

C–H activation by organometallics: the role of matrix isolation studies

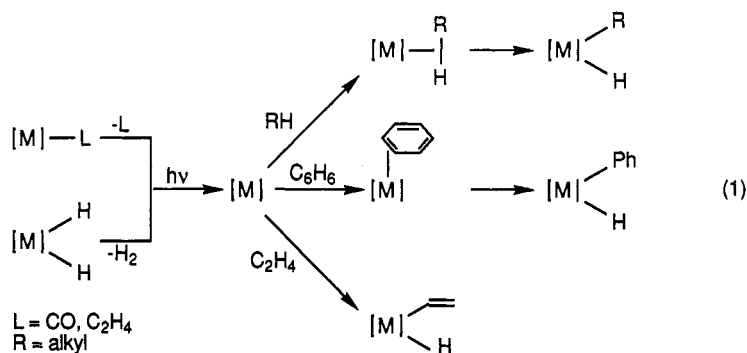
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Abstract Advances are reported in the application of matrix isolation in combination with solution techniques to the study of C–H activation reactions of organometallics. Laser-induced fluorescence proves applicable to all the open-shell metallocenes studied, $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}$ ($\text{M} = \text{Mo}, \text{W}, \text{Re}$) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}$. Studies with pulsed dye-lasers allow the determination of excitation spectra and the emission lifetimes. Three types of situation are encountered when the behaviour of photoproducts in matrices is compared with that in solution. In the type 1 situation, a coordinatively unsaturated intermediate is stabilised by the matrix. It may be observed in solution using time-resolved spectroscopy if the matrix and solution studies share a common spectroscopic technique (e.g. $\text{Ru}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$). In type 2 reactions, photolysis leads to an unstable isomer of the precursor. Such species may often be observed by NMR following photolysis of solutions or frozen solutions at low temperature. The cage formed by the matrix or viscous solvent may play a significant role in this type of reaction as, for instance, in the isomerisation of some metal-ethene complexes. Type 3 reactions involve intermolecular reaction in the matrix (e.g. $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ with methane), but the products of reaction may be very labile. The corresponding reactions with alkanes may be observed by laser flash photolysis with the aid of a common spectroscopic method.

INTRODUCTION TO C–H ACTIVATION

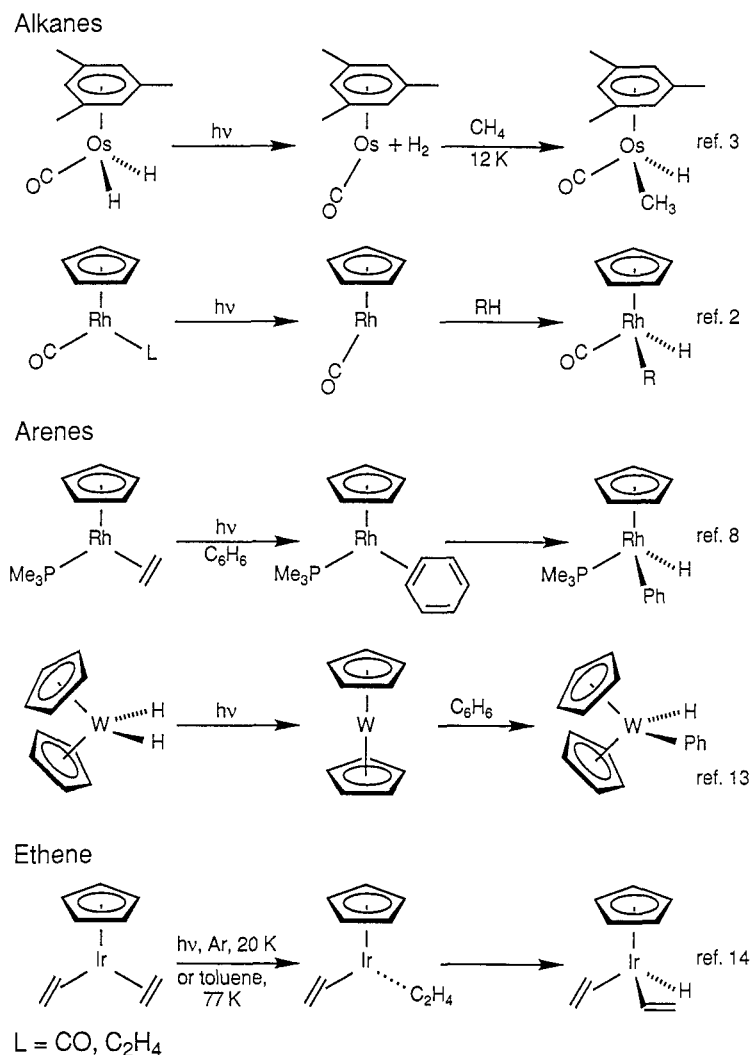
Photochemistry offers one of the principal entries into C–H activation by organometallics. It is now established that such reactions proceed via photolytic expulsion either of a 2-electron ligand or of dihydrogen from the precursor complex, generating a metal fragment which is coordinatively and electronically unsaturated (ref. 1 – 8). This fragment reacts with a hydrocarbon in a subsequent step (eq. 1), ultimately forming the insertion product.



As indicated in eq. 1, alkanes, arenes and alkenes are all reactive (see Scheme 1 for examples). There is abundant evidence that arenes react via η^2 -arene intermediates which serve to lower the activation energy for insertion into these strong C–H bonds (ref. 6, 8). Recent studies on isotopic exchange have also pointed to the existence of η^2 -alkane or σ -complexes in alkane insertion and elimination reactions (ref. 1, 9 – 11). The insertion of the metal fragment into the C–H bonds of ethene represents a special case, since the ethene π -complex is usually more stable than the (vinyl)hydride complex and is not an intermediate in the insertion process (ref. 12). Moreover, the photochemical conversion of an ethene complex into a (vinyl)hydride complex may be intramolecular in some instances (ref. 3).

Many of these reactions lend themselves to detailed mechanistic study by laser flash photolysis and matrix isolation methods. In York, we have employed matrix isolation and time-resolved methods in conjunction with the more conventional armoury of the synthetic chemist to probe the mechanisms of C-H activation reactions. Examples of some reactions studied are given in Scheme I.

Scheme 1 C-H Activation reactions studied by matrix isolation and/or laser flash photolysis.



In the next section of this account, I wish to point to advances in the techniques available to the matrix spectroscopist for the study of reaction intermediates, especially through the use of laser-induced fluorescence (LIF). In the final section, I will examine the relationship between reactivity in solution and in matrices. Again, it is through major improvements in techniques that such comparative studies have advanced.

MATRIX SPECTROSCOPY AND THE APPLICATION OF LASER-INDUCED FLUORESCENCE

The power of the matrix isolation method lies in the application of spectroscopic techniques appropriate to the problem in hand. The diversity of methods available is illustrated by the $(\eta^6\text{-arene})_2\text{V}$ (arene = benzene, toluene, mesitylene) complexes and the reactive metallocenes, Cp_2M (M = Mo, W, Re, Cp = $\eta^5\text{-C}_5\text{H}_5$). The vanadium arene complexes are stable at room temperature, but give much more highly resolved IR and UV/vis spectra in matrices. Their paramagnetism can be investigated by ESR in matrices, since they possess ^2A ground states (ref. 15).

The metallocenes have been generated by photolysis of a variety of precursors isolated in low-temperature matrices including the hydrides, Cp_2MH_2 ($M = \text{Mo}, \text{W}$) and Cp_2ReH . All three have been proved to possess parallel ring structures by a combination of IR and UV/vis spectroscopy and their paramagnetism has been demonstrated by magnetic circular dichroism (ref. 13). This technique provides an optical method of following magnetisation which highlights the presence of both spin and orbital contributions to the magnetic properties of these molecules. The measurements make use of their intense ligand-to-metal charge-transfer (LMCT) band in the near UV or visible.

Several years ago, we demonstrated that laser excitation into the LMCT transition of Cp_2Re and Cp^*_2Re ($\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$) resulted in intense fluorescence with vibrational fine structure even better resolved than in the absorption spectrum. This study was facilitated by the overlap of the absorption band with several lines of the Ar^+ or Kr^+ laser (ref. 16). In our current work, we have employed pulsed dye lasers and shown that LIF is exhibited by all these open-shell metallocenes and by Cp^*_2Re . In contrast, recent experiments show that laser excitation of the corresponding band of $(\eta^5\text{-arene})_2\text{V}$ results in resonance Raman scattering with a progression once again in the symmetric (ring)-metal-(ring) stretching mode.

The LIF spectrum is illustrated for Cp_2Re (figure 1, ref. 17). The emission spectra show several sets of vibrational progressions with relative intensities which vary with excitation wavelength. The different sets of progressions are associated with different conformers or sites in the matrix. The improvement in resolution of the LIF spectra over the absorption spectra is now seen to arise

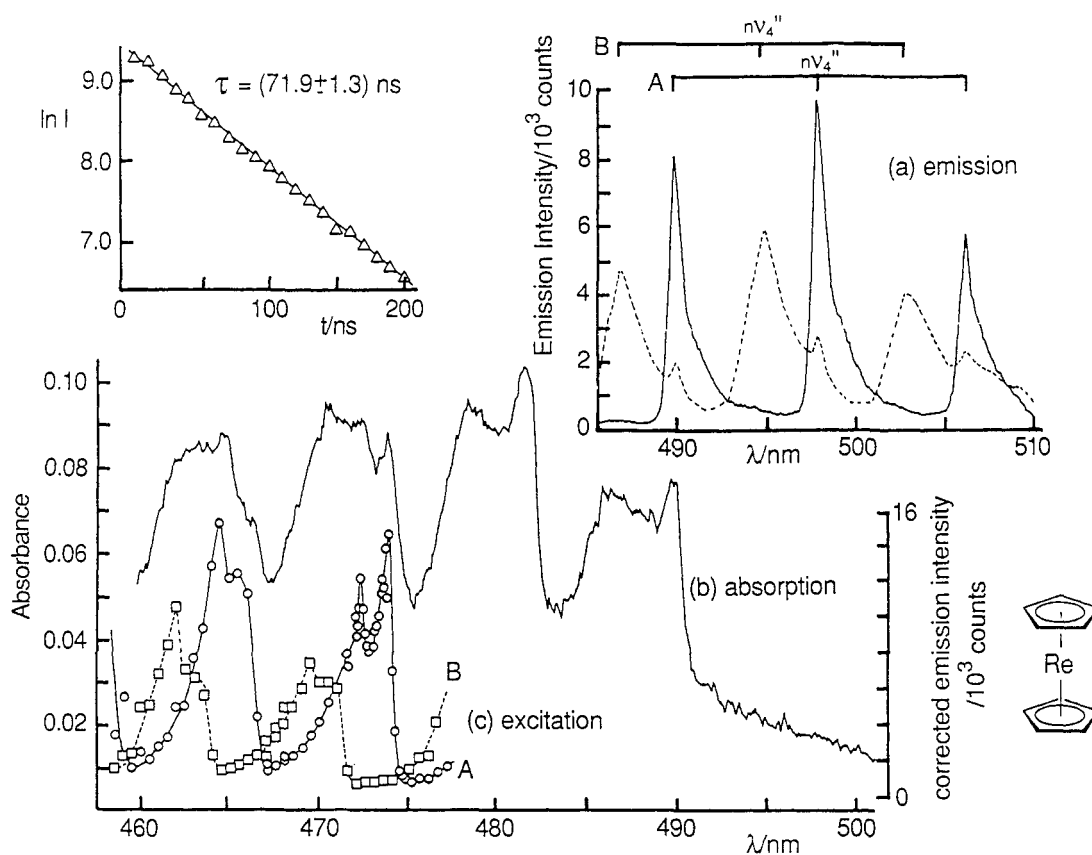


Fig. 1 (a) Emission spectrum of Cp_2Re in a N_2 matrix at 12 K. — $\lambda_{\text{ex}} = 473.5$ nm, --- $\lambda_{\text{ex}} = 469.5$ nm. The inset shows the logarithmic plot of emission intensity yielding fluorescence lifetime. (b) — Absorption spectrum of Cp_2Re in N_2 matrix. (c) Excitation spectra for Cp_2Re : o-o-o- excitation spectrum for $\lambda_{\text{em}} = 498.0$ nm corresponding to full line in spectrum a; - - - - excitation spectrum for $\lambda_{\text{em}} = 494.8$ nm corresponding to broken line in spectrum a. (λ_{ex} = excitation wavelength, λ_{em} = emission wavelength). Reproduced with permission from Journal of Physical Chemistry. Copyright American Chemical Society.

because the laser excitation is site-selective; the absorption spectra represent the sum of several overlapping spectra of different conformers/sites. The contribution of each site is 'deconvoluted' experimentally by the determination of the excitation spectra (figure 1c). As expected, the lifetimes of these excited states are short (72 ns for Cp₂Re and < 10 ns for Cp₂W and Cp₂Mo). The spectra also allow the determination of several totally symmetric vibrations in the ground electronic state which are inaccessible by IR spectroscopy. LIF has long been exploited in studies of small molecules in matrices and in the gas phase because of its high selectivity and sensitivity. The emission data not only provide new information about the reactive metallocenes in their ground and excited states, but suggest new approaches to the detection of reactive organometallics in other phases.

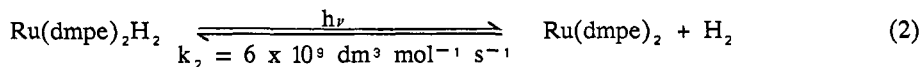
COMPARISONS OF PHOTOCHEMISTRY IN SOLUTION AND MATRICES

The compatibility of matrix and solution behaviour is always a point of contention. Even among those in the field of matrix isolation, there are some who highlight the differences and others who emphasise the similarities. However, the drastic improvement in time-resolved spectroscopy and in NMR techniques means that the comparative behaviour is subject to experimental test. There are already several comparisons in the organometallic literature, for instance that for Fe(CO)₄ (ref. 18). The question of multiple CO loss from group VI hexacarbonyls is also of particular interest. In matrices, multiple CO loss to form 14-electron or 12-electron fragments occurs sequentially, requiring one photon for each CO group lost. In solution, only 16-electron fragments are formed, but in the gas phase multiple CO loss may occur as a result of absorption of a single photon if its energy is sufficient (ref. 19). Here I will attempt to classify the behaviour which we have observed in cyclopentadienyl and phosphine complexes. In doing so, I will also illustrate the interplay of matrix and solution studies, the detection of reaction intermediates and the mechanisms of several C-H activation reactions.

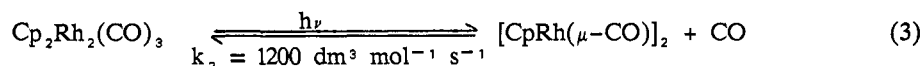
Type 1. Unsaturated intermediate in matrices, transient in solution

A matrix stabilises an organometallic fragment in its ground electronic state with minimal change in geometry from fluid phases (ref. 20). Such a fragment is likely to be a short-lived transient in solution or the gas phase. Proof of a common intermediate in matrices and in solution requires a common spectroscopic technique. In the case of Cp₂Mo, the matrix studies provide detailed characterisation of electronic and molecular structure (see above), and show that the molecule has a sharp UV absorption centred at 396 nm. This feature may be used to detect the same molecule by laser flash photolysis in solution. These experiments show that Cp₂Mo decays within a few microseconds either by reaction with 2-electron donors or by C-H insertion into its precursor, Cp₂MoH₂ (ref. 21).

Perhaps, the most striking example of identification through a common UV spectrum is that of Ru(dmpe)₂ (dmpe = Me₂PCH₂CH₂PMe₂). This molecule was proposed as an intermediate in some of the first intermolecular C-H activation reactions investigated by Chatt and Davidson (ref. 22), but it was then generated thermally from Ru(dmpe)₂(naphthyl)H. We have generated it photochemically from Ru(dmpe)₂H₂ or Ru(dmpe)₂D₂. The photoproduct shows a characteristic three-band UV/vis spectrum, whether generated in matrices or by flash photolysis (figure 2, ref. 23). There is essentially no dependence on the matrix. Ru(dmpe)₂ reacts at a diffusion-controlled rate with H₂, so reducing the utility of the dihydride as a precursor for C-H activation.



When a ligand is lost from a dinuclear complex, there is the possibility of compensation by increasing the bond order of the metal-metal bond. In practice, the resulting stabilisation is not necessarily sufficient to make the photoproduct isolable. Thus, photolysis of Cp₂Rh₂(CO)₃ yields the deep purple [CpRh(μ-CO)]₂, which has a formal metal-metal double bond. This complex may be detected in solution either by time-resolved visible or infrared spectroscopy. In the absence of CO, it has a lifetime of a few seconds at room temperature (eq. 3, ref. 2).



Sometimes, as in the case of Cr(CO)₅, the organometallic fragment is stabilised by specific solvation by a matrix atom or molecule: even argon may be effective. Such solvation is also observed in solution so that the spectra in a methane matrix resemble those in alkane solution. Cr(CO)₅ provides an example in which both IR and visible spectroscopy have been used to great effect to demonstrate the similarity of the structure and electron accepting behaviour in matrices and fluid phases (ref. 19, 24-25). The interaction of alkanes with Cr(CO)₅ represents a model for the putative η²-alkane intermediate in alkane activation.

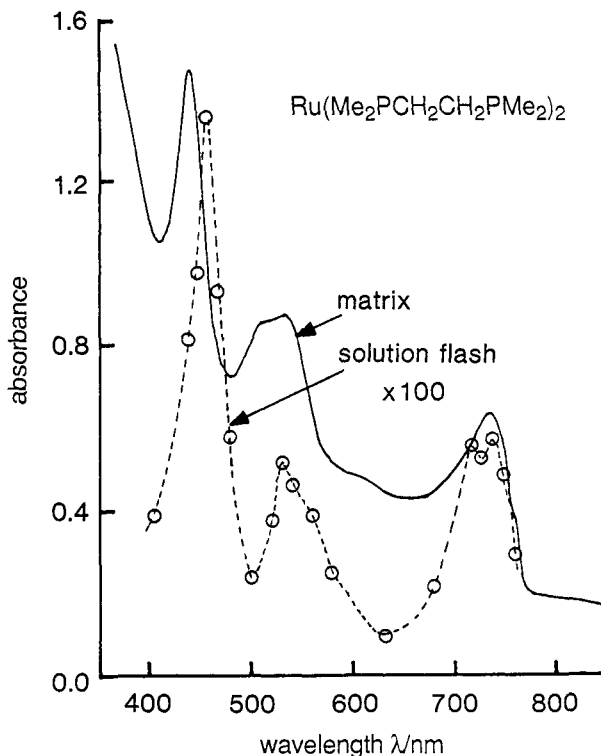
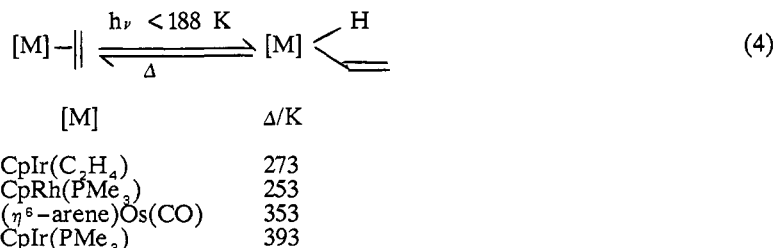


Fig. 2 Absorption Spectra of $\text{Ru}(\text{dmpe})_2$ generated by photolysis of $\text{Ru}(\text{dmpe})_2\text{H}_2$. Solid line: spectrum in methane matrix at 12 K. Broken line: difference spectrum measured 5 μs following laser flash (308 nm) of solution in cyclohexane.

Type 2. Formation of unstable isomers by C-H insertion

The last few years have seen the discovery of several examples of photo-induced isomerisation of metal-ethene complexes to metal(vinyl)hydrides (ref. 12, 26). Some examples studied in York are shown in eq. 4 and Scheme 1 (ref. 3, 14).



These reactions were first observed by photolysis in matrices, but in each case the (vinyl)hydrides can also be made by photolysis of cold or frozen solutions of the precursor in toluene. The resulting products vary widely in stability: approximate temperatures for their thermal isomerisation back to ethene complexes are given in eq. 4. Several observations point to a mechanism which involves formation of an intermediate cage complex $[\text{M}\dots\text{C}_2\text{H}_4]$ rather than a straightforward intramolecular mechanism:

(i) The isomerisation of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ and $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ proceeds cleanly in frozen toluene at 77 K, but not in toluene solution even at temperatures as low as 188 K. If photolysed in toluene solution, insertion into toluene competes with insertion into ethene.

(ii) When either $\text{CpIr}(\text{C}_2\text{H}_4)_2$ or $\text{CpM}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Rh}, \text{Ir}$) is photolysed in reactive CO matrices, formation of carbonyl-substituted products competes with isomerisation. In the case of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$, the only product is $\text{CpRh}(\text{PMe}_3)\text{CO}$.

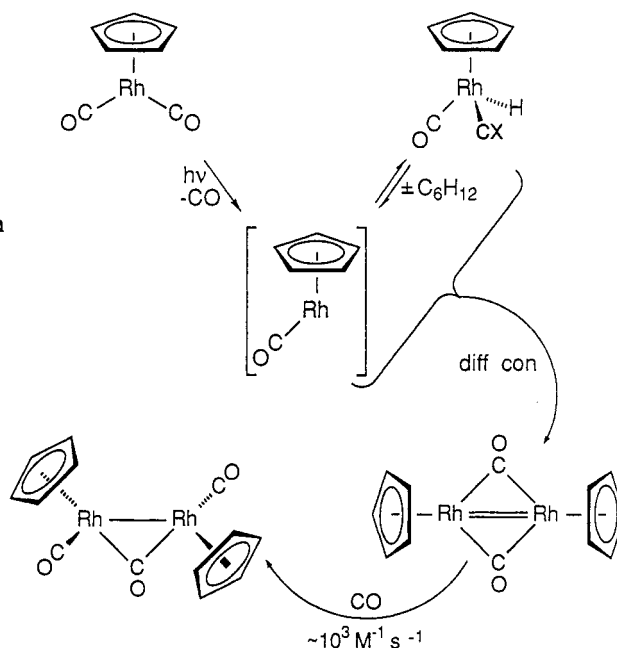
(iii) When $(\eta^6\text{-mesitylene})\text{Os}(\text{CO})(\text{C}_2\text{H}_4)$ is photolysed at 188 K in C_2D_4 -saturated toluene $(\eta^6\text{-mesitylene})\text{Os}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$ is the exclusive product (ref. 3).

The best explanation of these observations is that the reactions proceed via a cage-complex, and that there is a gradation of interaction between ethene and metal fragment, which follows a similar order to the thermal stability of the (vinyl)hydrides. Thus, the reaction of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ is close to intramolecular, while that of its rhodium analogue involves a weakly interacting cage-complex which is readily disrupted by other ligands. In conclusion, the cage formed by the matrix or a viscous/frozen solvent has a profound effect on the outcome of reactions of type 2. Moreover, the formation of the more thermally unstable products would not have been detected without matrix isolation.

Type 3. Intermolecular C–H insertion leading to labile products

Insertion of metals into C–H bonds of alkanes was long sought after. When eventually found, it did not require an exotic new compound, but one as familiar as $\text{Cp}^*\text{Ir}(\text{CO})_2$ (ref. 27). The question arose whether such processes had been missed in other simple organometallics. Rest *et al.* (ref. 5) found good evidence from the CO–stretching vibrations that $\text{CpRh}(\text{CO})_2$ yielded CpRhCO on photolysis in an argon matrix, but $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$ in a methane matrix. We found the same products on photolysis of $\text{CpRh}(\text{C}_2\text{H}_4)_2\text{CO}$ and were able to improve the evidence by locating the rhodium–hydride stretching vibration (ref. 4). Yet why had $\text{CpRh}(\text{CO})(\text{alkyl})\text{H}$ complexes never been detected in solution? Laser flash photolysis of $\text{CpRh}(\text{CO})_2$ in alkane solution with UV detection provided the means to show that the photoproduct is either $\text{CpRh}(\text{CO})(\text{alkane})$ or $\text{CpRh}(\text{CO})(\text{alkyl})\text{H}$, but not to distinguish the two possibilities (ref. 2). The matrix experiments had shown that CpRhCO and $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$ differed in $\nu(\text{CO})$ frequency by 57 cm^{-1} , so it was evident that time-resolved infrared (TRIR) spectroscopy was the technique required to ascertain which species was formed in solution. TRIR experiments provided unequivocal evidence for the C–H insertion process, and showed that $\text{CpRh}(\text{CO})(\text{cyclohexyl})\text{H}$ decayed with the same kinetics as the transient detected by UV spectroscopy (ref. 2). Intriguingly, the immediate product of decay in the absence of added ligand turns out to be $[\text{CpRh}(\mu\text{-CO})]_2$ (see above and Scheme 2). In summary, matrix isolation and solution experiments are consistent, but the C–H insertion products are too labile to observe by static spectroscopy at room temperature.

Scheme 2 Photochemistry of $\text{CpRh}(\text{CO})_2$ in cyclohexane solution in absence of added ligand, deduced from time-resolved studies (cx = cyclohexyl, diff. con. = diffusion controlled).



Weiler *et al.* have conducted a parallel and most remarkable series of TRIR experiments on the reaction of $\text{Cp}^*\text{Rh}(\text{CO})_2$ in liquid krypton and xenon in the presence of alkanes (ref. 7). They also found the corresponding (alkyl)hydride complexes, but in addition they found evidence for prior formation of alkane and noble gas complexes.

Of course, the products of C–H insertion need not be so labile. For instance, the formation of $(\eta^6\text{-mesitylene})\text{Os}(\text{CO})(\text{CH}_3)\text{H}$ was observed first in matrices, but it proved possible to synthesise this complex by other means and sublime it directly into a matrix for comparison (ref. 3).

If this account makes the relationship between matrix and solution chemistry straightforward, this is not always so. Matrix photolysis of $\text{CpRh}(\text{C}_2\text{H}_4)_2$ generates $\text{CpRh}(\text{C}_2\text{H}_4)$. Solution flash photolysis of the same material gives two transients A and B; B has a lifetime about 10^3 times longer than A (ref. 28). The former has a spectrum resembling the matrix species, yet the matrix cannot stabilise an excited state. The latter is a solvent–complex, $\text{CpRh}(\text{C}_2\text{H}_4)\text{S}$, but we find no sign of B in the matrix. What is the difference in electronic structure between A and B? At present, these problems remain unsolved.

CONCLUSIONS

The combined use of matrix isolation and solution techniques offers a very effective method of extending our knowledge of C-H bond activation processes. Such reactions usually follow the same course in matrices as in solution during the initial stages, but it may require low-temperature spectroscopy or time-resolved spectroscopy to demonstrate the similarity. A significantly different course may be taken in matrices (or frozen solution) from that observed in fluid solution if the reaction occurs within the matrix cage, as in the isomerisation of some metal ethene complexes.

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