform the carbonyl complex. The mechanism of the latter process apparently

$$2\,RhCl(PPh_3)_2 \xrightarrow{k_6} [RhCl(PPh_3)_2]_2 \qquad (6)$$

$$[RhCl(PPh_3)_2]_2 + 2\,CO \xrightarrow{k_7} 2\,RhCl(CO)(PPh_3)_2 \qquad (7)$$

involves a unimolecular rate-limiting step with a k_7 value of 1.8 ± 0.1 s^{-1} (monitored at 390 nm). The stopped-flow kinetics of the reaction between $[RhCl(PPh_3)_2]_2$, prepared thermally,[3] and CO (P_{CO} = 0.05 to 0.5 atm) to give $RhCl(CO)(PPh_3)_2$ also proved exponential with k_{obsd} values independent of [CO] and experimentally indistinguishable (1.7 ± 0.4 s^{-1} at 298 K) from the flash photolysis result.

The rate constant k_6 for the formation of the dimer B can be estimated from the percentage of this species actually formed when the flash photolysis of $RhCl(CO)(PPh_3)_2$ was carried out in the absence of other added ligands. Determining the extent of dimerization of A in the absence of added CO requires knowing the concentration of A formed in the flash, i.e., an estimate of the extinction coefficients of this transient at the wavelengths of observation. This was done by making the assumption that the experiment with a large excess of PPh_3 (0.05 M, above) trapped all A as $RhCl(PPh_3)_3$. From the known spectrum of the latter species,[13] the initial absorbance changes (Figure 2) and the assumption that the efficiency for the formation of A is independent of other reactants, the initial concentrations and the extinction coefficient for A (8×10^2 M^{-1} cm^{-1} at 410 nm) were determined. With these values, it was estimated that about 40% of A dimerized to give B in competition with the back reaction with photoliberated CO to give starting material. Given the value $k_3 = 6.9 \times 10^7$ M^{-1} s^{-1} for the latter reaction, the value $k_6 = (2.6 \pm 0.6) \times 10^7$ M^{-1} s^{-1} was estimated for the dimerization. (The earlier estimate[1a] of 5×10^7 M^{-1} s^{-1} was in error by a factor of 2 owing to our failure to take the stoichiometric factor into account.)

Careful examination of the flash photolysis ($\lambda_{irr} > 315$ nm) of $RhCl(CO)(PPh_3)_2$ in benzene under relatively high pressures of CO (0.1–1.0 atm, 0.0007–0.007 M) demonstrated that A and B are not the only transients which are formed. Under these conditions, where A would be consumed within the lifetime of the flash via reaction with CO, a small transient bleaching was observed over the spectral range 380–430 nm. This new transient D, which would be obscured in the presence of any significant concentration of A, decayed exponentially back to $RhCl(CO)(PPh_3)_2$ with a k_{obsd} of $1.3 \pm 0.1 \times 10^3$ s^{-1}. Both the spectral properties and the exponential decay rate of this apparently minor product proved to be independent of [CO] or $[PPh_3]$ under these conditions.[14]

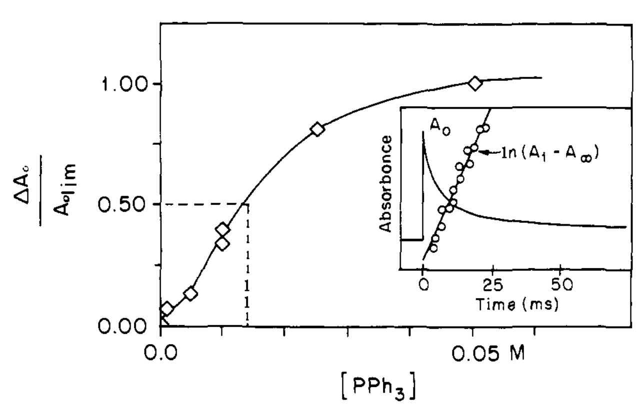

Figure 5. Plot of the change in initial absorbance (ratioed to the limiting value) vs. $[PPh_3]$ for the flash photolysis of $RhCl(CO)(PPh_3)_2$ in the presence of excess CO (0.0006 M) and various concentrations of PPh_3. Inset: The temporal absorbance changes at 440 nm resulting from the flash photolysis under these conditions. The initial absorbance change is denoted by A_0.

Solvent effects on the transient photochemistry of $RhCl(CO)(PPh_3)_2$ were briefly examined by carrying out the flash photolysis studies in rigorously deaerated methylene chloride and THF solution as well. In each case, a transient was observed to have spectral properties qualitatively the same as A (transient absorption over the spectral region 410–500 nm); however, in THF solution there was no appreciable formation of the dimer B. In THF, it was further demonstrated that flash photolysis in the presence of an excess of PPh_3 (0.003 M) led to the immediate formation of $RhCl(PPh_3)_3$ in agreement with presumed labilization CO as the primary photoreaction. With the assumption of identical extinction coefficients for reactants and transients in all three solvents, the rate constants for the second-order decay of A followed the order CH_2Cl_2 > benzene > THF with the relative values (normalized to benzene) 1.8:1.0:0.27. Although the above assumption is questionable from a quantitative standpoint, it is clear that A in THF is significantly less reactive than in the other two solvents.

Reaction of $RhCl(PPh_3)_2$ with PPh_3. As noted above, flash photolysis of $RhCl(CO)(PPh_3)_2$ (2×10^{-4} M) in the presence of a large excess of PPh_3 leads to the immediate appearance of absorbances which are attributed to the formation of $RhCl(PPh_3)_3$ followed by relatively slow reaction with CO to reform the starting complex. In order to assess the rate constant for the reaction between A and PPh_3, a competition method was employed. This entailed measuring the absorbance change $\Delta A°$ (at 440 nm) of such a solution with a fixed [CO] (6×10^{-4} M) but with $[PPh_3]$ varied over the range 0.001–0.05 M immediately subsequent to the flash. Under these conditions $RhCl(PPh_3)_2$ was completely consumed within the lifetime of the flash owing to the competitive capture by CO or PPh_3 (eq 2 and 3). Thus, $\Delta A°$ reflected the amount of $RhCl(PPh_3)_3$ formed under the reaction condition and approached a limiting value $\Delta A°_{lim}$ at high $[PPh_3]$ where all the $RhCl(PPh_3)_2$ formed was captured by the phosphine. With all other parameters held constant, the ratio $\Delta A°/\Delta A°_{lim}$ ranged from 0 at $[PPh_3]$ = 0.00 M to 1.0 (Figure 5). For $\Delta A°/\Delta A°_{lim} = 0.50$ (0.014 ± 0.002 M PPh_3), the relationship $k_2[CO] = k_3[PPh_3]$ must hold. From the data [CO] = 0.0006 M, $[PPh_3]$ = 0.014 ± 0.002 M, and $k_2 = 6.9 \times 10^7$ M^{-1} s^{-1}, the value $k_3 = (3.0 \pm 0.5) \times 10^6$ M^{-1} s^{-1} was calculated.

For each of these experiments, the initially formed $RhCl(PPh_3)_3$ reacted further with CO to regenerate $RhCl(CO)(PPh_3)_2$. Under these conditions (excess CO) the latter absorbance changes were exponential, and the k_{obsd} values (136 ± 15 s^{-1}) calculated from first-order rate plots were independent of $[PPh_3]$ over the 10-fold range investigated. Division of this k_{obsd} value by [CO] (0.0006 M) gives the value (2.27 ± 0.25) × 10^5 M^{-1} s^{-1} for k_5. This k_5 value agrees with the second-order rate constants derived from the flash photolysis and stopped-flow experiments noted above.

Reaction of $RhCl(PPh_3)_2$ with Dihydrogen. Flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene under H_2 (1.0 atm, 0.0028 M[12])

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(14) (a) These conditions parallel those used by Kunin and Eisenberg (ref 14b) who recently demonstrated that photolysis of $RhCl(CO)(PPh_3)_2$ in benzene under 1 atm P_{CO} leads to the reversible carbonylation of benzene, e.g.,

$$C_6H_6 + CO \xrightleftharpoons{h\nu,\ RhCl(CO)(PPh_3)_2} C_6H_5CHO$$

The transients seen here under 1 atm P_{CO} showed transient bleaching at longer wavelength suggestive of oxidative addition products. Conceivably, the initial excited state or a subsequent species undergoes some oxidative addition of benzene (or orthometallation) to form a species such as $HRhCl(C_6H_5)(CO)(PPh_3)_2$ as a minor intermediate observable only under conditions where the much more strongly absorbing $RhCl(PPh_3)_2$ transient is quickly trapped by CO. Such a Rh(III) species could decay via unimolecular reductive elimination of C_6H_6 or via migratory CO insertion into the Rh–C_6H_5 bond followed by elimination of benzaldehyde. At present, the limited experimental data as well as some ambiguity regarding the possible role of the dicarbonyl species $RhCl(CO)_2(PPh_3)_2$ under these conditions (ref 14c) leaves this interpretation in a rather speculative mode. (b) Kunin, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 535–536. (c) Sanger, A. R. *Can. J. Chem.* **1985**, *63*, 571–575.

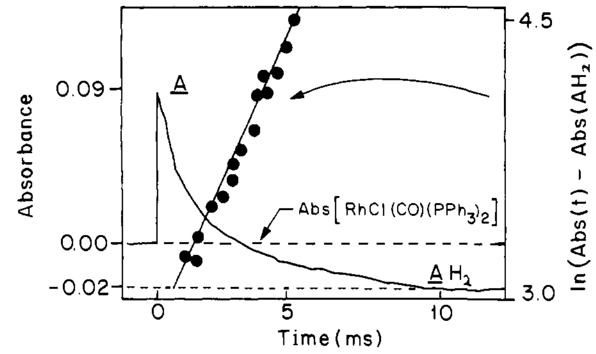

Figure 6. Curve: Temporal absorbance changes at 420 nm resulting from the flash photolysis of $RhCl(CO)(PPh_3)_2$ in H_2 saturated benzene. Line: First-order rate plot of these data.

led first to the absorbance changes characteristic of A formation followed by first-order decay ($k_{obsd} = 280 \pm 14\ s^{-1}$) to a new transient having absorbances smaller than those of the starting complex over the wavelength range 400–440 nm (Figure 6). The spectral properties of this bleached transient would be consistent with the formation of a rhodium(III) dihydride[15]

$$RhCl(PPh_3)_2 + H_2 \xrightarrow{k_8} H_2RhCl(PPh_3)_2 \qquad (8)$$

Similar transient behavior was observed when the flash photolysis was carried out on solutions equilibrated with a lower H_2 pressure (0.5 atm, 1.4×10^{-3} M); however, in this case, the kinetics of the relatively slow reaction with dihydrogen were affected somewhat by the competitive reaction of A with CO, so only an approximate k_{obsd} value of $135 \pm 40\ s^{-1}$ was obtained. Nonetheless, this lower k_{obsd} does indicate the second-order nature of the H_2 addition, i.e.

$$d[H_2RhCl(PPh_3)_2]/dt = k_8[RhCl(PPh_3)_2][H_2] \qquad (9)$$

From the experiment at $[H_2] = 0.0028$ M, a k_8 value of $(1.00 \pm 0.05) \times 10^5\ M^{-1}$ was calculated.

Flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene under D_2 (1.0 atm, 0.0028 M) gave similar transient behavior with a k_{obsd} value of $190 \pm 40\ s^{-1}$, giving a second-order rate constant of $(6.8 \pm 1.3) \times 10^4\ M^{-1}\ s^{-1}$. This value leads to a kinetic isotope effect k_8^h/k_8^d of 1.5.

The bleached transient formed from the reaction of A with dihydrogen reacted further over a longer time scale to reform $RhCl(CO)(PPh_3)_2$ via first-order kinetics. The rate constant for this decay ($2.6 \pm 0.3\ s^{-1}$) was independent of the concentration of dihydrogen and showed no deuterium isotope effect.

Reaction of $RhCl(PPh_3)_2$ with Alkenes. Flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene equilibrated with ethene (1.0 atm, 0.14 M)[3,12] resulted in the formation of a new transient with increased absorption over the range 400–500 nm (λ_{max} about 415 nm, $\Delta\epsilon_{max}$ $2.3 \times 10^3\ M^{-1}\ cm^{-1}$) and decreased absorption at 370–390 nm within the deadtime of the flash apparatus (20 μs). These spectral properties are consistent with formation of the known ethene complex $RhCl(C_2H_4)(PPh_3)_2$ (eq 10).[3] This transient decayed via second-order kinetics to regenerate the starting complex, presumably owing to the reaction of the ethylene adduct with CO (eq 11). Identical transient behavior was noted for the flash photolysis of $RhCl(CO)(PPh_3)_2$ under a reduced pressure of ethene (0.01 atm, 0.0014 M) with either argon or dihydrogen (0.99 atm, 0.0028 M) making up the difference.

$$RhCl(PPh_3)_2 + C_2H_4 \xrightarrow{k_{10}} RhCl(C_2H_4)(PPh_3)_2 \qquad (10)$$

$$RhCl(C_2H_4)(PPh_3)_2 + CO \xrightarrow{k_{11}} RhCl(CO)(PPh_3)_2 + C_2H_4 \qquad (11)$$

The immediate formation of the ethene complex (within 20 μs) at 0.0014 M C_2H_4 indicates that, if the reaction of A with ethene is second order as expected, the lower limit for k_{10} would be about $4 \times 10^7\ M^{-1}\ s^{-1}$. More remarkable is the apparent rate of reaction 11. Use of the extinction coefficient difference between $RhCl(C_2H_4)(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$ (above) and the slope of the second-order plot (Abs^{-1} vs. t) give a k_{11} value of $(1.0 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$. This kinetics behavior was checked by carrying out the flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene under both ethene (1.0 atm, 0.14 M) and CO (0.01 atm, 6×10^{-5} M). Under these conditions, the formation of $RhCl(C_2H_4)(PPh_3)_2$ was followed by exponential reformation of $RhCl(CO)(PPh_3)_2$ with a k_{obsd} value of $(6.0 \pm 0.1) \times 10^3\ s^{-1}$. Division of this value by [CO] gives $k_{11} = (1.0 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$ in agreement with the above result.

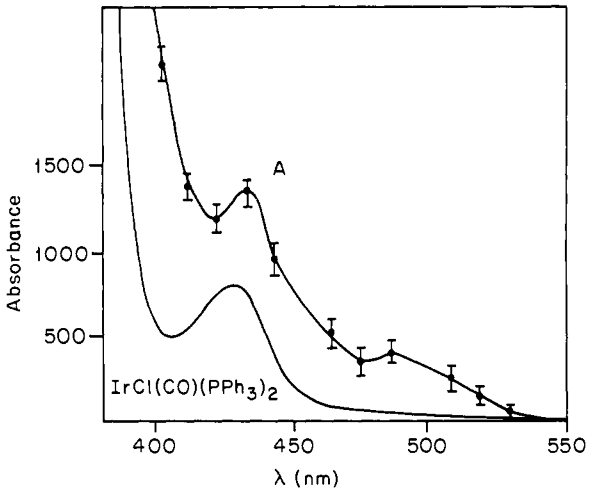

Figure 7. Transient absorption spectrum of the intermediate E formed as the result of the flash photolysis ($\lambda_{irr} > 290$ nm) of $IrCl(CO)(PPh_3)_2$ in benzene.

Flash photolysis ($\lambda_{irr} > 315$ nm) of $RhCl(CO)(PPh_3)_2$ in deaerated benzene under argon was also carried out with added cyclohexene (0.05 M, cyclohexene purified by alumina chromatography and subsequent vacuum distillation). The transient spectrum observable immediately subsequent to the flash (λ_{max} about 450 nm, $\Delta\epsilon_{max}$ $1.4 \times 10^3\ M^{-1}\ cm^{-1}$) decayed via second-order kinetics to regenerate the starting material with a rate constant of about $1 \times 10^8\ M^{-1}\ s^{-1}$. There was no formation of any dimer. (Immediate formation of the transient under these conditions implies a second-order rate constant of $>1 \times 10^7\ M^{-1}\ s^{-1}$ for the reaction of A with cyclohexene.) The same solution was then equilibrated with dihydrogen (1 atm) and again subjected to flash photolysis under identical conditions. The resultant transient absorption and second-order decay rates were identical with those seen in the absence of H_2.

B. Flash Photolysis of $IrCl(CO)(PPh_3)_2$. Flash photolysis of $IrCl(CO)(PPh_3)_2$ in scrupulously deaerated benzene under argon ($\lambda_{irr} > 260$ nm; however, the solvent UV absorbance limited the useful excitation to >295 nm) resulted in the formation of a transient species E with the spectrum shown in Figure 7. This transient decayed via simple second-order kinetics (Figure 8) to regenerate the original base line. There were no net spectral changes for the photolysis solution even after flashing the solution repeatedly (e.g., 20 pulses with the micropulser set at 450 J/flash), consistent with the earlier report that $IrCl(CO)(PPh_3)_2$ showed no net photochemistry under continuous photolysis at 366 nm in benzene solution.[16] The reluctance of $IrCl(CO)(PPh_3)_2$ to undergo irreversible photochemistry was also confirmed in this laboratory by examining the continuous photolysis of this complex in degassed benzene, methylene chloride, THF, and chloroform solutions. Only in the last solvent did long-term irradiation with polychromic light from a high-pressure mercury lamp ($\lambda_{irr} > 315$ nm) lead to any net photochemistry as indicated by changes in the electronic spectrum. The product in this case was not

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[15] Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762–2774.

[16] Geoffroy, G. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3933–3936.

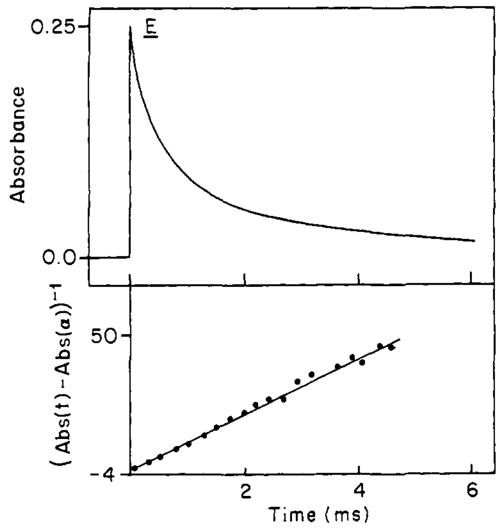


Figure 8. Upper curve: Temporal absorbance changes at 460 nm resulting from the flash photolysis of $IrCl(CO)(PPh_3)_2$ in deaerated benzene. Lower: Second-order rate plot of these data.

characterized; however, the in situ IR spectrum displayed a ν_{CO} band at 2030 cm^{-1} (compared to a ν_{CO} frequency of 1965 cm^{-1} for $IrCl(CO)(PPh_3)_2$), suggesting that the observed photoreaction led to the oxidation of the iridium center.

The second-order kinetics for the decay of E suggested that photoexcitation of $IrCl(CO)(PPh_3)_2$ leads to the reversible labilization of one ligand as seen above for the rhodium(I) analogue. When the flash photolysis experiment was carried out in benzene under various CO pressures (0.005–0.02 atm), the transient spectrum due to E was observed immediately after the flash; however, the decay of E to $IrCl(CO)(PPh_3)_2$ was substantially accelerated and occurred via first-order kinetics. Thus, it was concluded that E is $IrCl(PPh_3)_2$, the product of CO photodissociation (eq 12), and that the observed relaxation process is the reaction of $IrCl(PPh_3)_2$ with CO to regenerate $IrCl(CO)(PPh_3)_2$ (eq 13). A plot of the above first-order rate constants k_{obsd} vs. [CO] gave a k_{13} value of $(2.7 \pm 0.7) \times 10^8$ M^{-1} s^{-1} (the experimental uncertainty being the result of the limited time response of the flash apparatus). Knowing k_{13} plus the slopes of second-order plots such as shown in Figure 8 allows calculation of extinction coefficient differences from between $IrCl(CO)(PPh_3)_2$ and E; for example, a $\Delta\epsilon_{420}$ value of 1300 ± 325 M^{-1} cm^{-1} was thus calculated.

$$IrCl(CO)(PPh_3)_2 \xrightarrow{h\nu} IrCl(PPh_3)_2 + CO \qquad (12)$$

$$IrCl(PPh_3)_2 + CO \xrightarrow{k_{13}} IrCl(CO)(PPh_3)_2 \qquad (13)$$

Notably, flash photolysis of the Ir(I) dinitrogen complex $IrCl(N_2)(PPh_3)_2$ in deaerated benzene under either argon or dinitrogen led to a transient spectrum within experimental uncertainty the same as shown in Figure 7. In this case, the photodissociation of N_2 to form E was apparently irreversible. As a consequence, the decay of this reactive intermediate was much slower and led to unidentified products. The disappearance of E was accompanied by first-order spectral changes (k_{obsd} = 0.9 ± 0.1 s^{-1}) to give a new absorption spectrum (bleaching in the spectral region 334–460 nm) consistent with the formation of Ir(III) products. In addition, the proton NMR spectrum of the product solutions of the continuous photolysis (λ_{irr} 405 nm) of $IrCl(N_2)(PPh_3)_2$ in C_6D_6 under otherwise analogous conditions displayed a −22.5-ppm resonance indicating the formation of an iridium(III) hydride,[17] presumably a product of the internal orthometalation of a coordinated triphenylphosphine.

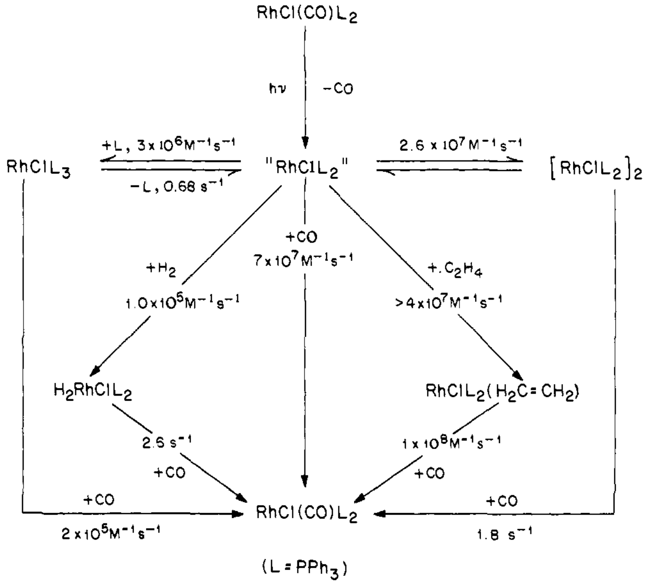
Table I. Second-Order Rate Constants for the Reaction of $RhCl(PPh_3)_2$ with Various Substrates in Benzene[a]

$$RhCl(PPh_3)_2 + L' \xrightarrow{k_j} RhCl(PPh_3)_2L'$$

M	L'	k_j (in M^{-1} s^{-1})
Rh(I)	CO	$(6.9 \pm 0.2) \times 10^7$
	C_2H_4	$>4 \times 10^7$
	$RhCl(PPh_3)_2$	$(2.6 \pm 0.6) \times 10^7$
	PPh_3	$(3.0 \pm 0.5) \times 10^6$
	H_2	$(1.00 \pm 0.05) \times 10^5$
	D_2	$(0.68 \pm 0.13) \times 10^5$
Ir(I)	CO	$(2.7 \pm 0.7) \times 10^8$
	PPh_3[b]	$(1.3 \pm 0.4) \times 10^7$

[a] Results obtained by flash photolysis at 23 ± 1 °C. [b] Reference 18.

Scheme I. Reactions of $RhCl(PPh_3)_2$ and Other Species Formed Subsequent to the Flash Photolysis of $RhCl(CO)(PPh_3)_2$



Discussion

A. Reaction Dynamics of the Intermediates $RhCl(PPh_3)_2$ and $IrCl(PPh_3)_2$. The observations described above clearly indicate that when benzene solutions of $RhCl(CO)(PPh_3)_2$ are subjected to flash photolysis ($\lambda_{irr} > 315$ nm) the resulting transient A is $RhCl(PPh_3)_2$, the product of CO photodissociation. Table I summarizes the rate constants for the second-order reactions of this species with various substrates. The variation in k_j demonstrates that while A is certainly very reactive it is selective even among simple two-electron donors, i.e., the reaction with CO has a rate constant about 23-fold larger than that for the reaction with PPh_3. As expected, given that considerable electronic and structural rearrangement is required, the reaction with H_2 (eq 8) is substantially slower. However, it is particularly significant that A, which is tricoordinated or weakly solvated, reacts with H_2 at a rate more than four orders of magnitude faster than does the tetracoordinated $RhCl(PPh_3)_3$ (k_{14} = 4.8 M^{-1} s^{-1})[4]

$$RhCl(PPh_3)_3 + H_2 \xrightarrow{k_{14}} H_2RhCl(PPh_3)_3 \qquad (14)$$

Notably, the k_8 (1.0×10^5 M^{-1} s^{-1} at 23 °C) measured for the reaction of A with H_2 agrees well with the value ($>7 \times 10^4$ M^{-1} s^{-1}) estimated by Halpern and Wong[4a] from a stopped-flow kinetics investigation of the hydrogenation mechanism for $RhCl(PPh_3)_3$.

For each of the products formed by the reaction of A with a ligand L', subsequent reaction with CO was observed to reform $RhCl(CO)(PPh_3)_2$ over a relatively short time scale. These observations confirm the earlier report[11] that $RhCl(CO)(PPh_3)_2$ undergoes no *net* photoreaction when irradiated in deaerated benzene solutions. (However, recent studies have noted photocatalytic behavior under these conditions.[14b]) The reactions of

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[17] Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983–6994.

A and of subsequent products are illustrated in Scheme I.

The flash photolysis of $IrCl(CO)(PPh_3)_2$ leads to the formation of a quite analogous transient $IrCl(PPh_3)_2$. This species is about four times as reactive with CO as is A; however, it is notable that the relative reactivities of E toward CO and PPh_3 (a ratio of about 20)[18] proved nearly the same as those for the Rh(I) homologue.

The question as to the structure of the transient A (and correspondingly of E) is not well resolved. The reactivity patterns following flash photolysis of $RhCl(CO)(PPh_3)_2$ in CH_2Cl_2 and benzene are nearly identical, but the absence of dimer formation and lower reactivity toward CO in THF suggest that a solvated species such as $RhCl(S)(PPh_3)_2$ might be the intermediate, at least in this solvent. In this context, it is notable that de Croon and co-workers[19] have argued from thermal kinetic studies that A is solvated in benzene and proposed the configuration $RhCl(PPh_3)_2(\eta^2\text{-benzene})$. Nevertheless, a closely analogous three-coordinate 14-electron species $RhCl(PCy_3)_2$ has been spectroscopically characterized,[20] so a transient tricoordinate structure for A would appear to be quite reasonable, at least in a weakly coordinating solvent.

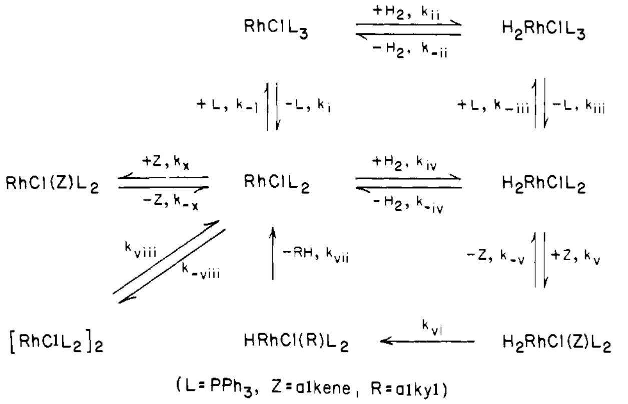
The reaction (eq 5) of CO with $RhCl(PPh_3)_3$, formed by the flash photolysis of $RhCl(CO)(PPh_3)_2$ in excess PPh_3, was confirmed by stopped-flow kinetics to be second order ($k_5 = 2 \times 10^5$ M^{-1} s^{-1}). Furthermore, the lifetime of $RhCl(PPh_3)_3$ in the presence of added CO (e.g., see inset in Figure 5) was found to be much too short to be accountable to the known thermal dissociation of PPh_3 from $RhCl(PPh_3)_3$ to give A ($k = 0.7$ s^{-1});[4a] thus, the second-order kinetics must reflect an associative (or interchange) ligand substitution mechanism as commonly observed for other square-planar complexes.[21] Notably, the analogous reaction of $IrCl(PPh_3)_3$ with CO[18] is also second order with a rate constant 8×10^4 M^{-1} s^{-1}, just a factor of 3 smaller than that for the rhodium(I) analogue.

More remarkable is the much greater reactivity of the ethene complex $RhCl(C_2H_4)(PPh_3)_2$ toward CO (eq 11), which displays a second-order rate constant comparable to that seen for the analogous reaction of A and more than two orders of magnitude larger than that for the reaction of CO with $RhCl(PPh_3)_3$ (eq 5). Given the relative stability of $RhCl(C_2H_4)(PPh_3)_2$,[15] it is probable that eq 11 is an associative reaction. One possible explanation for the relative facility of this reaction may be the lesser steric crowding expected in the transition state of eq 11 than in eq 5. Notably, qualitative NMR evidence in toluene solution has previously demonstrated rapid exchange between this complex and free ligand.[15]

Unlike the ethene and PPh_3 adducts, the dimer $(RhCl(PPh_3)_2)_2$ and the dihydrogen adduct $H_2RhCl(PPh_3)_2$ both react with CO via first-order kinetics. For the former species, this behavior was confirmed by stopped-flow experiments. In both cases, a dissociative mechanism might be assumed. Alternatively, the same kinetics would be consistent with associative reaction of the adduct with solvent in a rate-limiting reaction followed by displacement of solvent by CO.[21] There is no ready differentiation of these two mechanisms from the present data.

For the dihydrogen adduct, it is easy to see how a different mechanism would be required to displace H_2 from the d^6 Rh(III) species than, for example, to displace PPh_3 from the Rh(I) adduct $RhCl(PPh_3)_3$. One explanation of the first-order kinetics of the rate-limiting step would be a concerted dihydrogen elimination from the Rh(III) dihydride $H_2RhCl(PPh_3)_2$ or from the solvated analogue $H_2RhCl(PPh_3)_2S$. An alternative mechanism might involve rate-limiting first-order dissociation of a ligand, e.g., S, from the hexacoordinate solvated species followed by H_2 elimination, a mechanism which would be compatible with the earlier observations that reductive elimination from Ir(III) centers occurs much more readily from the pentacoordinate dihydrides than from analogous hexacoordinate species.[1b,18,22] However, the tris(phosphine) species $H_2RhCl(PPh_3)_3$ is reported[6] to labilize PPh_3 with a considerably larger first-order rate constant (see below), so rate-limiting dissociation of S from $H_2RhCl(PPh_3)_2S$ appears unlikely. Although other mechanisms can be envisioned,[23] the first-order decay observed in limited studies under the flash photolysis would appear most consistent with direct H_2 elimination from $H_2RhCl(PPh_3)_2$. If so it is noteworthy that H_2 elimination from this five-coordinate complex is nearly four orders of magnitude faster than from the six-coordinate $H_2RhCl(PPh_3)_3$.[6]

Scheme II. Reactions Relevant to the Proposed Mechanism for the Hydrogenation of Alkenes Catalyzed by $RhCl(PPh_3)_3$[a]



[a] Subscripts for rate constants were chosen to be consistent with those listed in the similar scheme described in ref 6.

It is less clear why a mechanism change is necessary for reaction of CO with the dimer B for which each rhodium(I) is in the formal oxidation state I. If indeed the rate-limiting step for the reaction depicted in eq 7 involves the unimolecular dissociation of the dimer to give two A's (the reverse of eq 6), then the rate constant ratio $k_6/k_7 = (1.4 \pm 0.3) \times 10^7$ M^{-1} represents the equilibrium constant for eq 6. A value of $>1.7 \times 10^5$ M^{-1} had previously been estimated.[6]

B. Applications to Wilkinson's Catalyst. Scheme II depicts the reactions commonly accepted to be the important features of the hydrogenation of alkenes by Wilkinson's catalyst. (The Roman numeral subscripts for Scheme II rate constants were chosen to be consistent with the numbers used in the recent review by Tolman and Faller.)[6] Several of the rate constants listed in Table I or described in the Results are particularly relevant to this cycle. Perhaps the most important of these is the rate constant k_{-i} for the reaction of PPh_3 with A which was determined by the flash photolysis technique to be 3.0×10^6 M^{-1} s^{-1} (i.e., k_i above). This reaction is the reverse of the phosphine dissociation from Wilkinson's catalyst to form the tricoordinate reactive intermediate. Thus, since the PPh_3 dissociation rate constant k_i (0.7 s^{-1}) has been determined by stopped-flow kinetics studies, the equilibrium constant K_i for PPh_3 dissociation from $RhCl(PPh_3)_3$ in benzene can be calculated from the k_i/k_{-i} ratio to be 2.3×10^{-7} M. This value is consistent with the previous estimate ($<10^{-5}$ M)[4] and with the failure to observe A when benzene solutions of $RhCl(PPh_3)_3$ were studied by NMR spectroscopy.[14]

Another key parameter is the rate constant k_{iv} (i.e., k_8 above) for the reaction of A with H_2. The value measured by flash photolysis (1.0×10^5 M^{-1} s^{-1}) is four orders of magnitude larger than k_{ii}, clearly showing the advantage A has over $RhCl(PPh_3)_3$ in activating H_2 as previously argued.[4a] The rate constant ratio

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(23) One such mechanism would be the fast reaction of $H_2RhCl(PPh_3)_2$ with CO to give $H_2RhCl(CO)(PPh_3)_2$ followed by H_2 elimination to give $RhCl(CO)(PPh_3)_2$ directly. While such a mechanism would appear likely at high [CO] (D. Wink, Ph.D. Dissertation, U.C.S.B, 1985), the low stoichiometric concentrations of CO generated in the flash photolysis experiments would require second-order kinetics for this pathway under these conditions.

k_{-i}/k_{iv}, which represents the relative reactivities of A toward PPh_3 or H_2, is about thirty. The greater reactivity of the tricoordinate intermediate toward the more basic phosphine is not surprising although the ratio of 30 is higher than that previously estimated.[4,6]

In accord with the above discussion, the first-order rate constant for the reaction of $H_2RhCl(PPh_3)_2$ with CO to give $RhCl(CO)(PPh_3)_2$ would represent the *upper limit* for unimolecular H_2 elimination from this adduct in benzene, i.e., k_{-iv}. If indeed $k_{-iv} \leq 2.6\ s^{-1}$, several other numerical parameters can be calculated for the model described in Scheme II. First, the equilibrium constant K_{iv} for H_2 addition to A (k_{iv}/k_{-iv}) would be $\geq 4 \times 10^4\ M^{-1}$ (23 °C), somewhat larger than the value reported for K_{ii} ($6.4 \times 10^3\ M^{-1}$, 25 °C).[24] Second, given that the relationship $K_{iii} = K_iK_{iv}/K_{ii}$ must hold, the values of K_i and K_{iv} described here plus the reported value of K_{ii} would give a $K_{iii} \geq 1.4 \times 10^{-6}$ M, surprisingly larger than K_i (2.7×10^{-7} M). In addition, the rate constant k_{iii} for PPh_3 dissociation from $H_2RhCl(PPh_3)_2$ has been reported[6] from NMR exchange experiments to be 500 s^{-1} in 25 °C (CH_2Cl_2). If it is assumed that the rates are little affected by the solvent differences, a k_{-iii} limit of $\leq 4 \times 10^8\ M^{-1}\ s^{-1}$ results. This value would appear to be rather high, although the reaction represented is between an unsaturated d^6 complex and a two-electron donor. The reported[6] k_{iii} also appears high for the dissociation of a two-electron donor from Rh(III), although this might be explainable by the probable position of the labilized phosphine being trans to a hydride ligand.

In summary, the above flash photolysis studies have successfully interrogated the quantitative reaction dynamics of the tricoordinate intermediate $RhCl(PPh_3)_2$ and related reactive intermediates. These results have proved consistent with the generally accepted mechanism for the $RhCl(PPh_3)_3$ catalysis of alkene hydrogenation but have provided a much firmer experimental basis for proposed reactivities of several key intermediates.

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Registry No. $RhCl(CO)(PPh_3)_2$, 13938-94-8; $RhCl(PPh_3)_2$, 68932-69-4; $RhCl(PPh_3)_3$, 14694-95-2; $H_2RhCl(PPh_3)_2$, 12119-41-4; $RhCl(C_2H_4)(PPh_3)_2$, 12120-14-8; $[RhCl(PPh_3)_2]_2$, 14653-50-0; $IrCl(CO)(PPh_3)_2$, 14871-41-1; $IrCl(PPh_3)_2$, 31690-54-7; CO, 630-08-0; PPh_3, 603-35-0; C_2H_4, 74-85-1; H_2, 1333-74-0; D_2, 7782-39-0; $IrCl(PPh_3)_3$, 16070-58-9.

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(24) This value of K_{ii} is taken from ref 6 but corrected from that reported (9×10^3 M) owing to that source's use of a different solubility for H_2 in benzene (0.002 mol L^{-1} atm^{-1}) than used here (0.0028 mol L^{-1} atm^{-1}) (taken from ref 12).

Synthesis of (±)-Catharanthine, (+)-Anhydrovinblastine, and (−)-Anhydrovincovaline

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Abstract: An efficient total synthesis of (±)-catharanthine (**1**) has been accomplished. Diels–Alder reaction of **8** with α-chloroacryloyl chloride followed by reaction with MeOH gave **9**. Treatment of **9** with Me_3SiI gave **10**, and reaction of **10** with indole-3-acetyl chloride provided **11**, which was converted to **13**. Irradiation of **13** in CH_3CN/H_2O with a 450-W Hanovia mercury lamp through a Pyrex filter provided **14**. Reduction of **14** by treatment with Et_3OBF_4 and $NaBH_3CN$ gave (±)-catharanthine (**1**). The coupling of synthetic (±)-catharanthine with natural (−)-vindoline (**2**) via modified Polonovski reaction provided (+)-anhydrovinblastine (**15a**) and (−)-anhydrovincovaline (**17a**), which could be easily separated by flash chromatography.

The dimeric *Catharanthus* alkaloids vinblastine (**3a**) and vincristine (**3b**) are efficacious, clinically useful anticancer agents which are used routinely for the treatment of a number of human cancers.[2] These compounds have been shown to block mitosis with metaphase arrest by binding to the cell protein tubulin and preventing the assembly of microtubules.[2] Unfortunately, the isolation and purification of these compounds is a difficult process. For example, vincristine (**3b**) constitutes only 0.00025% of the dry weight of the leaves of *Catharanthus roseus* and must be separated from over sixty other alkaloids.[3]

It has recently become possible to prepare **3a** and **3b** with the correct C(16′*S*) configuration. The coupling of (+)-catharanthine (**1**) and (−)-vindoline (**2**), both obtained from *Catharanthus roseus*, gives (+)-anhydrovinblastine (**15a**); subsequent elaboration of **15a** provides **3a** and **3b**.[4] Although (−)-vindoline is the major alkaloid in *Catharanthus roseus* and is readily isolated and purified,[5] this approach is severely limited since (+)-catharanthine is only a minor constituent and is substantially more difficult to

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(1) Fellow of the Alfred P. Sloan Foundation (1980–1984). Recipient of an NIH Research Career Development Award CA 00864 (1983–1988).

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