Volumes of Activation for Kinetically Labile Organometallic Complexes: Solvent Displacement from *cis*-[$(C_6H_5Cl)(PPh_2R)W(CO)_4$] [R = Ph, $(CH_2)_4CH{=}CH_2$] in Chlorobenzene Solution

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Large, positive, and similar volumes of activation, indicative of dissociative desolvation mechanisms, have been observed for chlorobenzene displacement by pyridine and through chelate ring closure, respectively, from *cis*-[$(C_6H_5Cl)(PPh_2R)W(CO)_4$] complexes [R = Ph, $(CH_2)_4C{=}CH_2$] produced *via* pulsed laser flash photolysis.

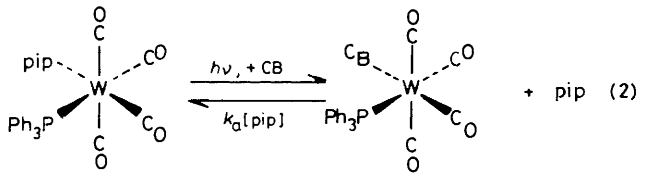
The investigation of reaction rates at variable pressure has contributed significantly to the assignment of reaction mechanisms in organometallic chemistry.[1] Flash photolysis studies through which rates of reaction have also been determined for intermediates produced during thermal reactions have added much to this knowledge.[2] Here we report variable pressure studies (up to 150 MPa) of the displacement of chlorobenzene solvent by pyridine and through chelate ring closure, respectively, from *cis*-[$(C_6H_5Cl)(PPh_2R)W(CO)_4$] [R = Ph, $(CH_2)_4CH{=}CH_2$]. Investigations of this type have afforded volumes of activation for thermal reactions of kinetically labile species produced after pulsed laser flash photolysis[3]† which, in contrast to the corresponding entropies of activation, are diagnostic of mechanism.

Pulsed laser flash photolysis of *cis*-[$(pip)(L)W(CO)_4$] complexes (pip = piperidine) (**1a**), reaction (1), has been shown to induce W–pip bond fission, which is followed by rapid solvation to afford *cis*-[$(solvent)(L)W(CO)_4$] transients (**1b**) as predominant reaction species.[4,5]‡ Rates of solvent displacement from these transients to reform (**1a**) or *cis*-[$(L)(L')W(CO)_4$] products (**1c**) have been investigated employing either pip or a variety of Lewis bases co-ordinating through P (L').[5] Chosen here for flash photolysis/high pressure (f.p./h.p.) study were transients (**1b**) in which L = PPh_3, $PPh_2(CH_2)_4CH{=}CH_2$, and which react in chlorobenzene (CB) solution as shown in reactions (2) and (3), respectively. These reactions were selected so as to maximize the difference in the chemical nature of the Lewis base functionality displacing the solvent molecule and to minimize the extent of net reaction accompanying mutliple photolysis shots: for reaction (2) the predominant photolysis product was the substance photolysed, (**2a**), while for reaction (3), the product (**3c**) was also observed to produce the solvated transient (**3b**) upon photolysis.[6,7]

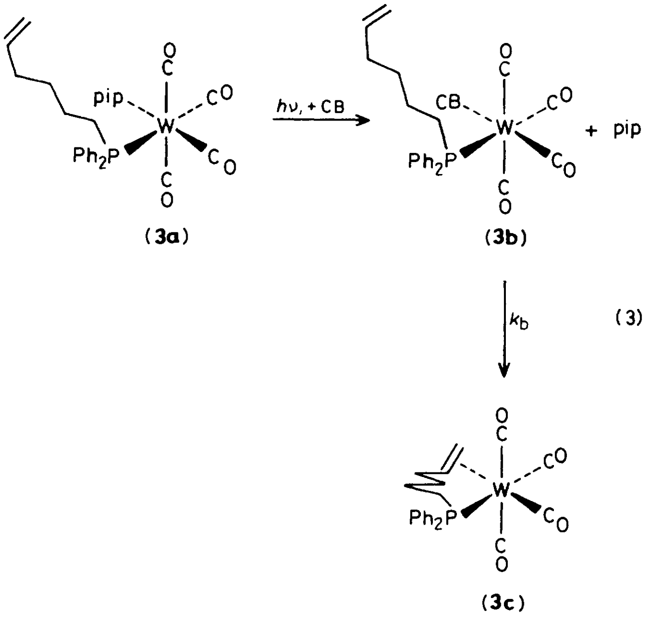
Photolysis of the substrates was carried out using a Nd:YAG laser operating in the frequency-tripled mode (355 nm); 430 nm was the analysing wavelength. The photolysis equipment and experimental procedures,[8] together with the high pressure apparatus,[9] have been described elsewhere.

$$\begin{tikzcd}
\textit{cis}\text{-}[(\text{pip})(\text{L})\text{W}(\text{CO})_4] \arrow[r, shift left, "h\nu,\ +\text{S}"] & \textit{cis}\text{-}[(\text{S})(\text{L})\text{W}(\text{CO})_4] + \text{pip} \arrow[l, shift left] \arrow[d, "+\text{L}'"] \\
 & \textit{cis}\text{-}[(\text{L}')(\text{L})\text{W}(\text{CO})_4]
\end{tikzcd} \qquad (1)$$

(**1a**) (S = solvent) (**1b**) (**1c**)



(**2a**) (**2b**)



(**3a**) (**3b**) (**3c**)

$$\begin{tikzcd}
\textit{cis}\text{-}[(\text{pip})(\text{L})\text{W}(\text{CO})_4] \arrow[r, shift left, "h\nu"] & {[(\text{L})\text{W}(\text{CO})_4]} + \text{pip} \arrow[l, shift left, "k_{-1}\,[\text{pip}]"] \arrow[d, shift right, "k_2\,[\text{CB}]"'] \\
 & \textit{cis}\text{-}[(\text{CB})(\text{L})\text{W}(\text{CO})_4] \arrow[u, shift right, "k_{-2}"']
\end{tikzcd} \qquad (4)$$

(**1a**) (**1b**)

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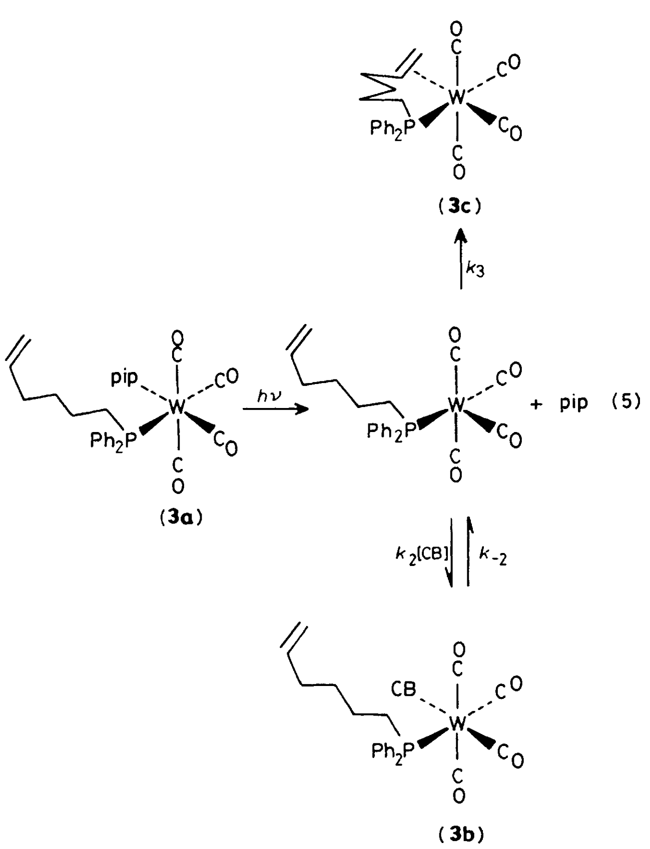
† Similar methods have been used to investigate the physical and chemical behaviour of photogenerated excited states; ref. 3.

‡ The analogous *trans* solvate also is produced; it reacts on a much slower time-scale.



A quartz 'pill-box' observation cell[9] was contained within an autoclave fitted with two perpendicular pairs of sapphire windows to allow passage of the photolysis and observation beams. Values of the pseudo first-order rate constants, k_{obs}, were determined from averages of 5—10 photolysis shots employing the same sample (*vide supra*); two to four independent determinations of k_{obs} were carried out at 5, 50, 100, and 150 MPa and 24.5 °C. For reactions of (**2b**), $k_{obs} = k_a[\text{pip}]$, while for (**3b**), $k'_{obs} = k_b$, where k_a and k_b are overall second- and first-order rate constants, repectively.

Plots of absorbance *vs.* time for reaction (3) at 5 and 150 MPa, illustrating the decrease in rate observed with increased pressure, are shown in Figure 1. Figure 2 depicts plots of ln k_{obs}, reactions (2) and (3), *vs.* pressure for the systems in question. From the slopes of these plots were obtained values of $\Delta V^\ddagger$ of 11.3(4) and 10.5(3) cm^3 mol^{-1} for reactions (2) and (3), respectively. The large positive values of $\Delta V^\ddagger$ strongly support a solvent displacement mechanism which involves significant W–CB bond breaking. On the other hand, activation entropies calculated for CB displacement from *cis*-[(CB)(L)W(CO)$_4$] transients by pip [L = P(OPr^i)$_3$, P(OEt)$_3$, P(OCH$_2$)$_3$CMe, PMe$_2$Ph] are all similar and near zero:[5] 4.6(121), −15.9(46), 10.0(192), and −7.9(171) J K^{-1} mol^{-1}, respectively, and thus are equivocal in the assignment of mechanism. However, studies of the disappearance of (**1b**) *via* reaction (1) for L = P(OPr^i)$_3$ in cyclohexane–CB–pip mixtures have demonstrated that the Lewis bases pip and CB compete for an intermediate, which must be [(L)W(CO)$_4$], and thus provide strong evidence that the mechanism for reaction (1) is dissociative as shown in reaction (4). For this mechanism $k_{obs} = k_{-1}k_{-2}[\text{pip}]/(k_{-1}[\text{pip}] + k_2[\text{CB}])$, or $k_{obs} = k_{-1}k_{-2}[\text{pip}]/k_2[\text{CB}]$ under the conditions we have employed, in which $k_2[\text{CB}] \gg k_{-1}[\text{pip}]$. The dissociative mechanism suggested for (**3b**), outlined in reaction (5), affords the expression $k'_{obs} = k_{-2}k_3/(k_2[\text{CB}] + k_3)$, or, where $k_2[\text{CB}] \gg k_3$, $k'_{obs} = k_{-2}k_3/k_2[\text{CB}]$. From these relationships it follows that $\Delta V^\ddagger$s determined from the pressure dependence of k_{obs} are given by equations (6) and (7), respectively. It is realistic to expect that $\Delta V^\ddagger(k_{-1})$, $\Delta V^\ddagger(k_3)$, and $\Delta V^\ddagger(k_2)$ will all be negative since these rate constants all govern bond formation, and therefore that the overall large, positive, and similar $\Delta V^\ddagger$s observed in both systems largely present the contribution of $\Delta V^\ddagger(k_{-2})$ to equations (6) and (7). Thus these values are diagnostic of W–CB bond dissociation, and, as has been demonstrated elsewhere,[10] provide mechanistic evidence for systems in which entropies of activation do not.

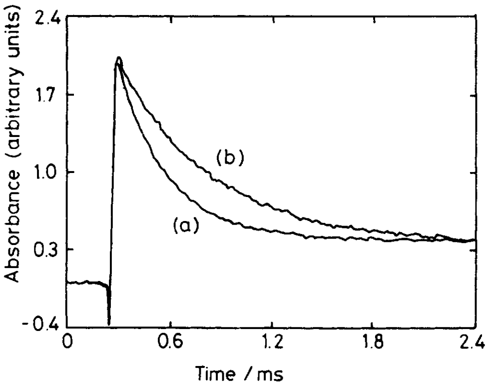


Figure 1. Plots of absorbance (arbitrary scale) *vs.* time for the thermal reaction of *cis*-[(CB)PPh$_2$(CH$_2$)$_4$CH=CH$_2$W(CO)$_4$] (**3b**) in chlorobenzene (CB) at 24.5 °C at (a) 5 and (b) 150 MPa pressure.

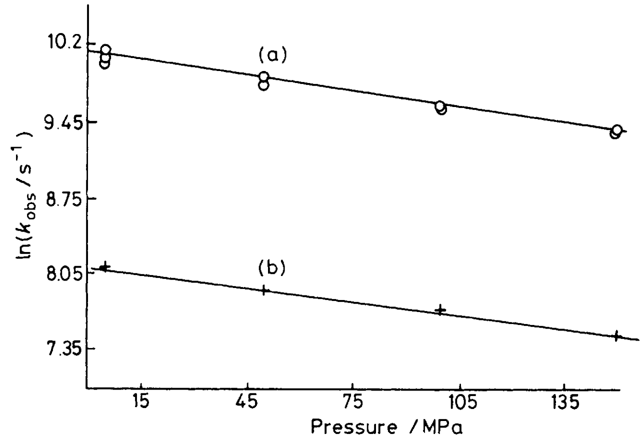


Figure 2. Plots of ln k_{obs} *vs.* pressure for thermal reactions (a) of *cis*-[(CB)(PPh$_3$)W(CO)$_4$] (**2b**) with pip, and (b) of *cis*-[(CB)-PPh$_2$(CH$_2$)$_4$CH=CH$_2$W(CO)$_4$] (**3b**) *via* unimolecular ring closure, both in chlorobenzene (CB) at 24.5 °C.

Pulsed laser f.p./h.p. studies of the reactivities of organometallic transients should prove valuable in the diagnosis of reaction mechanisms, particularly of homogeneous catalysis,[11] since such studies can access for temporal investigation at high pressure species which are steady-state intermediates under catalytic conditions.

$$\Delta V^\ddagger_{obs} = \Delta V^\ddagger(k_{-1}) + \Delta V^\ddagger(k_{-2}) - \Delta V^\ddagger(k_2) \quad (6)$$

$$\Delta V^{\ddagger\prime}_{obs} = \Delta V^\ddagger(k_{-2}) + \Delta V^\ddagger(k_3) - \Delta V^\ddagger(k_2) \quad (7)$$

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Austin, U.S.A., employing high pressure equipment constructed at the University of Frankfurt, F.R.G. The CFKR is supported jointly by the Biotechnology Research Technology Program of the Division of Research Resources of the U.S. National Institutes of Health (Grant No. RR00886) and by the University of Texas at Austin. We thank the Robert A. Welch Foundation (Grant No. B-434), the U.S. National Science Foundation (Grant No. CHE 84-15153), the NTSU Faculty Research Fund, and the Deutsche Forschungsgemeinschaft for financial support, and Charles B. Dobson for experimental assistance.

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