THE PHOTOCHEMISTRY OF MONOSUBSTITUTED TRI(PHENYLPHOSPHINE)
DERIVATIVES OF SOME METAL CARBONYL COMPLEXES

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by

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Declaration

I declare that the work presented in this thesis is based entirely on my research carried out at Dublin City University under the supervision of Dr. Conor Long.

Barry Crocock
TO MY PARENTS
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Abstract

The photochemistry of some d^6 metal carbonyl complexes is investigated. In particular, the effect of the substitution of a carbon monoxide ligand by a triphenylphosphine ligand on the reactivity of the intermediates formed on photolysis of these complexes is examined. The manganese complexes (η^5-C_5H_4CH_3)Mn(CO)_3 and (η^5-C_5H_4CH_3)Mn(CO)_2PPh_3 are investigated by laser flash photolysis (λ = 355 nm). The laser flash photolysis (λ = 266 nm, 355 nm) of the Group VI M(CO)_5PPh_3 (M = Cr, Mo or W) complexes is also reported.

The crystal structures of the (η^5-C_5H_4CH_3)Mn(CO)_2L (L = pyridine, cis-cyclooctene) complexes are presented and examined to see the effects of a good σ donating ligand and a good π accepting ligand on the (η^5-C_5H_4CH_3)Mn(CO)_2 unit.

A program written in GWBASIC for transient capture and analysis is described.
CHAPTER 1

INTRODUCTION
1.0 INTRODUCTION

Photolysis of metal carbonyl compounds has become of increasing interest and importance in recent times. The potential use of these compounds in synthesis and as homogeneous catalysts has been known for many years. Homogeneous catalysts frequently function efficiently under milder conditions than their heterogeneous counterparts. The use of heterogeneous catalysts outweighs the use of homogeneous catalysts in industrial processes primarily because they can easily be removed from the reaction medium. However, in some processes the use of homogeneous catalysts has become almost exclusive. One such process is the production of ethanal which is synthesised by the Wacker process in which an aqueous HCl solution of PdCl₂/CuCl₂ is used to convert ethene to ethanal by air oxidation. Another process involves the carbonylation of methanol to produce acetic acid under low pressures of carbon monoxide (30 - 40 atm) using the rhodium based catalyst [RhI₂(CO)₃]. Other reactions use homogeneous catalysts to effect highly specific organic transformations. Industrially, these are small scale processes producing chemicals of interest to the pharmaceutical sector. Homogeneous catalysts have proved to be very effective in the areas of hydrogenation, olefin isomerisation, carbonylation, oligomerisation and polymersation of organic molecules. Certain metal carbonyl complexes are known to be homogeneous catalysts. Among these are Ni(CO)₄ which is used in the hydrocarboxylation of olefins and (arene)Cr(CO)₃ or photoactivated Cr(CO)₆ which are used in the selective hydrogenation of some conjugated dienes.

The central process in these reactions is the displacement of a carbonyl group by a nucleophilic ligand. Thermal replacement of the carbonyl ligand is often difficult whereas photochemical decarbonylation can proceed with quantum yields approaching 1. Knowledge of the structure and reactivity of these intermediates has important applications in the areas of synthesis and design of homogeneous catalytic...
processes\textsuperscript{1,2} Therefore it is important to understand these processes. A variety of procedures has been employed to elucidate the structure, identity and reaction kinetics of these intermediates. Among the most successful have been low temperature matrix isolation and laser flash photolysis. The advantages and disadvantages of these methods will be given with respect to the photochemical study of metal carbonyl complexes. In addition the photochemistry of MeCpMn(CO)\textsubscript{2}L (L = CO, PPh\textsubscript{3}) and of the GroupVIB pentacarbonyl tritylphosphine complexes will be discussed as these are the prime concern of this thesis.

1.1 Low temperature matrix isolation

This technique was developed in the 1950 by Pimentel\textsuperscript{6} and is the oldest method employed in the detection of metal carbonyl photofragments. The metal complexes are dispersed in a matrix, usually an inert noble gas at low temperature (1.5-60K). Alternative matrices such as N\textsubscript{2}, O\textsubscript{2}, CO and CH\textsubscript{4} have also been used. The advantage of this technique is that reactive fragments, which would not have a long lifetime at room temperature, can be stabilised. These fragments are molecules or ions which are present in vapours or discharges at high temperature, weakly bound to other molecules or transients of short lifetimes in reactions. The matrices stabilise molecular ground states not excited states and the lifetimes of these species are reduced relative to gas phase\textsuperscript{7}. After irradiation of these matrices, spectroscopic techniques e.g. UV/visible and infra red spectroscopy, can be used to study the metal carbonyl photofragments produced. This would not normally be possible because of the short lifetimes of the metal carbonyl intermediates. Infra red spectroscopy is particularly useful because the carbonyl bands are sharp and to a good approximation no coupling is involved with other molecular vibrations.

One of the requirements of the matrix isolation technique is that the matrix should be inert towards the photofragments produced. In the majority of cases no
interaction can be observed with the noble gases or with nitrogen and methane matrices. However, evidence has been found for coordination by the photoproducts to the matrix, examples of which are $\text{Cr(CO)}_5\text{N}_2^8$, $\text{Fe(CO)}_4(\text{CH}_4)^9$, $\text{Cr(CO)}_5\text{Ar}^{10}$ and $\text{Mn(CO)}_5\text{Kr}^{11}$. This demonstrates the reactivity of these photochemically produced coordinately unsaturated species.

Apart from matrices of inert gases, low temperature solvent glasses are also used. These consist of hydrocarbons e.g., isopentane, methylcyclohexane, and are maintained at higher temperatures (77K) than the inert gas matrices$^{12}$. The spectroscopic techniques used for species detection are the same as for matrix studies. However, carbonyl bands in the infra red tend to be broader and may occlude other spectral features needed for accurate structural determination. This problem may be overcome in some cases by isotopic enrichment of the matrix. In addition, these glasses may not be inert and therefore are more likely to interact with the photofragments produced. Other disadvantages which apply to both matrices and glasses are that they cannot be easily used for charged species, very little kinetic information can be obtained because of the restricted temperature range and the frozen rigid structure of the matrix can block some pathways in photochemical processes. The last disadvantage is not thought to be so important in frozen glasses because of a less closely packed arrangement.

As a complementary technique to matrix isolation, low temperature solutions of liquefied noble gases have been used to characterise unstable carbonyl compounds. The advantage of this technique over the others is the total lack of absorption by the solvent in the infra red. When combined with Fourier transform infra red spectroscopy, this allows weak absorptions arising from coordinated ligands to be detected. One such example is the detection in liquid xenon of the H-H stretching vibration of coordinated...
dihydrogen in Cr(CO)$_5$H$_2$ which is too weak to be detected using matrix isolation techniques.\(^\text{13}\)

Problems associated with low quantum yields for loss of ligand species in metal carbonyl complexes using conventional light sources have been overcome by the use of lasers for excitation.\(^\text{14}\) An example using a laser as the excitation source is the loss of hydrogen from HMn(CO)$_5$.\(^\text{15}\) Using a conventional mercury lamp HMn(CO)$_4$ is generated in a solid argon matrix but not Mn(CO)$_5$ because of low quantum yield for H loss. Alternatively, Mn(CO)$_4$ is generated only in a CO matrix because recombination with CO removes HMn(CO)$_4$. When an ArF excimer laser (193nm) is used as an excitation source in an argon matrix both species are observed.

1.2 Flash photolysis

Conventional flash photolysis was developed in the 1950's by Nomsh and Porter\(^\text{16}\) for which they received the Nobel prize. They were able to identify reactive intermediates present in many photochemical systems. Stationary concentrations of atoms, radicals or excited species are normally too low for intermediates to be detected by spectroscopic techniques. The concentrations of these intermediates can be increased by using a very high intensity flash of light e.g. a discharge lamp or laser. From spectroscopic observations the spectra and lifetimes of the intermediates can be obtained. Nasielski pioneered flash photolysis with UV/visible detection on metal carbonyl systems with the analysis of Cr(CO)$_6$.\(^\text{17}\) Metal carbonyl intermediates are relatively easy to detect because their quantum yields for formation are high and their UV/visible absorptions are intense. Solvent absorptions can be overcome by using solvents with suitable cut-off wavelengths. The basic technique involves excitation of the sample solution with a high intensity flash e.g. a laser pulse, while simultaneously passing a monitoring beam, e.g. from a xenon arc lamp, through the sample. Changes in absorption in the monitoring beam reflect the formation of intermediates or depletion.
of parent compound (or both). Spectra are recorded using a spectrograph or are built up point by point by changing the wavelength of a monochromator. Fast transient digitizers are used to record the change in voltage output from a suitable photomultiplier. A diagram of a conventional flash photolysis system is shown in Figure 1.2.1.

While UV/visible monitored flash photolysis is quite adequate for obtaining electronic spectra, transient decay kinetics and their variation with reaction conditions, little structural information is available from this technique. Since the number of infrared bands is dependent on the symmetry of molecules, finite infrared spectral shifts are associated with minor structural changes in molecules. Therefore infrared spectra have more easily accessible structural information.

Figure 1.2.1. A schematic diagram of a typical conventional flash photolysis system.

This technique is ideal for metal carbonyl compounds as CO stretching frequencies are relatively uncoupled to other vibrational modes and their positions are dependent on
the electron density on the metal\textsuperscript{18}. The system for spectral and kinetic data collection is similar to that used in the UV/visible monitored technique. Differences arise in the absorption data and obviously the monitoring beam source. The spectrometers only measure changes in infrared absorption; i.e., bands arising from the parent compound appear negative and the photoproducts as positive. Monitoring sources can be normal infrared sources such as a glowbar or the high-intensity CO laser which is tunable over the carbonyl vibrational region.

1.3 Photochemistry of MeCpMn(CO)\textsubscript{2}L, L=CO, L=PPh\textsubscript{3}

Reports on photochemical reactions involving MeCpMn(CO)\textsubscript{2}L, MeCp=(η\textsubscript{5}-CH\textsubscript{3}C\textsubscript{5}H\textsubscript{4})\textsubscript{2}, L=CO, L=PPh\textsubscript{3}, are not very common. However, reactions involving the related CpMn(CO)\textsubscript{3} complex (Cp = η\textsubscript{5}-C\textsubscript{5}H\textsubscript{5}) have been comprehensively studied and are reported to behave similarly to MeCpMn(CO)\textsubscript{3}\textsuperscript{19,20}. Photochemical reactions of the monosubstituted phosphine complex MeCpMn(CO)\textsubscript{2}PPh\textsubscript{3} are rarely reported\textsuperscript{21}. As in the case of nearly all the metal carbonyl complexes, the primary photoreaction is reported to be the dissociative loss of a CO ligand\textsuperscript{22} (Reaction 1.3.1). The primary photoproduct in the photolysis of CpMn(CO)\textsubscript{3} is also thought to be loss of a CO ligand (Reaction 1.3.2). Strohmeier et al. reported the quantum yield for this reaction to be unity\textsuperscript{5}. It is now known that the quantum yield is ~0.65 which is still quite high for dissociative loss of CO and approximates that of the isoelectronic Group VIB hexacarbonyls (Φ = 0.67\textsuperscript{19}).

\begin{alignat}{2}
\text{MeCpMn(CO)\textsubscript{3}} & \xrightarrow{hv} \text{MeCpMn(CO)\textsubscript{2}} + \text{CO} & (1.3.1) \\
\text{CpMn(CO)\textsubscript{3}} & \xrightarrow{hv} \text{CpMn(CO)\textsubscript{2}} + \text{CO} & (1.3.2)
\end{alignat}

Low temperature matrix isolation studies of CpMn(CO)\textsubscript{3} in argon\textsuperscript{23,24}, methane\textsuperscript{23,24}, methylcyclohexane/Nujol\textsuperscript{25}, and nitrogen\textsuperscript{23,24} also reveal the dicarbonyl species as the primary photoproduct. The difference in the carbonyl stretching frequencies for the
different matrices and glasses is an indication of the charge on the metal nucleus. For example, the $\nu_{\text{CO}}$ for the CpMn(CO)$_2$ fragment in argon matrix are 1972 and 1903 cm$^{-1}$ and the corresponding values in Nujol are 1955 and 1886 cm$^{-1}$. This is indicative of a 'stronger' interaction with Nujol as the CO stretching frequencies in the argon matrix approach the stretching vibration for free CO (2143 cm$^{-1}$). In the case of the nitrogen matrix a complex was formed by replacement of the lost CO ligand with dinitrogen which agreed with the band positions found in an n-heptane solution for an authentic sample of CpMn(CO)$_2$N$_2$.

Other low temperature studies on CpMn(CO)$_3$ were performed in mixed matrices. A photochemical experiment carried out on CpMn(CO)$_3$ in a CO matrix revealed no observable photochemical reactions. However, irradiation in a $^{13}$CO doped (5%) methane matrix showed that enrichment of the CpMn(CO)$_3$ complex occurs. Prolonged photolysis yielded mono-, di- and tri-$^{13}$CO enriched CpMn(CO)$_3$ as well as the expected coordinately unsaturated photofragments. Irradiation of CpMn(CO)$_3$ in a methylcyclohexane/isopentane 4:1 glass gave CpMn(CO)$_2$ and CpMn(CO) as photoproducts. The addition of ethers (L) to the glass produced CpMn(CO)$_2$(L) and CpMn(CO)(L)$_2$. A similar type experiment was performed with alcohol glasses. The production of rotamers was observed because of steric constraints involved in coordination of the alcohol to the metal centre arising from matrix interaction (Figure 1.3.1).

Photosubstitution reactions of CpMn(CO)$_3$ have been well documented and can result in the nucleophilic substitution of a CO ligand ($^{19}$) (Reaction 13.3) or oxidative addition ($^{27}$) (Reaction 13.4) depending on the nature of the entering ligand.

$$\text{CpMn(CO)}_3 + X \xrightarrow{h\nu} \text{CpMn(CO)}_2X + \text{CO} \quad (13.3)$$

$$\text{CpMn(CO)}_3 + Y-Z \xrightarrow{h\nu} \text{CpMn(CO)}_2(Y)(Z) + \text{CO} \quad (13.4)$$
Figure 13.1 The rotamers produced in the photolysis of CpMn(CO)$_3$ in a methylcyclohexane/isopentane 4:1 glass at 77K. ROR' = alcohol or ether, n = 5.

The photochemical reactive state in CpMn(CO)$_3$ is thought to be a LF state and not a MLCT state. Wrighton et al. examined the photosubstitution behavior in CpMn(CO)$_2$X (X = pyridine and substituted pyridine) complexes and the results showed that the only observed reaction was pyridine substitution (Reaction 13.3). The quantum yields for these reactions were high (Φ = 0.65). An examination of the analogous rhenium complexes showed that substitution depended to a great extent on the accepting ability of the ligand. This variation was attributed to the presence of a low lying MLCT state which could lie above or below the LF excited state depending on the nature of the ligand. For the manganese complexes, it was concluded that even though irradiation into the MLCT states produced photochemical substitution reactions of the pyridine ligands, the reactivity was consistent with a LF state. These reactions were also independent of the nature and concentration of the entering nucleophile but dependent on the nature of the metal and the leaving ligand.
The observations are characteristic of the photosubstitution reactions of d⁶ metal carbonyl complexes.

Oxidative addition products were formed in the photolysis of ($\eta^5$-MeCp)Mn(CO)₂L (L = CO, PPh₃, P(OPh)₃, P(OEt)₃, PBu₃ or PMe) in the presence of H₂SiPh₂ at -10°C to give the appropriate MeCpMn(CO)(L)(H)SiPh₂H compounds. The rates of the reaction were reported to be controlled by steric rather than electronic effects. The same authors also prepared similar hydrido silyl complexes containing Mn-H-Si three centred bonds. Reductive elimination, as in Reaction 13.5, can be observed when triphenyl silyl (Y) and hydrogen (Z) are replaced by addition of PPh₃ to produce CpMn(CO)₂PPh₃ and regenerate triphenyl silane.

$$\text{CpMn(CO)₂(Y)(Z)} + \text{L} \xrightarrow{\text{hγ}} \text{CpMn(CO)₂L} + \text{Y-Z} \quad (13.5)$$

The cyclopentadienyl ligand is inert to substitution. Photolysis of LMn(CO)₃ (L = $\eta^5$-C₅H₅, $\eta^5$-indenyl, $\eta^5$-fluorenyl) in the presence of PPh₃ has shown that changes in the $\eta^5$ ligand has little or no effect on the rates for carbonyl group substitution.

Many other photochemical reactions involving the CpMn(CO)₂ moiety are found in the literature. Photolysis of the carbene complex CpMn(CO)₂(CPh₂) in THF does not lead to any ligand substitution but to heterolytic cleavage of the Mn-carbene bond (Reaction 13.6). The photoreactive state was a carbene centred charge transfer (CT) state. In the excited CT state the complex was roughly described as containing a high spin d⁵ manganese(II) and a diphenyl carbene radical anion ligand. Photolysis in tetrahydrofuran (THF) provided evidence for this state as photochemical cleavage of the carbene ligand did not produce the expected CpMn(CO)₂(THF) solvent adduct. The carbene anion was identified by the low temperature 366nm irradiation of CpMn(CO)₂(CPh₂) in a protic solvent to produce the HCPH₂⁺ species which was subsequently identified by electron spin resonance and emission spectroscopy.
\[ \text{CpMn(CO)}_2(\text{CPh}_2) \xrightarrow{hv} \text{Mn(II)} + \text{CPh}_2^- \quad (136) \]

Intramolecular photochemical reactions have been observed on CO loss for ring substituted cyclopentadienyl manganese tricarbonyl complexes. Examples of this type of reaction are \((\text{C}_2\text{H}_4\text{CH}_2\text{OCH}_2\text{CHCH}_2)\text{Mn(CO)}_3\)\(^{32}\), in which the vinyl group on the allyloxymethyl substituent coordinates to the metal centre (Figure 13.2 (a)) and \((\text{Ph}_2\text{PCH}_2\text{CH}_2\text{C}_3\text{H}_4)\text{Mn(CO)}_3\)\(^{33}\) which forms a chelate via the phosphine group (Figure 13.2 (b)). The photolysis of tetrahydrofurfurylcymantrene at 77K in Nujol produced a dicarbonyl species in which the oxygen on the tetrahydrofurfuryl was coordinated to the manganese centre to form an intramolecular chelate complex (Figure 13.2 (c))\(^{34}\).

Several examples of dinuclear complexes formed from the photolysis of \(\text{CpMn(CO)}_3\) in the presence of a bidentate ligand are known\(^{35}\). There are two types of dinuclear species produced, ones containing metal-metal bonds, and ones with a bridging ligand with no metal-metal bonding. The metal-metal bond complexes usually have a two electron bridging ligand e.g. \(\text{CH}_2\)\(^{36}\) or \(\text{C}_8\text{H}_6\)\(^{37}\) in which one electron is donated to each metal centre. Examples of these type complexes are given in Figure 13.3 (a), (b). The bridging non-metal bonding complexes have ligands such as cyclopentadiene\(^{38}\) or hex-2,4-diyne\(^{39}\) which have two coordinating sites. These dinuclear complexes are usually formed from the reaction of photochemically produced \(\text{CpMn(CO)}_2S\) \((S = \text{donor solvent})\) with the parent complex and the bridging ligand (Figure 13.4 (a), (b)). Another example of a bridging ligand complex is \(\text{MeCpMn(CO)}_2(\mu-\text{VP})\text{MeCpMn(CO)}_2\) where \(\text{VP} = 4\text{-vinylpyridine}\)\(^{40}\) In this complex the nitrogen on the vinylpyridine ligand was \(\sigma\) coordinated to one of the manganese centres while the other was \(\eta^2\) coordinated through the vinyl group (Figure 13.4 (c)).
Figure 1.3.2. Examples of intramolecular coordination in CpMn(CO)₃ complexes
Photolysis of MeCpMn(CO)$_3$ with 4,5-dimethyl 2-phenylphosphonn yielded a dinuclear complex where a manganese dicarbonyl moiety was $\sigma$ coordinated via the lone pair on the phosphorus in the phosphonin ring and a second manganese was, by loss of its three carbonyl ligands, $\eta^6$ coordinated to the phosphonin ring already attached to the first manganese$^{41}$ (Figure 1.3.5.

(a)

(b)

Figure 1.3.3 Dinuclear species formed from the photochemical reactions of ($\eta^5$-C$_5$H$_4$R)Mn(CO)$_3$ (R = H, Me) containing a Mn-Mn bond and a two electron bridging ligand
Figure 13.4. Dinuclear species formed from the photolysis of $(\eta^5$-$C_5H_4R)\text{Mn(CO)}_3$ (R = H, Me) with bidentate bridging ligands and containing no Mn-Mn bond.
Figure 1.3.5 The unusual coordination of two manganese centres via a triphenyl phosphon bond

MeCpMn(CO)$_3$ has been observed as a photocatalyst in the cyclotrimensation of aryl isocyanates$^{42}$ Photolysis of MeCpMn(CO)$_3$ at 366nm in THF produced the solvent adduct MeCpMn(CO)$_2$(THF). Addition of isocyanate to the solution produced the cyclotrimensation product phenylisocyanurate. The THF adduct was believed to be the active catalyst.

1.4 Photochemistry of M(CO)$_5$L compounds (M = Cr, Mo, W).

The photochemically and thermally reactive states in M(CO)$_5$L (M = Cr, Mo, W) complexes is thought to be one and the same$^{43}$ Therefore both the thermal and photochemical reactions of these complexes will be discussed with emphasis being placed on the photochemical reactions. The photochemistry of M(CO)$_5$L compounds (M = Cr, Mo, W) is complicated by the fact that three photoproducts are possible and
that the ratio of the photoproducts produced is directly dependent on the nature of the monosubstituted ligand L (Reaction 141)

\[
\text{M(CO)\textsubscript{3}L} + h\nu \rightarrow \text{M(CO)\textsubscript{5}L} + \text{L} \quad (141)
\]

\[
\text{M(CO)\textsubscript{4}L} + \text{CO} \quad \text{or} \quad \text{trans-M(CO)\textsubscript{4}L} + \text{CO}
\]

The importance of the monosubstituting ligand L is reflected in the W(CO)\textsubscript{3}CS complex where thermal substitution reactions involved CO loss and the products were in the trans position\textsuperscript{44}. Irradiation of this complex at 405nm produced substitution reactions of very low quantum yield ($\Phi < 0.01$)\textsuperscript{45}. In the series where M = Cr\textsuperscript{46}, Mo\textsuperscript{46}, W\textsuperscript{47} and L = pyndine or substituted pyndine, substitution of the pyndine ligand occurs with high quantum yields ($\Phi = 0.6$). And in the case where M = Mo\textsuperscript{48}, W\textsuperscript{45} and L = PPh\textsubscript{3}, the major reaction was the loss of a CO ligand cis to L with the production of a significant amount of trans product usually in the expected statistical ratio. It is obvious that the $\pi$-accepting/donating ability of the ligand L is affecting the substitution reactions. This ability is also important in determining which isomers of the pentacoordinated photofragments are the most stable. The position of the electronic excited states determines the photoreactivity of these compounds and these are ultimately controlled by the ligand.

Matrix isolation studies of complexes of the type M(CO)\textsubscript{3}L coupled with infrared detection has provided valuable information in the identification of the photofragments produced on photolysis. The photochemical behaviour of Cr(CO)\textsubscript{3}L (L = PMe\textsubscript{3}\textsuperscript{49}, PCl\textsubscript{3}\textsuperscript{50}) was examined in an argon matrix at 12K\textsuperscript{49}. CO loss was observed for L = PMe\textsubscript{3} and unique ligand loss for L = PCl\textsubscript{3}. These results were explained by the existence of two photoactive states. The position of these states was dependent on the ability of the ligand L to undergo $\pi$ backbonding with the metal centre. Studies of
Ci(CO)₅(pyridine) in argon matrix at 10K have been carried out with the dominant photoreaction being loss of the pyridine ligand at irradiation wavelengths greater than 334nm and loss of CO at wavelengths less than 313nm⁵⁰,⁵¹.

Irradiation of W(CO)₅(alkene) at 77K in methylcyclohexane produced evidence that twice the amount of alkene was lost on 313nm excitation than on irradiation at 254nm². Longer wavelength excitation favours alkene loss by virtue of the fact that alkenes are weaker field ligands than CO and therefore the lowest excited state has more d₂ character. The wavelength dependency was consistent with reactivity from different one-electron excited states, the lower one having more d₂ character and the upper one having more d₂,₂ character even though there is little difference in the alkene and CO bonding (σ donor, π acceptor). Photolysis (436nm) of Cr(CO)₅(pyrazine) in an argon matrix at 10K gave one product, Cr(CO)₅, which was identified by infra red spectroscopy⁵¹. Irradiation at 229nm also afforded one product. However, this product was the cis form of Cr(CO)₅(pyrazine). The difference in product formation at the two wavelengths was attributed to the different energies of the σ antibonding d₂ and d₂,₂ orbitals. Short wavelength irradiation would preferentially result in the occupation of the d₂,₂ antibonding orbital causing loss of a CO ligand to form cis-Cr(CO)₄(pyrazine). On the other hand photolysis at longer wavelengths results in the population of the antibonding d₂ orbital and the result is to labilize the pyrazine ligand.

Thermal substitution may occur via one or several competing pathways⁵³. The first and the most common mechanism was dissociation of a CO or other ligand as the rate determining step. Other mechanisms included associative processes, ligand migration to an adjacent CO and radical abstraction. The general rate term for thermal reactions in metal carbonyl complexes is,
\[
\frac{-d[R]}{dt} = [R](k_1 + k_2[L])
\]

where \([R]\) is the concentration of the thermally generated reactive species. The rate law indicates both associative and dissociative processes. The term \(k_2\), first order in \(R\) and in entering ligand \(L\), was often of negligible importance and therefore indicating the dominance of dissociative substitution reactions. The magnitude of \(k_2\) was determined by the basicity of ligand \(L\), the covalent radius of the metal atom in the complexes and obviously the concentration of \(L\). Similar two term rate laws have been observed for photochemical systems\(^{54,55}\).

Two further questions arise from the dissociation process with respect to \(M(\text{CO})_5L\) (\(M = \text{Cr}, \text{Mo}, \text{W}\)) complexes, (a) what are the influences of the other ligands in the complex on the dissociation rate and (b) what is the effect of the departing ligand on those which remain. The substitution of a CO ligand by \(\text{PPh}_3\) in \(\text{Cr}(\text{CO})_6\) increased the lability of the \(\text{cis}\) CO groups by a factor of 300\(^{53}\). Similar rate changes were seen in \(\text{Mo}(\text{CO})_5\text{PPh}_3\)\(^{56}\) and in \(\text{cis} - \text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{pipene})\)\(^{57}\). This indicates that \(\text{cis}\) labilisation is not confined to CO loss. In addition the extent of the \(\text{cis}\) labilisation appears to be influenced by the degree of the \(\pi\) bonding between the metal and the CO \textit{trans} to a weaker \(\pi\) accepting ligand. The presence of a strong electron releasing ligand produces the greatest labilisation of \textit{trans} ligands. Ligands which are weaker \(\pi\) acceptors than CO labilise preferentially in the \(\text{cis}\) position. This is a generalisation as there is difficulty in separating the steric and electronic ground state effects and their importance in ligand substitution reactions.

Crystal structure data on the \(\text{Cr}(\text{CO})_5L\) (\(L = \text{phosphine}\)) complexes indicate that the shortest Cr-P bond is found for the strongest \(\pi\) accepting ligand (\(\text{P(OPh)}_3\))\(^{58}\) < \(\text{P(CH}_2\text{CH}_2\text{CN)}_3\))\(^{59}\) < \(\text{PPh}_3\)\(^{58}\). A similar series was noted for \(\text{Mo}(\text{CO})_5L\) complexes\(^{60}\). Therefore the bond distances in the complexes may reflect an energy minimum.
composed of the maximum orbital overlap with minimum steric hindrance of the ligand.

* cis-trans*/*trans-cis* isomerisation of the reaction intermediates in thermal and photochemical reactions of $\text{M(CO)}_5\text{PPPh}_3$ has been noted in many cases. The five coordinate intermediates are normally fluxional on the timescale of their expected lifetime. Therefore the site of CO loss is not necessarily the position where the substituting ligand enters. Daresbourg and Murphy reported that in the photolysis of $\text{Mo(CO)}_5\text{PPPh}_3$ with $^{13}\text{CO}$ the $\text{Mo(CO)}_4\text{PPh}_3$ intermediate could undergo rearrangement from the higher energy $C_{4v}$ isomer, with the PPh$_3$ in the axial position, to the more stable $C_4$ configuration. In the photolysis of $\text{Mo(CO)}_5$(amine) with $^{13}\text{CO}$ the reaction yields exclusively the *cis*-Mo($\text{CO})_4$($^{13}\text{CO}$)(amine) species. The explanation forwarded was that the rate constant for the rearrangement process to the more favourable $C_4$ isomer in the amine complexes must be greater than the rate constant for the photochemical substitution reaction. Therefore the rate constant for rearrangement in the triphenylphosphine complex must be of the same order of magnitude as the reaction rates of the photochemically produced $C_{4v}$ isomers and so ligand scrambling can occur. Other evidence points to steric crowding as an influence on the reaction intermediate. *cis*-Mo($\text{CO})_4$P(OMe)$_3$(pipendine) reacts with P(OMe)$_3$ to form mainly *trans*-Mo($\text{CO})_4$(P(OMe)$_3$)$_2$. This is in contrast to its reaction with $^{13}\text{CO}$ where the only product is *cis*-Mo($\text{CO})_4$($^{13}\text{CO}$)P(OMe)$_3$.

The relative size of the phosphorus ligands are known to affect the reactivities of the transition metals to which they are attached. To quantify this reactivity, Tolman introduced the concept of the cone angle $\theta$. It is defined as the apex angle of a right cylindrical cone centred 2.28 Å from the centre of a phosphorus atom that just touches the van der Waals radius of the outermost atoms. Mosbo *et al.* conducted a study on the relative size of the phosphorus ligands on the reaction of W($\text{CO})_5$(L)(pyndine) (L
= phosphines) with various phosphines. The distribution of the cis and trans products were measured by 31P NMR and the ratios were found to decrease as the cone angle of the ligand increased. Furthermore, observations in the synthesis of the W(CO)₅(L)(pyridine) complex from W(CO)₄(pyridine)₂ and the desired phosphine ligand demonstrated that large phosphine ligands (i.e., ones with large cone angles) facilitated the loss of the second pyridine ligand. This was in contrast to the smaller phosphines, which produced predominantly the monopyridine product indicating that the larger ligands accelerated loss of the cis ligand upon initial coordination displacing one of the pyridines.

Daresbourg examined the substitution of L from cis-Mo(CO)₄L₂ by CO (L = Phosphine) cis-Mo(CO)₄L₂ reacted with ¹³CO to form specifically the cis ¹³CO derivative. The rate of dissociation was enhanced by the size of the phosphorus ligand and therefore with Tolman cone angle. In Mo(CO)₅L complexes CO loss was found to occur preferentially from equatorial sites and increased in the order PPh₃ > P₄-n-Bu₃ > P(OCH₂)₂CC₂H₅. Experiments in the substitution of trans-Mo(CO)₅L with ¹³CO produced cis ¹³CO labelled product indicating fluxionality with respect to the loss of a ligand trans to the remaining ligand. This indicated that the rate of cis-trans isomerisation was slower than the dissociative loss of PPh₃ from cis-Mo(CO)₅(PPh₃)₂. Smaller phosphorus ligands, e.g., P(n-Bu)₃, PEt₃, underwent isomerisation by non-bond breaking processes which implied that the barrier to rotation with smaller ligands was less than Mo-P bond cleavage.

The metal centre is not necessarily the site for attack in metal carbonyl complexes as Basolo et al. reported on the mechanism for the CO substitution of Mo(CO)₅PPh₃ with L in the presence of (CH₃)₃NO. The reaction was believed to take place by the rate determining attack of (CH₃)₃NO on a CO atom cis to the phosphorus ligand in the complex. This was followed by rapid loss of CO₂ and the
uptake of PPh₃ present in the solution to form \textit{cis}-Mo(CO)₄(PPh₃)₂ exclusively. The sole production of the \textit{cis} product was explained by the tighter bonding of the CO \textit{trans} to the unique ligand in the pentacarbonyl species because the ligand was not a good π acceptor relative to CO. This greater electron density on the \textit{trans} CO, with respect to the \textit{cis} CO ligands, made it less susceptible to nucleophilic attack by (CH₃)₃NO. The oxygen atom transfer takes place because the carbon atoms of CO have a partial positive charge while the oxygen atom of (CH₃)₃NO has a partial negative charge. The different reactivities of the Group VIB metal centres to the (CH₃)₃NO has been attributed to the σ donor capacities of CO in the complexes to the metal centre (W > Mo > Cr) and to the metal size (Cr < Mo < W). This indicates that there was a correlation between π backbonding in the metal complexes and the reactivity of the carbon atom on CO to nucleophiles.

Irradiation into the LF band is believed to produce the photochemistry observed with these complexes i.e. ligand loss. The MLCT band is reported as being unreactive with any photochemistry associated with MLCT irradiation arising from intersystem crossing to the reactive LF state. Therefore the depopulation of the dπ orbitals involved in the backbonding to a ligand orbital does not appear to cause sufficient destabilization to cause M-CO dissociation. LF excitation would result in the population of a σ* level (either dₓ² or dₓ²-y² in origin) which would be expected to labilise a σ donating ligand. In addition, the promoted electron would also have been involved in the backdonation of electron density from the metal into the ligand orbitals and so affect the metal-ligand π bonding. Therefore any ligand involved in the σ and π bonding would be expected to be labilised upon excitation into the LF band. This in effect means that CO loss and unique ligand loss would be expected in the irradiation of M(CO)₅PPh₃ (M = Cr, Mo, W) complexes. A point to note is that irradiation into the MLCT band of W(CO)₄(1,10 phenanthroline) in the presence of PEt₃ produces photochemistry \textit{vs} an associative mechanism. This means in effect that the
depopulation of the weakly backbonding orbitals producing a partially oxidised metal centre provides a route for an associative mechanism. This may explain in part why the rate laws in the photosubstitution of metal carbonyl complexes have two competing terms, one dissociative and one associative (vide supra).

The ligand photosubstitution reactions in THF solutions of Mo(CO)₅PPh₃ at 366 nm in the presence of PPh₃ and ¹³CO have shown that both cis and trans products were observed. The yield of the cis product was much higher than the corresponding trans analogue in the reactions with both ligands. In the reaction with ¹³CO a small quantity of ¹³CO enriched Mo(CO)₆ was produced indicating loss of the unique ligand trans-Mo(CO)₅(PPh₃)₂ photoisomerised to the cis form by loss of PPh₃, rearrangement to the C₄ form and recapture of PPh₃. Thermal rearrangement back to the trans isomer was possible at elevated temperatures where the more energetic form of the intermediate (C₄v) predominates. Therefore, the loss of a trans ligand was thermodynamically less favourable at ambient temperature with rearrangement of the intermediate to the less energetic C₄ form.

The excitation wavelength is also important in ligand labilisation. In many cases wavelength dependent substitution of M(CO)₅L, (M = Mo, L = PPh₃, M = W, L = pyridine, L = alkene) complexes has been observed. In Mo(CO)₅PPh₃ the reaction displays a significant decline in quantum efficiency on irradiation at shorter wavelengths. The reason proposed was that longer wavelength irradiation promotes an electron preferentially into a dₓ² antibonding orbital and therefore labilise along the z axis as opposed to shorter wavelength irradiation which could populate both the antibonding σ* orbitals and labilise on all axes. In the W(CO)₅(pyridine) case, irradiation across the region of LF singlet absorption produces an increase in quantum yield as the excitation wavelength decreases. Irradiation into the LF triplet region produces quantum yields smaller relative to the LF singlet region. This was
explained in terms of more efficient substitution on irradiation into the lower electronic state $^1E$ rather than the upper state $^1A$ ($^1E$ and $^1A$ are components of $C_4v$ symmetry) $^1E$ irradiation gives an excited state relaxation pathway which releases a pyridine ligand, $^1A$ excitation leads to a relaxation pathway which exposes a CO ligand not a pyridine ligand.

Wavelength dependence was also observed for the photochemical substitution of $W(CO)_5L \ L = \text{pyridine, piperidine}$ with 1-hexene$^{70}$ This dependency was attributed to solvent effects as the quantum yields varied from solvent to solvent In the piperidine and pyridine complexes, irradiation at 436nm populates the $^1E$ excited state directly. This was thought to be the reactive state as excitation at this wavelength produces higher yields However the yields were less than unity and it was assumed that competition between intersystem crossing to the $^3E$ (488nm) state and radiationless decay were responsible The quantum yields varied from 0.68 in CC1$_4$ to 0.41 in CH$_2$Cl$_2$ This was accounted for by collisions with the solvent molecules The CC1$_4$ molecule is considerably larger than the corresponding CH$_2$Cl$_2$ molecule. It was suggested that collisions with CC1$_4$ lead to inefficient energy transfer which prolongs the excited state and allows for greater internal conversion between the $^1A$ and the $^1E$ states and greater intersystem crossing between $^1E$ and $^3E$ states This would explain the observation that the quantum yield decreases with decreasing excitation wavelength therefore allowing an increase in intersystem crossing to the $^3E$ state which was less reactive.

In time resolved spectroscopy the solvent interactions have been the subject of much interest Flash photolysis studies on the Group VIB metal hexacarbonyls has provided evidence that the $M(CO)_5$ photoproducts are solvated in alkane solutions within picoseconds of irradiation to form $M(CO)_5S$ ($S = \text{alkane}$)$^{71}$ Flash photolysis studies of Cr(CO)$_6$ in alcohol$^{72}$ and alkyl bromide$^{73}$ solvents demonstrated that the
coordinately unsaturated photofragment, generated in the flash reacts with the solvent molecule either at the alkane end or the functional end (i.e., -OH or Br). The alkane intermediate then rearranges to a more stable complex coordinating either to the oxygen of the hydroxyl group or to the bromide atom depending on the solvent used. Similar observations were for noted for picosecond studies carried out in tetrahydrofuran solvent. In alkane nitrite solvents, the photofragment coordinates preferentially at the cyano end of the solvent molecule. The reaction dynamics were faster in nitrite solvent than in the corresponding alcohol series. This was accounted for by the preferential coordination of the pentacarbonyl photofragment to the dipolar end of the nitrite solvent molecule. Photolysis in benzene solution produces a Cr(CO)₅(η²-benzene) complex where the benzene was coordinated to Cr via an 'isolated' carbon double bond. The strength of the solvent interaction with the photo-generated metal pentacarbonyl fragment appears in the order perfluoralkane < alkane < arene < alcohol < nitrite. Two mechanisms were proposed for the displacement of the solvent molecule by ligands from the metal/solvent complex. The first process involved an interchange between the solvent and the incoming ligand (path A). The second involved dissociation of the solvent molecule from the photogenerated metal complex followed by a reaction with the ligand (path B).

\[
\begin{align*}
\text{Cr(CO)}_5(\text{solvent}) & \xrightarrow{k_1} [\text{Cr(CO)}_5] + \text{solvent} \\
\text{A interchange} & \xrightarrow{k_3[L]} \text{solvent} \\
\text{B dissociative} & \xrightarrow{k_2[L]} \text{Cr(CO)}_5(L)
\end{align*}
\]

The contribution of each mechanism to the overall reaction was influenced by the type of solvent and the size of the metal atom. An interchange mechanism was proposed for the solvent displacement of n-heptane and a dissociative mechanism for arenes based
on the observed volumes of activation. The contribution of the solvent interchange process was found to increase in the order Cr < Mo - W.

Flash photolysis of the $M(CO)_5L$ ($L$ = ligand) complexes has been investigated but only in modified experiments where one of the CO ligands was replaced by a nitrogen based ligand which would be labilized preferentially to a CO and so reduce the number of primary photoproducts. Dobson et al. carried out pulsed laser time resolved studies on $Mo(CO)_4(NP)$ ($NP = 1$-(diethylamino)-2-(diphenylphosphino)ethane). The reaction proceeds by cleavage of the Mo-N bond to form a solvated complex where the vacant coordination sites were $cis$ and $trans$ to the coordinated phosphorus. The formation of a $trans$ species from the parent complex was indicative of a ligand scrambling process. This process is thought to occur prior to solvation, which when measured for other carbonyl complexes e.g. Cr(CO)$_5$, using picosecond spectroscopy occurred in under 1ps. In other words, the excited state species, following loss of a carbonyl ligand, decayed by a ligand randomization process to form two square pyramidal species, one with the phosphorus ligand in the axial site and one with the ligand in an equatorial site, at a rate faster than the solvation process. The reactivities of the $cis$ and $trans$ solvated complexes were different by a factor of 100. The effect of the phosphorus atom on the $trans$ site would be more stabilising on the solvent-metal interaction because of the electron releasing nature of the phosphorus atom. Similar type experiments were also carried out by Dobson et al. on $cis$-$W(CO)_4(L)(L')$, where $L$ = PPh$_3$ and $L'$ = pipendine, using both time resolved UV/visible and infra red detection. He observed loss of the pipendine ligand to form $[cis$-$W(CO)_4L]$ which reacted with chlorobenzene to form the solvated intermediate $cis$-$W(CO)_4L$(chlorobenzene). This subsequently reacted with $L''$ ($L''$ = phosphines) to form the $cis$-$W(CO)_4LL''$ complex which may undergo thermal isomensation to the $trans$ product.
The investigation of the lower metal to ligand charge transfer state of W(CO)$_5$(4-cyanopyndine) was carried out using time resolved infra red spectroscopy. Visible irradiation of the complex resulted in a shift to higher frequency for the CO stretching vibrations indicating that an electron was lost from the metal centre. This excited state decays to the ground state via an LF state and fragments into W(CO)$_5$ and 4-cyanopyndine.

1.5 Summary

Both the manganese and the Group VIB complexes are very photoreactive and the dominant photoreaction appears to be the loss of a CO ligand. The $\pi$ accepting/donating effect of the unique ligand in the pentacarbonyl compounds affects the extent of the CO loss. The cyclopentadienyl ring is substitutionally inert in the manganese carbonyl complexes. Ligand loss in both types of compounds is thought to occur via the LF state by promotion of an electron from the $t_{2g}$ orbitals to the antibonding $e_g$ orbitals. In the Group VIB complexes these $e_g$ orbitals are split and this splitting is believed to account for the wavelength dependency observed in their photochemical reactions. The lowest energy MLCT states appear to be unreactive but evidence exists that implicates these states as accounting, in part, for the associative term in the two term rate law noted in the photochemical reactions of the Group VIB systems, particularly the larger metal complexes.
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CHAPTER 2

355nm LASER FLASH PHOTOLYSIS OF MeCpMn(CO)₃ AND MeCpMn(CO)₂PPh₃ WITH UV/VISIBLE MONITORING
2.0 Laser flash photolysis of MeCpMn(CO)₃

The laser flash photolysis with UV/visible monitoring of MeCpMn(CO)₃ (MeCp = \( \eta^5-C_5H_4CH_3 \)) in cyclohexane at 355nm produced evidence for the formation of two transient species. The first transient species was identified as the solvated MeCpMn(CO)₂(cyclohexane) complex from its UV/visible difference spectrum and its reaction kinetics. A second transient species was observed and similarly identified as the dinuclear MeCp₂Mn₂(CO)₃ complex.

2.1 Electronic spectrum of MeCpMn(CO)₃

A UV/visible spectrum of MeCpMn(CO)₃ in cyclohexane solution is shown in Figure 2.11. The low energy absorption spectrum of MeCpMn(CO)₃ is dominated by a band centred at 330nm. This band has been assigned as a charge transfer (CT) transition, having mainly Mn \( \rightarrow \) (\( \eta^5-C_5H_4CH_3 \)) CT character.

![UV/visible spectrum of MeCpMn(CO)₃](image)

**Figure 2.11** A UV/visible spectrum of MeCpMn(CO)₃ (1.08 x 10⁻³ mol dm⁻³) in cyclohexane.
This region of the spectrum is also thought to contain the LP transitions which are obscured by the more intense Mn \( \rightarrow \left( \eta^1-C_7H_4CH_3 \right) \) CT transition. The large absorption at ~250nm is probably a Mn \( \rightarrow \pi^*\text{CO} \) CT transition.

2.2 Primary photoproduct: MeCpMn(CO)_2(cyclohexane)

Photolysis of MeCpMn(CO)_3 in hydrocarbon glasses at 80K is reported to undergo loss of CO as the primary photoprocess. The resulting photoproduct has been identified by infrared spectroscopy as the coordinately unsaturated 16e\(^-\) complex MeCpMn(CO)_2. These highly reactive 16e\(^-\) species of metal carbonyl complexes are known to coordinate weakly to the matrices and even those consisting of inert noble gases. The coordinately unsaturated isoelectronic M(CO)_5 (M = Cr, Mo, W) complexes are now recognised as coordinating to solvent molecules in solution photolysis. This rate of this coordination has been measured, using picosecond spectroscopy, in alkane solvent to occur within 1ps of the flash. Consistent with CO loss from the M(CO)_6 complexes the isoelectronic manganese complex CpMn(CO)_3 is also known to lose a CO ligand and coordinate a solvent molecule when photolyzed in solution. MeCpMn(CO)_3 has been shown to behave similarly to CpMn(CO)_3 in photochemical reactions, i.e. the primary photoproduct is reported to be loss of a CO ligand. Therefore on the 355nm photolysis of MeCpMn(CO)_3 (ε = 650 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)) the first transient species observed was MeCpMn(CO)_2(cyclohexane) and this species was probably formed within the duration of the flash (10ns) as in the case of the Group VIB pentacarbonyl solvated species. The reaction is summarized in Equation 2.2.1.

\[
\text{MeCpMn(CO)}_3 \xrightarrow{hv} \text{MeCpMn(CO)}_2 + \text{CO} \xrightarrow{S} \text{MeCpMn(CO)}_2S \quad (2.2.1)
\]

S = cyclohexane
Figure 2.2.1 Transient for the decay of the MeCpMn(CO)$_2$(cyclohexane) complex at 640nm

Figure 2.2.2 A UV/visible difference spectrum of MeCpMn(CO)$_2$(cyclohexane) obtained in cyclohexane solution 1 $\mu$s after the laser pulse
A typical transient obtained in the 355nm photolysis of MeCpMn(CO)$_3$ monitored at 640nm is shown in Figure 2.1 where the decay curve corresponds to the decay of the solvated complex MeCpMn(CO)$_2$(cyclohexane). This assignment can be supported by evidence from the 308nm TRIR (TRIR = Time Resolved Infra Red) spectroscopy studies of CpMn(CO)$_3$ in hydrocarbon solvents where the first observable species was the solvated CpMn(CO)$_2$S (S = n-heptane$^6$) complex. A parallel study of CpMn(CO)$_3$ carried out in cyclohexane solution using UV/visible detection obtained a UV/visible difference spectrum of the solvated complex CpMn(CO)$_2$(cyclohexane) 5μs after the flash. This spectrum consisted of a broad band with a maximum near 580nm. The UV/visible difference spectrum of MeCpMn(CO)$_2$(cyclohexane) (Figure 2.2.2) has two maxima at 290nm and 580nm. The broad absorption at 580nm is similar to that obtained for CpMn(CO)$_2$(cyclohexane). The region less than 300nm was not measured in the CpMn(CO)$_3$ experiment so the strong absorption at 290nm was not observed in the spectrum obtained for CpMn(CO)$_2$(cyclohexane)$^6$. The valley in the UV/visible spectrum of MeCpMn(CO)$_3$ (Figure 2.1.1) corresponded to the maximum at 290nm for MeCpMn(CO)$_2$(cyclohexane) in the UV/visible difference spectrum.

As with CpMn(CO)$_2$S (S = cyclohexane$^6$, n-heptane$^6$) the addition of CO to the solution reduced the lifetime of the solvated complex but had little effect on its overall yield. However, the second order rate constant for the reaction of MeCpMn(CO)$_2$(cyclohexane) with CO (Figure 2.2.3) was twice that of the corresponding rate for the unsubstituted nng complex CpMn(CO)$_2$(cyclohexane) (Table 2.2.1). In the manganese complexes, the electron donating effect of the methyl substituent on the cyclopentadienyl nng should decrease the reaction rate by forming a more stable manganese dicarbonyl complex. This should increase the stability of the dicarbonyl photofragment and so decrease its reaction rate. However, the opposite was observed and this suggests that steric effects are involved in the coordination of cyclohexane to the metal centre.
Figure 2.2.3 A plot of concentration of CO (mol dm$^{-3}$) against the observed rate constant for the reaction of CO with the MeCpMn(CO)$_2$(cyclohexane) complex at 298K
<table>
<thead>
<tr>
<th>(C₅H₄R)Mn(CO)₂S</th>
<th>CO</th>
<th>(C₅H₄R)Mn(CO)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=H</td>
<td>3.4 x 10⁵</td>
<td>1.1 x 10⁶</td>
</tr>
<tr>
<td>R=Me</td>
<td>7.2 x 10⁵</td>
<td>1.08 x 10⁶</td>
</tr>
</tbody>
</table>

Table 2.2.1 Second order rate constants (dm³ mol⁻¹ s⁻¹) for the reaction of (C₅H₄R)Mn(CO)₃S (S = cyclohexane) with CO and parent compound in cyclohexane solution *ref 6

This trend was also observed in the TRIR studies of pentasubstituted cyclopentadienyl manganese tricarbonyl complexes in n-heptane solution® The two fold increase in the second order rate observed in these experiments for the monomethylsubstituted complex in cyclohexane corresponded to a two fold increase for the pentamethylsubstituted complex in n-heptane. This suggests that the orientation of the single methyl group on the cyclopentadienyl ring has a steric influence on the solvent coordination site and that this effect is independent of the number of methyl substituents. Therefore this indicates that the substitution on the cyclopentadienyl ring affects the rates of reaction of these solvated intermediates and that it is more likely to be a steric effect rather than an electronic one.

An interesting point to note is the difference in rate constants between experiments carried out in n-heptane and cyclohexane solutions. The rates observed in n-heptane are approximately twice as fast as those observed in cyclohexane. This shows that different interaction energies are involved in the coordination of cyclohexane to the metal as chemically both solvents are the same, differing only in shape. This difference has also been noted indirectly in photoacoustic calorimetry experiments of the metal-ligand bond dissociation energies of CpMn(CO)₃ in n-heptane⁹ Using previously obtained activation parameters for the substitution
reaction of $\text{CpMn(CO)}_2(\text{cis}-\text{cyclooctene})$ by $\text{PPh}_3$ in methylcyclohexane and comparing it to data which they calculated in n-heptane they found that the activation energy for the Mn-ligand bond strength was 42 kJ mol$^{-1}$ greater in methylcyclohexane solution than in the corresponding n-heptane solution. This suggests that the higher activation energy associated with methylcyclohexane may be attributed to stronger coordination of the methylcyclohexane molecule to the metal centre and perhaps to steric effects or a different mechanism of desolvation.

The possibility exists of photochemical nng slippage as a primary photoprocess. However, photochemically induced nng slippage has not been observed in $\eta^3$-cyclopentadienyl coordinated manganese complexes. The $\eta^3$ coordinated nng slipped dianion $[\eta^3-\text{MeCpMn(CO)}_3]^2-$ has been synthesised and indicates that nng slippage in $\text{MeCpMn(CO)}_3$ appears to be a function of charge on the metal centre. If nng slippage did occur in the photolysis of $\text{MeCpMn(CO)}_3$, this species would be expected to be stabilised under 1 atm atmosphere of CO, forming a tetracarbonyl complex. No new transients were observed in photolysis experiments under CO.

2.3 Secondary photoprocess: $\text{MeCp}_2\text{Mn}_2(\text{CO})_5$

The second transient species observed in the 355nm laser flash photolysis of $\text{MeCpMn(CO)}_3$ has been attributed to the dinuclear $\text{MeCp}_2\text{Mn}_2(\text{CO})_5$ species. The UV/visible difference spectrum obtained at 1700μs for the longer lived transient decay (Figure 23.1) was identical to that which was observed for the $\text{CpMn(CO)}_3$ system with two maxima at 360nm and 530nm. The 360nm region of the spectrum is often assigned to metal $\sigma$-$\sigma^*$ transitions in dinuclear species and the presence of the methyl group on the cyclopentadienyl nng should not affect this transition. The corresponding TRIR spectrum for the $\text{CpMn(CO)}_3$ system revealed four CO bands which were assigned to the single carbonyl bridging $\text{Cp}_2\text{Mn}_2(\text{CO})_5(\mu\text{-CO})$ complex.
MeCpMn(CO)₃ has often been reported to have photochemical behaviour very similar to CpMn(CO)₃⁷ Therefore it was unlikely that MeCpMn(CO)₃ formed a different dinuclear complex given the close agreement in the UV/visible difference spectra.

The MeCp₂Mn₂(CO)₅ complex must be formed by reaction of the solvated primary photoprodut MeCpMn(CO)₂(cyclohexane) with unreacted parent (Reaction 2 3 2).

\[
\text{MeCpMn(CO)₂(S) + MeCpMn(CO)₃ \rightarrow S \rightarrow MeCp₂Mn₂(CO)₅} \quad (2 3 2)
\]

\( S = \text{cyclohexane} \)

The transient in Figure 2 3 2 shows the 'grow-in' of the dinuclear species As in experiments carried out on the CpMn(CO)₃ complex the rate of reaction of MeCpMn(CO)₂(cyclohexane) was found to increase linearly with increasing MeCpMn(CO)₃ concentration (Figure 2 3 3) The second order rate constant for this reaction was \( 1.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). This was consistent with \( 1.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for CpMn(CO)₃. Kinetic observations in the photoreactions of various pentasubstituted cyclopentadienyl manganese compounds in n-heptane indicated that PPh₃ reacts with the solvated intermediates of these complexes at the same rate regardless of the cyclopentadienyl substitution. This was attributed to the steric factors in the approach of the PPh₃ ligand. Similarly large steric interactions would be expected in the reaction of MeCpMn(CO)₂S (S = cyclohexane) with the parent complex. This would explain the close second order rate constant agreement between the reaction of the nng substituted and unsubstituted cyclopentadienyl manganese dicarbonyl solvent complexes with their respective parent complexes.

The decay of the dinuclear species was dependent on the concentration of CO (Figure 2.3.4) The CO dependence indicated that the dinuclear species reacted with CO in solution to regenerate parent complex (Reaction 2 3 3)
Figure 2.3.1 A UV/visible difference spectrum of MeCp$_2$Mn$_2$(CO)$_5$ in cyclohexane obtained after 1700$\mu$s

MeCp$_2$Mn$_2$(CO)$_5$ + CO $\rightarrow$ 2MeCpMn(CO)$_3$ (2.3.3)

A typical transient for the decay of the dinuclear species is shown in Figure 2.3.5. The second order rate constant for this reaction was calculated as 5.733 x 10$^3$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$. The lifetime of this species (~80ms) was longer than that observed for the Cp$_2$Mn$_2$(CO)$_5$ complex (~50ms). This extra stability is most likely from the presence of the electron donating methyl group on the cyclopentadienyl ring.

Activation parameters have been calculated for the reaction of MeCpMn(CO)$_2$ (cyclohexane) with parent compound (Figure 2.3.6). The value for $E_{\text{act}}$ of 34.5 kJ mol$^{-1}$ was very similar to the value calculated for the reaction of the CpMn(CO)$_2$(cyclohexane) species with parent complex of 32 kJ mol$^{-1}$. In a study of the activation parameters for CpMn(CO)$_2$(cyclohexane) with various ligand types, the value for the activation energies showed no significant difference from 30 kJ mol$^{-1}$. 13
This value was very similar to the value reported for the low temperature oxidation of a range of \( R_3SiH \) compounds to \( \text{CpMn(CO)}_3 \). The \( \Delta S^f \) value for the reaction with parent complex was slightly negative. This indicates that the reaction was associative in nature. However \( \Delta S^f \) is subject to large errors and the data were inconclusive.

2.4 Infra red monitored photolysis of \( \text{MeCpMn(CO)}_3 \)

Infra red experiments involving solution cell laser photolysis (355nm) of \( \text{MeCpMn(CO)}_3 \) in argon degassed cyclohexane indicate the formation of 5 new bands (Figure 2.4.1). These bands to some extent are in agreement with the \( \nu CO \) 's obtained in TRIR experiments in n-heptane solution and in low temperature matrix isolation experiments at 77K in nujol (Table 2.4.1). Differences in the frequencies could be accounted for by the difference in solvent and in timescale in the recording of the spectra. The dinuclear species observed in the time resolved experiments had a lifetime...
of ~80 ms The unknown species was observed to have a longer lifetime as its infra red spectrum was recorded ~30 seconds after 355 nm photolysis with the laser. The lifetime of this species indicated that it was not the MeCp₂Mn₂(CO)₄(μ-CO) complex proposed in the photolysis of MeCpMn(CO)₃. It was therefore another dinuclear species perhaps formed from the thermal decay of the MeCp₂Mn₂(CO)₄(μ-CO) dinuclear complex. The lower frequencies could be accounted for by the extra electron density on the metal centre because of the donating effect of the methyl group on the cyclopentadienyl ring. The presence of a weak vibration at 1777 cm⁻¹ shows that this photoproduct contained a bridging carbonyl ligand with the same frequency as the Cp₂Mn₂(CO)₃ complex. The close agreement of the bands in Table 2.4.1 indicated that this species may be a cis or trans analogue of MeCp₂Mn₂(CO)₄(μ-CO). The species observed in the time resolved experiments may have the cyclopentadienyl rings in a cis configuration while the species observed in the infra red experiments may be the more stable trans analogue.

<table>
<thead>
<tr>
<th>Compound</th>
<th>vCO terminal (cm⁻¹)</th>
<th>vCO bridge (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂Mn₂(CO)₅⁺</td>
<td>1993, 1955, 1934,</td>
<td>1777</td>
</tr>
<tr>
<td></td>
<td>1907</td>
<td></td>
</tr>
<tr>
<td>MeCp₂Mn₂(CO)₅⁻</td>
<td>1973, 1948, 1920,</td>
<td>1762</td>
</tr>
<tr>
<td></td>
<td>1885</td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td>1991, 1963, 1907,</td>
<td>1777</td>
</tr>
<tr>
<td></td>
<td>1880</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4.1 Infra red data for the vCO of the dinuclear species from the photochemical reactions of CpMn(CO)₃. *Ref 6 in n-heptane solution after 1500 μs. †Ref 13 at 77K in nujol. ‡this work in cyclohexane solution.
Figure 23.3 Plot of $k_{obs}$ for the reaction of MeCpMn(CO)$_3$(cyclohexane) against the initial concentration of MeCpMn(CO)$_3$ in cyclohexane at 298K.
$k_{[CO]} = 5.733 \times 10^3 \pm 73.2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

Intercept = $12.89 \pm 0.6 \text{ s}^{-1}$

Corr coeff = 0.999

Figure 2.3.4 Plot of CO concentration (mol dm$^{-3}$) against the observed rate constant for the decay of the dinuclear MeCp$_2$Mn$_2$(CO)$_5$ complex at 298K
Figure 2.3.5 Transient for the decay of MeCp₂Mn₂(CO)₅ monitored at 370nm under 10 atmosphere of argon
\[ \frac{1}{T} \times 10^{-3} \quad \ln k_{obs} \quad \ln \frac{k_{obs}}{[M]^a} \quad \ln \frac{k_{obs}}{[M]^a T} \]

<table>
<thead>
<tr>
<th>( \frac{1}{T} \times 10^{-3} )</th>
<th>( \ln [M]^a )</th>
<th>( \ln \frac{k_{obs}}{[M]^a T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5211</td>
<td>8.521</td>
<td>9.410</td>
</tr>
<tr>
<td>3.4783</td>
<td>8.705</td>
<td>9.542</td>
</tr>
<tr>
<td>3.4423</td>
<td>8.888</td>
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</tr>
<tr>
<td>3.3670</td>
<td>9.173</td>
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<tr>
<td>3.3445</td>
<td>9.347</td>
<td>10.084</td>
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<tr>
<td>3.3058</td>
<td>9.360</td>
<td>10.086</td>
</tr>
<tr>
<td>3.2573</td>
<td>9.637</td>
<td>10.348</td>
</tr>
</tbody>
</table>

\( a = [M] \) concentration of MeCpMn(CO)\(_2\) = 1.6 x 10\(^{-3}\) mol dm\(^{-3}\)

Arrhenius plot

slope = -4148 ± 207  
intercept = 2314 ± 0.7  
Corr. Coeff = 0.994

Eyring plot

slope = -3853 ± 207  
intercept = 229 ± 0.704  
Corr. Coeff = 0.993

\( E_{act} = 34.5 \pm 1.7 \) kJ mol\(^{-1}\)  
\( \Delta H = 32.0 \pm 1.7 \) kJ mol\(^{-1}\)  
\( \Delta S = -7.5 \pm 20 \) J mol\(^{-1}\) K\(^{-1}\)

Table 2.3.2 Experimental data for the calculation of the energy, enthalpy and entropy of activation for the formation of MeCp\(_2\)Mn\(_2\)(CO)\(_5\) as determined from UV/visible flash photolysis experiments
Figure 2.3.6 (a) Arrhenius and (b) Eyring plots for the formation of MeCp₂Mn₅(CO)₅ obtained from 355nm laser flash photolysis experiments of MeCpMn(CO)₃.
Figure 2.4.1 An infra red spectrum of the carbonyl region obtained after 355nm photolysis of MeCpMn(CO)$_3$ in an argon degassed cyclohexane solution.
2.5 Conclusion

Flash photolysis experiment of MeCpMn(CO)\textsubscript{3} demonstrated that the reactions of this complex are analogous to those reported for CpMn(CO)\textsubscript{3}. Differences arise from kinetic data which demonstrated that the methyl group on the cyclopentadienyl ring has an influence on the solvation/desolvation of the cyclohexane molecule from the metal coordination sphere. Reactions of the solvated dicarbonyl species are twice as fast with CO as the corresponding CpMn(CO)\textsubscript{2}(cyclohexane) species. This was probably because of a more weakly coordinated cyclohexane arising from the steric influence of the methyl group. It appears that the methyl group has a direct influence on the coordination site as previous work carried out in n-hexane produced a two-fold increase for the pentamethylsubstituted Me\textsubscript{5}CpMn(CO)\textsubscript{3} complex\textsuperscript{8}. The solvated complex MeCpMn(CO)\textsubscript{2}(cyclohexane) also reacts with parent tricarbonyl complex to form a dinuclear species. The existence of the dinuclear species was confirmed by its UV/visible difference spectrum. This spectrum was similar to one identified in the photolysis of CpMn(CO)\textsubscript{3}\textsuperscript{6}. TRIR studies of CpMn(CO)\textsubscript{3} identified the dinuclear complex as a pentacarbonyl compound with four terminal CO's and a bridging CO. A similar structure was postulated for MeCpMn(CO)\textsubscript{3}. The dinuclear complex reacted with CO presumably to reform the parent complex. Solution infrared studies indicated the possibility of a second and more stable dinuclear complex.
2.6 Laser flash photolysis of MeCpMn(CO)$_2$PPh$_3$

UV/visible photolysis of MeCpMn(CO)$_2$PPh$_3$ (MeCp = \(\eta^5\)-C$_5$H$_4$CH$_3$) in n-heptane solution (\(\lambda = 366\)nm) was reported to lose a CO molecule as its primary photoprocess\(^{16}\). No loss of the triphenylphosphine ligand was observed as shown by experiments performed in the presence of CO and the absence of PPh$_3$. Laser flash photolysis experiments on MeCpMn(CO)$_2$PPh$_3$ at 355nm produced evidence for the production of one dominant transient species. This species was identified and proposed as the non-solvated MeCpMn(CO)PPh$_3$ complex principally from its reaction kinetics and from its UV/visible difference spectrum. Evidence exists for other transient species which were presumably formed as a result of loss of a triphenylphosphine ligand from MeCpMn(CO)$_2$PPh$_3$.

2.7 Electronic spectrum of MeCpMn(CO)$_2$PPh$_3$

Figure 2.7.1 contains the electronic absorption spectrum of MeCpMn(CO)$_2$PPh$_3$ in cyclohexane solvent. The first low energy absorption band appears at -350nm with the next lowest absorption at ~290nm in MeCpMn(CO)$_2$PPh$_3$. In the corresponding tricarbonyl complex, the lowest absorption band was found at 330nm in alkane solvent. This band was assigned to a Mn to (\(\eta^5\)-CH$_3$C$_5$H$_4$) charge transfer (Mn \(\rightarrow\) CpCT) band\(^1\). In addition, the LF transitions were also assigned unresolved to the same energy region. It is likely that the band at 350nm is the LF transition because of a lowering of the LF energy on the coordination of the triphenylphosphine ligand. The substitution of a carbonyl group in MeCpMn(CO)$_3$ by a ligand with less accepting power than a CO ligand has the effect of inducing a higher negative charge on the metal. This charge can be distributed over the metal centre and on the remaining carbonyl groups. The cyclopentadienyl ring has been shown in infrared studies of CpMn(CO)$_3$ not to accept any electron density as a result of carbonyl...
substitution with most of the charge distribution occurring over the carbonyl groups. Therefore the Mn→CpCT band for MeCpMn(CO)₂PPh₃ is present unresolved at 330 nm. The assignment of the transition at 290 nm may possibly be a Mn→dπ* CT band arising from the phosphine ligand as this band was absent in the UV/visible spectrum of MeCpMn(CO)₃ (Figure 2.11). The band at 250 nm is probably a Mn→COπ*CT transition.

Figure 2.7.1 A UV/visible spectrum of MeCpMn(CO)₂PPh₃ (6.3 x 10⁻⁴ mol dm⁻³) in cyclohexane solution.

2.8 355 nm Laser flash photolysis of MeCpMn(CO)₂PPh₃

MeCpMn(CO)₂PPh₃ is produced from the photoelimination of a CO ligand from the π²-methylcyclopentadienylmanganese(III)carbonyl complex MeCpMn(CO)₃. Flash photolysis of MeCpMn(CO)₂PPh₃ in cyclohexane at 355 nm (ε = 1367 dm³ mol⁻¹ cm⁻¹) produced one transient species. This species had an absorbance maximum.
Figure 2.8.1 A UV/visible difference spectrum of the MeCpMn(CO)PPh₃ complex in cyclohexane recorded after 10 μs under 1.0 atmosphere of argon

10 mV/div

Figure 2.8.2 Decay of the transient species, (a) under one atmosphere of argon and (b) under 0.25 atmospheres of carbon monoxide, monitored at 400 nm

50 us/div
at 400nm as can be seen in the UV/visible difference spectrum in Figure 28.1. This species was not MeCpMn(CO)$_2$(cyclohexane) as its UV/visible difference spectrum consisted of a broad band with a maximum at 580nm (Figure 28.2)

This transient species was originally thought to be the solvated MeCpMn(CO)PPh$_3$(cyclohexane) complex produced from photochemical loss of a CO ligand. Under 1 atmosphere of argon the decay of this photoproduct was detected and follows a first order decay process. However, under 1 atmosphere of CO the formation of this species was suppressed, the transient returned to baseline. The decay of the transient species again followed a pseudo-first order process. This indicated that this transient species was not a primary photoproduct as the addition of CO greatly affected its yield. Figure 28.2 demonstrates the loss in yield upon addition of CO to the sample solution. This suggests that perhaps two transient species of varying reactivity were formed, an extremely reactive one, with a lifetime too short to be measured on the present instrumentation (<200ns), and the one that was detected, a secondary photoproduct. Similar type behaviour was noted in the flash photolysis of CH$_3$Mn(CO)$_5$ in cyclohexane$^{18}$ Time resolved infra red and UV/visible detection were used to determine that the primary photoproduct was CH$_3$Mn(CO)$_4$ produced from the loss of a CO cis to the methyl group. Under an argon atmosphere this species was identified as the solvated cis-CH$_3$Mn(CO)$_4$(cyclohexane) complex. Under a CO atmosphere however, the yield of this solvatocomplex was reduced to one fifth its intensity under argon. The solution proposed was that the coordinately unsaturated species competed with CO and cyclohexane to form either the cis-CH$_3$Mn(CO)$_4$(cyclohexane) complex or parent CH$_3$Mn(CO)$_5$. This implied that the 16e- intermediate was not solvated as quickly as for example the Cr(CO)$_5$ species$^5$. The authors indicated some geometric rearrangement in CH$_3$Mn(CO)$_4$ to form a more stable trigonal-bipyramidal C$_3v$ complex to account for this behaviour. This species would have, because of geometric or electronic constraints, a sufficient lifetime to
discriminate in the coordination of a sixth ligand. The second order rate constant for
the reaction of $\text{CH}_3\text{Mn(CO)}_4$ with CO is $2.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The corresponding
second order rate constant for the reaction of $\text{MeCpMn(CO)}_2\text{PPh}_3$ with CO is $1.05 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Figure 2 8 3). The increase in rate constant by two orders of
magnitude indicates that perhaps a molecule of solvent does not occupy the vacant
coordination site in the $\text{MeCpMn(CO)}_2\text{PPh}_3$ photoproduct. The reacting species could
not be the $\text{MeCpMn(CO)}_2(\text{cyclohexane})$ complex as the second order rate constant for
the reaction of this species with CO is $7.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (vide infra). The
explanation for this observation may be in an intramolecular reaction and not in a
generic rearrangement as with $\text{CH}_3\text{Mn(CO)}_5$. Manganese carbonyl compounds are
well known in ortho-metallation reactions involving phosphine ligands. Triphenylphosphine is a very bulky ligand and could prevent the usual coordination
of a solvent to the vacant ligand site. This action would facilitate an ortho-metallated
type product. The CO molecule is small and would be able to coordinate to the metal
centre. This is important as it means that the intermediate can discriminate between
different sizes of molecules. This would account for the extremely fast second order
rate constant. The intermediate formed could compete with the ortho hydrogens on the
phenyl rings of the triphenylphosphine ligand and with CO in a similar fashion as the
$\text{CH}_3\text{Mn(CO)}_4$ intermediate competes with cyclohexane and CO. The reaction is
summarized in Scheme 2 8 1. Laser flash photolysis experiments of $\text{MeCpMn(CO)}_3$ in
cyclohexane indicated that the methyl group on the cyclopentadienyl ring had a direct
effect on the 'vacant' coordination site (vide infra). It is possible that the methyl group
also contributed in these experiments to the non-solvation of the $\text{MeCpMn(CO)}_2\text{PPh}_3$
species.

In solution, metal centres of electron rich complexes have been observed to
react with C-H bonds on their own ligands more rapidly than with saturated
hydrocarbons. Many examples exist showing this type of interaction.
(C5Me5)(PPh3)IrH2 irradiated in benzene solution undergoes loss of H2 to form a hydrido phenyl complex where the coordinately unsaturated intermediate formed on photolysis reacted with benzene solvent. In addition, an orthometallated complex was formed by intramolecular oxidative addition to the triphenylphosphine ligand. Irradiation in cyclohexane produced predominately the orthometallated product indicating that perhaps the intermediate in the reaction was not solvated on photolysis because of steric effects in coordinating a cyclohexane molecule. The methyl groups on the cyclopentadienyl ring remained uninvolved in the reaction. However, this is not always the case. Hydrogen atoms on the methyl group on the cyclopentadienyl ring can also participate in intramolecular C-H activation. (C5Me5)ZrH2 can activate a methyl group on the cyclopentadienyl ring via loss of the dihydrogen ligand. With respect to manganese, indium, and zirconium, have much larger atomic radii. The probability of a metallation reaction is increased for the larger metals. Manganese analogues would be expected to have shorter lifetimes arising from more unstable complexes because of increased ring strain.

\[
\begin{align*}
\text{(C5Me5)(PPh3)IrH2} & \rightarrow \text{(C5Me5)(PPh3)IrH} \rightarrow \text{(C5Me5)(PPh3)IrH2} \\
\text{hv} & \rightarrow \text{(C5Me5)(PPh3)IrH2} \\
\text{S} & = \text{cyclohexane}
\end{align*}
\]

Scheme 2.8.1 Scheme for the photolysis of MeCpMn(CO)2PPh3 in cyclohexane for loss of a CO ligand.
The intermediate may not necessarily involve an orthometallated type reaction. Many cases are known for the metal centre to coordinate to a benzene ring via 'double bond' or to an alkyl silane in a three centred Si-Mn-H bond. The possibility exists that a phenyl ring may coordinate via an 'isolated double' bond as postulated in the coordination of Cr(CO)₅ to benzene. Alternately the phenyl ring may be weakly coordinated via a three centred 'agostic' bond where the metal coordinates to the carbon hydrogen bond. A fourth possibility is 'end on' agostic bonding where the C-H σ bond interacts with the metal to form a linear weak σ bond. This type of interaction would provide the least strain in the proposed ring system.

Another explanation may be a rearrangement in the MeCpMn(CO)PPh₃ unit. Extended Huckel metal orbital calculations and perturbation theory have shown that the MeCpMn(CO)₂ species exists in a pyramidal geometry with the remaining ligands retaining a constant angle between them. This pyramidal geometry was very sensitive to the nature of the ligands and to the cyclopentadienyl ring. The effect of the electron donating methyl group and the replacement of a CO ligand with a PPh₃ may cause a planar ground state geometry to predominate and give a structure analogous to CpCo(CO)₂. Therefore the steric influence of the ligands would be greater, preventing coordination of the cyclohexane molecule and again facilitating coordination of smaller ligands to the metal. However, given the nature of the tnpPhosphine ligand i.e σ donor, π acceptor, the bonding for a tnpPhosphine ligand is not very different to a CO ligand and so it is likely that the pyramidal geometry would predominate.
$k_{\text{obs}} = 1.05 \times 10^8 \pm 6.88 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

Intercept = $-7075 \pm 6.5 \times 10^4 \text{s}^{-1}$

Corr coeff = 0.993

**Figure 2.8.3** A plot of the observed rate constant for the decay of MeCpMn(CO)PPh$_3$ against concentration of CO in cyclohexane solution at 298K
Ring dechelation is another possibility in the explanation of loss of yield on addition of CO\textsuperscript{10} However, the cyclopentadienyl ring has been shown in all photochemical reactions involving a manganese metal centre to be inert and therefore could be described as a rigid ligand\textsuperscript{11} Even when the cyclopentadienyl ring has been replaced by other $\eta^5$ ligands such as indenyl and fluorenyl no reaction involving these ligands was observed in contrast to the photochemical systems of the isoelectronic arene chromium tricarbonyl complexes\textsuperscript{26} Hapticity changes in the cyclopentadienyl ring from $\eta^5$ to $\eta^3$ has been observed in the thermal reactions of MeCpMn(CO)$_3$\textsuperscript{12} The production of this hapticity change involved the reduction of the manganese centre to produce the dianion [\eta$^3$-MeCpMn(CO)$_3$]$^2^-$ which was detected and identified by infra red spectroscopy If a photochemically induced ring slipped complex was formed in this experiment, it would be expected to be stabilised in the presence of CO forming a tricarbonyl complex No new transients were observed on addition of CO to the sample solution

The non-solvation of the MeCpMn(CO)$_3$PPh$_3$ complex because of steric hindrance from the intramolecular stabilisation reaction would also prevent the formation of a dinuclear species These dinuclear species are thought to be common in photochemical reactions of organometallic complexes and are unwanted side reactions as they would reduce the efficiency of these complexes as homogeneous catalysts The isoelectronic cyclopentadienyl manganese tricarbonyl, arene chromium tricarbonyl and cyclobutadienyl iron tricarbonyl complexes are known to form these dinuclear complexes\textsuperscript{13} The parent MeCpMn(CO)$_2$PPh$_3$ complex is much larger than a cyclohexane solvent molecule Since the triphenylphosphine ligand prevents coordination of a cyclohexane molecule it is also unlikely that the non-solvated intermediate would coordinate to MeCpMn(CO)$_2$PPh$_3$ This lack of a dinuclear complex greatly simplifies the task of transient identification and this was reflected in this experiment as only one transient was detected
The production of the dicarbonyl species cannot be ruled as infra red experiments which involved irradiating a solution of $\text{MeCpMn(CO)}_2\text{PPh}_3$ in argon degassed cyclohexane produced evidence for the production of the tricarbonyl complex (Figure 2.8.4). The irradiation was carried out using the 355nm line of the laser so as to reproduce the conditions in the transient experiments. The $\text{MeCpMn(CO)}_3$ complex could be produced from the loss of a trphenylphosphine ligand. The source of CO was most probably from the observed photoprodut, $\text{MeCpMn(CO)}_2\text{PPh}_3$. The weak band at 1836 cm$^{-1}$ may be the monocarbonyl complex $\text{MeCpMn(CO)}_2\text{PPh}_3$. Four weak bands were observed at 1975, 1961, 1919 and 1903 cm$^{-1}$. These bands correspond to similar ones observed in identical experiments with $\text{MeCpMn(CO)}_3$, and were assigned to an unknown dinuclear complex (Table 2.3.1). Under one atmosphere of argon, the transient decay of $\text{MeCpMn(CO)}_2\text{PPh}_3$ did not return to the baseline. This may indicate a reaction of the undetected $\text{MeCpMn(CO)}_2\text{(cyclohexane)}$ species with parent $\text{MeCpMn(CO)}_2\text{PPh}_3$ to form a dinuclear species. A UV/visible difference spectrum of this species is shown in Figure 2.8.5. $\text{MeCpMn(CO)}_2\text{(cyclohexane)}$ has been shown to react with parent in the laser flash photolysis of $\text{MeCpMn(CO)}_3$. In addition, the extinction coefficient of the $\text{MeCpMn(CO)}_2\text{(cyclohexane)}$ complex produced from the photolysis of $\text{MeCpMn(CO)}_3$ appeared to be very low and this may account for its non-detection in the laser flash photolysis of $\text{MeCpMn(CO)}_2\text{PPh}_3$. On the other hand, metal carbonyl dinuclear species have high extinction coefficients for metal centred $\sigma-\sigma^*$ transitions and so this would facilitate the detection of a photochemically produced transient dinuclear species. The strong absorption at 290nm detected in the time resolved spectrum of $\text{MeCpMn(CO)}_2\text{(cyclohexane)}$ would be absent in this experiment because there is no valley at 290nm in the absorbance spectrum of $\text{MeCpMn(CO)}_2\text{PPh}_3$. 
Figure 2.8.4 Infra red carbonyl region after the photolysis of MeCpMn(CO)$_2$PPh$_3$ in cyclohexane using the 355nm laser line. The bands at 1941 and 1881 cm$^{-1}$ correspond to the parent complex and at 2026 cm$^{-1}$ for MeCpMn(CO)$_3$. 
Figure 2.8.5 A UV/visible difference spectrum of the unknown dinuclear species taken after 300\,\mu s under 1\,\text{atmosphere of argon}

2.9 Conclusion

Photolysis of MeCpMn(CO)$_2$PPh$_3$ in cyclohexane solution produced evidence for the formation of two transient species. The first transient was identified from reaction kinetics as the non-solvated MeCpMn(CO)PPh$_3$ complex. The bulky tritylphenylphosphine ligand stenically prevented the cyclohexane molecule from coordinating to the metal centre. The coordinately unsaturated complex was stabilised by an intramolecular reaction. The nature of this interaction was unknown but is believed to involve possibly an orthometallation type reaction. The fast second order
rate constant for the reaction of this species with CO indicated that the CO molecule was able to coordinate to the manganese atom while the larger cyclohexane solvent molecule was not. The orientation of the methyl group may also have contributed to the non-solvation of the intermediate as it appears to directly influence the 'vacant' coordination site in experiments involving MeCpMn(CO)₃. Loss of tris(phenylphosphine) ligand was observed in infrared monitored solution photolysis of MeCpMn(CO)₂PPh₃. In time resolved experiments the presence of MeCpMn(CO)₂(cyclohexane) was not detected although it was thought to contribute to the transient decay not returning to the baseline in experiments carried out under argon. No dinuclear complex was formed from the MeCpMn(CO)PPh₃ species because of combined steric effects involving the tris(phenylphosphine) ligand and the cyclopentadienyl methyl group.
REFERENCES


CHAPTER 3

355nm AND 266nm LASER FLASH PHOTOLYSIS OF M(CO)₅PPh₃ COMPLEXES

(M = Cr, Mo or W)
3.1 Introduction

The irradiation into the LF bands of the GroupVIB hexacarbonyls produces loss of a CO ligand by depopulation of an electron from the \( t_{2g} \) orbitals, which are involved in the \( \pi \) backbonding from the metal to the CO ligands, and population of the \( e_g^* \) orbitals, which are antibonding with respect to the metal-CO \( \sigma \) bond. The substitution of a CO ligand in the \( \text{M(CO)}_6 \) complexes by a ligand with less \( \pi \) accepting capacity has the effect of splitting the doubly degenerate antibonding orbitals of \( e \) symmetry in the hexacarbonyl complex into two discrete orbitals having \( d_{z^2} \) and \( d_{xz} \) character in the pentacarbonyl complex. The extent of the splitting of the \( e \) orbitals is determined by the strength of the \( \pi \) accepting capability of the unique ligand. By convention, the unique ligand is placed on the \( z \) axis. Therefore, it should be possible by irradiating into the LF band, using different excitation wavelengths, to selectively labilise a ligand on the \( z \) axis or a CO group on the \( x \) and \( y \) axes. The loss of the unique ligand or a CO ligand on the \( z \) axis is dependent again on the extent of the \( \pi \) accepting ability of the unique ligand. However, this is a generalisation as the non radiative deactivation pathways of the excited states are not taken into account in this argument. The effect of these pathways was clearly seen in quantum yield measurements for the \( \text{Cr(CO)}_6 \) complex where a quantum yield of 1.0 was predicted for CO loss. The actual measurement was 0.67 with the difference being accounted for by recombination of the photoejected CO ligand with the \( \text{Cr(CO)}_5 \) photofragment.

A study of the fast photochemical reactions of the Group VIB monosubstituted triphenylphosphine pentacarbonyls in cyclohexane was undertaken to see the different effects produced on 355nm and 266nm laser irradiation. The major problem associated with such a study is the relatively similar UV/visible spectra of the three expected
photoproducts ($\text{M(CO)}_5$, cis-$\text{M(CO)}_4\text{PPh}_3$ and trans-$\text{M(CO)}_4\text{PPh}_3$ photocomplexes)

Such problems can be overcome to a certain extent by examining the relative reaction rates of the various photoproducts with CO which, in previous experiments using related compounds, have been shown to differ significantly

3.1.1 Electronic spectra of $\text{M(CO)}_3\text{PPh}_3$ ($\text{M} = \text{Cr, Mo or W}$).

The low energy absorption features of $\text{M(CO)}_3\text{PPh}_3$ ($\text{M} = \text{Cr, Mo or W}$) are shown in Figure 3.1.1.1. The first absorption band is noted at ~350nm for each of the complexes. This band has been assigned as the LF ($e^{4}b_2^2 \rightarrow e^{3}b_2^2a_1^1$) (LF = ligand field) transition. The more intense absorption at ~300nm corresponds to the M-$\pi^*\text{CO}$ CT (CT = charge transfer) band.

![Electronic spectra of M(CO)₃PPh₃](image_url)

**Figure 3.1.1.1** The electronic spectra of (a) Cr(CO)₃PPh₃ ($7 \times 10^{-4}$ mol dm⁻³) (b) Mo(CO)₃PPh₃ ($6.4 \times 10^{-4}$ mol dm⁻³) and (c) W(CO)₃PPh₃ ($7.9 \times 10^{-4}$ mol dm⁻³) in cyclohexane solution at room temperature.
3.2 Photolysis of Cr(CO)$_3$PPh$_3$

3.2.1 Infra red monitored photolysis of Cr(CO)$_3$PPh$_3$

Room temperature 355nm laser photolysis of argon degassed cyclohexane solutions of Cr(CO)$_3$PPh$_3$ in NaCl solution cells (path length = 0.1 mm) reveal the production of Cr(CO)$_6$ and a *trans* product (Figure 3.2.1.1). The bands at 2064, 1982 and 1944 cm$^{-1}$ correspond to the $A_1$, $A_2$ and $E$ modes of Cr(CO)$_3$PPh$_3$. These bands were depleted as a result of photolysis at 355 nm. New bands were observed at 2010, 1987, 1919, and 1895 cm$^{-1}$. The band at 1987 cm$^{-1}$ was characteristic of the $T_{1u}$ band observed for the Group VIB metal hexacarbonyl complexes and was assigned to Cr(CO)$_6$. The formation of the hexacarbonyl complex indicated that the triphenylphosphine ligand was lost from the parent compound. As the experiment was carried out in a sealed cell any CO released during the photolysis could react with the pentacarbonyl Cr(CO)$_5$ produced from photoliberation of triphenylphosphine. Triphenylphosphine loss has been observed in other related systems, i.e., Mo(CO)$_5$PPh$_3$ and occurred at low quantum yield for 366 nm excitation. The carbonyl stretching frequencies at 2010 and 1896 cm$^{-1}$ were indicative of the $A_{1g}$ and $E_u$ modes of a *trans* complex. This complex was probably formed from the reaction of a Cr(CO)$_4$PPh$_3$ intermediate, produced from photochemical loss of a CO ligand, with triphenylphosphine liberated from the parent complex. The small band at 1919 cm$^{-1}$ indicated the formation of some *cis* configuration Cr(CO)$_4$(PPh$_3$)$_2$. In order to investigate the reaction intermediates of the Cr(CO)$_3$PPh$_3$ further a photolysis study was carried out with excess triphenylphosphine in an argon degassed cyclohexane/Cr(CO)$_3$PPh$_3$ solution. The result of this experiment is presented in Figure 3.2.1.2. The parent complex bands correspond to 2064, 1982 and 1944 cm$^{-1}$ for the $A_1$, $A_2$ and $E$ modes respectively. New bands were observed at 2012, 1920 and 1895 cm$^{-1}$ and correlate well with those observed in the photolysis of Cr(CO)$_3$PPh$_3$ in the
absence of ligand. The band at 1895 cm\(^{-1}\) was the most intense and again suggests the formation of a trans-M(CO)\(_4\)L\(_2\) complex. The band intensity indicates the E\(_u\) mode of a trans complex. The weaker band at 2010 cm\(^{-1}\) corresponds to the A\(_{1g}\) band observed in trans complexes of the type M(CO)\(_4\)L\(_2\) (M = Cr, Mo or W). Another band, the B\(_{1g}\) mode at 1945 cm\(^{-1}\), is usually observed for these compounds but was masked in these experiments by the very intense E mode of the parent complex. The band at 1920 cm\(^{-1}\) again suggests the formation of some cis-Cr(CO)\(_4\)(PPh\(_3\))\(_2\). The other bands usually observed for cis complexes are at approximately 2010, 1901 and 1876 cm\(^{-1}\). The band at 2010 cm\(^{-1}\) is obscured by the 2010 cm\(^{-1}\) band of the trans complex. The other bands could be masked by the very intense E\(_u\) mode of trans-Cr(CO)\(_4\)(PPh\(_3\))\(_2\). A shoulder on the E\(_u\) band at 1870 cm\(^{-1}\) may correspond to the B\(_2\) mode observed in cis-M(CO)\(_4\)L\(_2\) complexes. From these results, it may be concluded that the room temperature photolysis of Cr(CO)\(_5\)PPh\(_3\) results in the formation of the trans-Cr(CO)\(_4\)(PPh\(_3\))\(_2\) complex as the major photoproduct with the formation of cis-Cr(CO)\(_4\)(PPh\(_3\))\(_2\) as a minor product. The loss of a triphenylphosphine ligand also occurs, however, this appears to be a minor photoproduct. No evidence for cis-trans photoisomeration was observed.
Figure 3.2.1.1 An infra red spectrum of the carbonyl bands produced following the 355nm photolysis of Cr(CO)$_3$PPh$_3$ in an argon degassed cyclohexane solution.
Figure 3.2.1.2 An infra red spectrum in the νCO region produced following the 355nm photolysis of Cr(CO)₅PPh₃ in an argon degassed cyclohexane solution with excess tBuPhosphine.
3.2.2 355nm laser flash photolysis of Cr(CO)$_5$PPh$_3$ with UV/visible monitoring

Laser flash photolysis of Cr(CO)$_5$PPh$_3$ using the 355nm line of the laser produced evidence for the formation of four transient species. These species were identified primarily from their reaction kinetics and to a lesser extent their UV/visible difference spectra. The species were identified as cis-Cr(CO)$_4$PPh$_3$, trans-Cr(CO)$_4$PPh$_3$ (cyclohexane), and two dinuclear species whose identities remain uncertain.

3.2.2.1 First transient species

The first observable transient species was cis-Cr(CO)$_4$PPh$_3$. This species was identified from its UV/visible difference spectrum and from kinetic studies of its reaction with CO. The UV/visible difference spectrum can be seen in Figure 3.2.2.11. The spectrum consists of a broad band with two maxima at 400nm and 500nm. This spectrum was different to that observed for Cr(CO)$_5$S (S = cyclohexane) which consisted of a single broad band with a maximum centred around 500nm. A spectrum of Cr(CO)$_6$(cyclohexane) obtained by photolysis of Cr(CO)$_6$ in cyclohexane solution under one atmosphere of CO can be seen in Figure 3.2.2.12. The absence of the small band at 400nm in the spectrum obtained for cis-Cr(CO)$_4$PPh$_3$ indicated that the UV/visible difference spectrum for this species was different to that obtained for Cr(CO)$_6$(cyclohexane).

The reaction of this species with CO demonstrates unequivocally that this species was not Cr(CO)$_5$(cyclohexane). The second order rate constant for the reaction of this first transient species was obtained by varying the concentration of CO in the cyclohexane solution. A typical transient for this reaction is given in Figure 3.2.2.13.
Figure 3.2.2.1.1 A UV/visible difference spectrum of \( \text{cis-Cr(CO)}_4\text{PPh}_3 \) obtained at 0.5 \( \mu s \) after the laser pulse.

Figure 3.2.2.1.2 A UV/visible difference spectrum of \( \text{Cr(CO)}_5(\text{cyclohexane}) \) obtained from 266nm laser flash photolysis of \( \text{Cr(CO)}_6 \) under 1.0 atmosphere of CO after 20\( \mu s \) after the laser pulse.
Figure 3.2.2.1.3 A typical transient obtained for the decay of \textit{cis}-\ce{Cr(CO)_4PPh_3}
obtained at 500 nm under 0.25 atmospheres of CO.

The data for the reaction of this transient species with CO and a graph of the concentration of CO (mol dm\(^{-3}\)) against the observed rate constant (s\(^{-1}\)) is shown in Figure 3.2.2.1.4. The slope of the line and hence the second order rate constant was \(2.0 \times 10^8\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). The second order rate constant for the reaction of CO with \ce{Cr(CO)_3(cyclohexane)} was quoted by Kelly \textit{et al.} as \(3.0 \times 10^6\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). The value obtained from the photolysis of \ce{Cr(CO)_6} under 1 atmosphere of CO in these experiments was \(2.8 \times 10^6\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). The second order rate constant obtained for the species obtained from the photolysis of \ce{Cr(CO)_3PPh_3} was almost two orders of magnitude greater than that obtained for \ce{Cr(CO)_3(cyclohexane)}. This confirms that the photoproduct observed was not \ce{Cr(CO)_3(cyclohexane)}. A possible explanation for the marked increase in the second order rate constant for this species could be that the \textit{cis} species cannot coordinate a solvent molecule because of the bulky trphenylphosphine ligand. However in the presence of CO, the \textit{cis} species may be able to coordinate.
Figure 3.2.2.1.4 A second order plot of the observed rate constant $k_{obs}$ (s$^{-1}$) for the reaction of cis-Cr(CO)$_4$PPh$_3$ against the concentration of CO (mol dm$^{-3}$) at 298K.
to a CO because a CO molecule is much smaller than a corresponding cyclohexane molecule. This would account for the increased rate for reaction of \textit{cis}-\textit{Cr(CO)}_4\text{PPh}_3 with CO. The rate constant was faster than that obtained for the non-solvated \textit{MeCpMn(CO)}\text{PPh}_3 intermediate and may, like \textit{MeCpMn(CO)}\text{PPh}_3, be stabilised by an intramolecular interaction with the bulky triphenylphosphine ligand. Chromium carbonyl complexes stabilised by intramolecular reactions have been observed. \textit{Cr(CO)}_3(\text{PCy}_3)_2 has been synthesised and characterised by X-ray crystallography where the sixth coordination site was occupied by an 'agostic' hydrogen from one of the cyclohexyl rings

In thermal reactions of complexes of the type \textit{Cr(CO)}_5L a site preference was shown for loss of a CO ligand, or other ligand, \textit{cis} to the unique ligand \textit{L}. Substitution of a CO ligand in \textit{Cr(CO)}_6 by phosphine ligands increased the lability of the \textit{cis} CO ligands by a factor of approximately 300. Time resolved infra red analysis of \textit{W(CO)}_5\text{PPh}_3 in n-heptane solution has demonstrated that the \textit{cis} CO loss intermediate reacted faster than the \textit{trans} intermediate and faster than the pentacarbonyl intermediate produced from photolysis of \textit{W(CO)}_6. Therefore the first transient species is proposed as \textit{cis}-\textit{Cr(CO)}_4\text{PPh}_3. If this is the case then this transient species would be a primary photoproduct produced from the loss of a CO group \textit{cis} to the triphenylphosphine ligand. Deconvoluting the transient decay curves using non linear regression (see experimental section) can give the initial absorbances of the species involved in the decay process. This can be used as an indicator at fast timescales to determine if the first species in the transient was a primary photoproduct as a steady absorbance value under various CO atmospheres would serve as evidence of a primary photoproduct. A plot of the absorbance values calculated from the transient decay curves obtained at various concentrations of CO against the concentration of carbon monoxide monitored at 500nm (Figure 3.2.2.1.5) revealed that the initial absorbance value calculated for the fast species remained constant regardless
of CO concentration. This indicates that the yield of this photoprodct was unaffected by the presence of CO and therefore a primary photoprodct. In photolysis experiments where a liquid pumping phase was omitted from the sample preparation, this first transient species was not observed. This indicates that the transient species is sensitive to impurities in the solvent, most probably water. Grevels et al. have shown that water can easily be removed from cyclohexane solutions by the addition of a liquid pumping phase to the sample preparation. The absence of this species when there is no liquid pumping phase suggests that it may be obscured by another band formed from the reaction of one of the other photoprodcts with water. Another explanation possible is that the reactivity of the first transient species with water may be beyond the detection range of the instrumentation.

![Initial Absorbance vs. [CO] mol dm$^{-3}$](image)

**Figure 3.2.2.1.5** A plot of the initial absorbances of cis-Cr(CO)$_4$PPh$_3$ against the concentration of CO.
3.2.2.2 Second transient species

The second transient species was assigned to trans-Cr(CO)_4PPh_3(cyclohexane). In the infrared monitored solution cell experiments, trans-products were identified as being the dominant photoproducts. A UV/visible difference absorption spectrum of trans-Cr(CO)_4PPh_3(cyclohexane) obtained from 355nm laser flash photolysis experiments in cyclohexane solution is shown in Figure 3.2.2.2.1. It consists of a broad band with a maximum at 480nm. Again, the Cr(CO)_5(cyclohexane) species can be ruled out as it has a maximum of ~500nm. A transient of this species is shown in Figure 3.2.2.2.2. This species reacts with CO and a graph of various concentrations of CO against the observed rate constant is depicted in Figure 3.2.2.2.3. The second order rate constant for the reaction of this species with CO was 2.0 x 10^6 dm^3 mol^-1 s^-1. This value was close to that obtained for the Cr(CO)_5(cyclohexane) complex at 3.0 x 10^6 dm^3 mol^-1 s^-1. However, given the difference in the UV/visible difference spectra, it was concluded that this species was the trans-Cr(CO)_4PPh_3(cyclohexane) complex. To further support this conclusion, the low temperature matrix isolation study of the related Cr(CO)_5PMe_3 complex in argon matrix at 10K revealed that two photoproducts were observed on photolysis between 229 and 366nm and identified as the cis and trans configurations of Cr(CO)_4PMe_3. A small amount of Cr(CO)_3 was also observed and consistent with the low quantum yield for unique ligand loss in other related systems, e.g., Mo(CO)_3PPh_3, W(CO)_5PPh_3. As before, deconvolution of the transients under various pressures of CO revealed that this species was a primary photoproduct, i.e., the yield of this species was unaffected by changing the CO concentration in solution. A graph of CO concentration against initial absorbance is shown in Figure 3.2.2.4. This species was probably solvated in solution. The loss of a CO ligand trans to the triphenylphosphine ligand would facilitate solvation of the trans-Cr(CO)_4PPh_3 intermediate.
Figure 3.2.2.2.1 UV/visible difference spectrum of *trans*-Cr(CO)$_4$PPh$_3$(cyclohexane) obtained at 10μs after the laser pulse.

Figure 3.2.2.2.2 A typical transient for *trans*-Cr(CO)$_4$PPh$_3$(cyclohexane) monitored at 500nm under 0.25 atmospheres of CO.


\[
k_{[CO]} = 1.92 \times 10^6 \pm 4.56 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

Intercept = \(1.47 \times 10^4 \pm 3.05 \times 10^2 \text{ s}^{-1}\)

Corr Coeff 0.999

**Figure 3.2.2.3** A second order plot of the observed rate constant \(k_{\text{obs}} (\text{s}^{-1})\) for the reaction of \(\text{trans-Cr(CO)}_4\text{PPh}_3\) (cyclohexane) against the concentration of CO (mol dm\(^{-3}\)) at 298K
Figure 3.2.2.4 A plot of initial absorbance of trans-Cr(CO)$_4$PPh$_3$(cyclohexane) against concentration of CO in solution.

The bulky triphenylphosphine ligand trans to the vacant site would provide the least steric effects to solvation.

3.2.2.3 Third transient species

The third transient species observed for the 355nm photolysis of Cr(CO)$_5$PPh$_3$ had a $\lambda_{\text{max}}$ at 460nm. A UV/visible spectrum of this species is shown in Figure 3.2.2.3.1. The $\lambda_{\text{max}}$ observed for this species was different to that observed for both cis-Cr(CO)$_4$PPh$_3$ and trans-Cr(CO)$_4$PPh$_3$(cyclohexane). A transient of this species obtained at 500nm is shown in Figure 3.2.2.3.2. The decay of the fast portion of the curve followed pseudo first order kinetics. A plot of the observed rate constant against concentration of CO (Figure 3.2.2.3.3) revealed that this species appeared not to react with CO. A plot of initial absorbance against concentration of CO in cyclohexane solution (Figure 3.2.2.3.4) indicated that yield of this species was affected by the
presence of CO and is therefore a secondary photoprodoot. This secondary photoprodoot may have been a dinuclear species formed from the reaction of a primary photoprodoot with parent or from an intramolecular reaction with one of the ligands. Such dinuclear species have been observed in the photochemical reactions of a number of metal carbonyl systems.\textsuperscript{14, 15, 16}

Another possibility is the formation of a water complex. Time resolved infra red studies carried out on Cr(CO)\textsubscript{6} in cyclohexane revealed the presence of Cr(CO)\textsubscript{5}(H\textsubscript{2}O) as a result of reaction of Cr(CO)\textsubscript{5}(cyclohexane) with trace amounts of water in the solvent.\textsuperscript{11} The infra red frequencies of this complex at 1946 and 1916 cm\textsuperscript{-1} indicated that H\textsubscript{2}O was a good donor ligand comparable with diethyl ether and tetrahydrofuran as ligands. Therefore it is possible that this intermediate was a water complex formed from the reaction of either \textit{cis}-Cr(CO)\textsubscript{4}PPh\textsubscript{3} or \textit{trans}-Cr(CO)\textsubscript{4}PPh\textsubscript{3}(cyclohexane) with H\textsubscript{2}O. However, in the time resolved infra red experiments on Cr(CO)\textsubscript{6}, it was reported that the water could easily be removed by a liquid pumping phase in the sample preparation.\textsuperscript{11} Therefore the inclusion of a liquid pumping phase in the sample preparation in the photolysis of Cr(CO)\textsubscript{5}PPh\textsubscript{3} should remove transient species produced as a result of reaction with water. This third transient species was present with and without a liquid pumping phase and was therefore not formed from the reaction of one of the photochemically produced intermediates with water.
Figure 3.2.2.3.1 A UV/visible difference spectrum of the third transient species obtained 1000\(\mu s\) after the flash under 10 atmospheres of argon.

Figure 3.2.2.3.2 A transient signal obtained for the third transient species monitored at 500nm under 0.25 atmospheres of CO.
Figure 3.2.2.3.3 A graphical representation and the experimental data of the concentration of CO (mol dm\(^{-3}\)) and the corresponding first order rate constants (s\(^{-1}\)) demonstrating the non-reaction of the third transient species with CO at 298K.
Figure 3.2.2.3.4 A plot of initial absorbance for the third transient species against concentration of CO

3.2.2.4 Fourth transient species

A fourth transient species was observed with a relatively long lifetime of ~10 seconds. A UV/visible difference spectrum of this complex is shown in Figure 3.2.2.4.1. It can be seen from this spectrum that the maximum absorption for this complex was also at 460nm. A transient obtained for this species is shown in Figure 3.2.2.4.2. This species reacted with CO to give a second order rate constant of 489 dm$^3$ mol$^{-1}$ s$^{-1}$ (Figure 3.2.2.4.3). The kinetic data obtained from long lived transient species are not as accurate as those obtained at shorter timescales because of the added effect of diffusion of photoproduct from the path of the monitoring beam. However, the diffusion effect is a systematic one and should not affect second order rate constant calculation. This species was not a primary photoproduct as again employing transient absorption deconvolution of the transient signal demonstrated that the yield of this species was sensitive to the presence of CO in solution (Figure 3.2.2.4.4).
Figure 3.2.2.4.1 A UV/visible difference spectrum of the fourth transient species taken after 40000\(\mu\)s

10 m\text{U}/\text{div}

Figure 3.2.2.4.2 A typical transient decay obtained for the decay of the fourth transient species monitored at 500nm under 0.25 atmospheres of CO

100000 \text{us}/\text{div}
Figure 3.2.2.4.3 A table of the concentration of CO (mol dm$^{-3}$) and the corresponding first order rate constants (s$^{-1}$) for the reaction of the fourth transient species with CO at 298K.

<table>
<thead>
<tr>
<th>[CO] mol dm$^{-3}$</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>3.59</td>
</tr>
<tr>
<td>0.006</td>
<td>5.04</td>
</tr>
<tr>
<td>0.009</td>
<td>7.04</td>
</tr>
<tr>
<td>0.012</td>
<td>7.82</td>
</tr>
</tbody>
</table>

$k_{[CO]} = 489 \pm 55$ dm$^3$ mol$^{-1}$ s$^{-1}$

Intercept $= 2.2 \pm 0.4$ s$^{-1}$

Corr coeff = 0.988
This fourth transient species was also presumed to be a dinuclear complex. It was present with or without a liquid pumping phase in the sample preparation and therefore was not the result of reaction with water in the solvent.

3.2.3 266nm laser flash photolysis of Cr(CO)$_5$PPh$_3$ with UV/visible monitoring

The 266nm laser flash photolysis of Cr(CO)$_5$PPh$_3$ in cyclohexane produced evidence for the formation of two transient species. These species were identified as a primary photoproduct and a secondary photoproduct. Other transient species were observed but were very weak and difficult to analyse. Room temperature infra red analysis of this species was not possible because of significant absorption of the infra red cells at 266nm.

3.2.3.1 First transient species
The first transient species observed for the 266nm photolysis of Cr(CO)$_5$PPh$_3$ was surprisingly not cis-Cr(CO)$_4$PPh$_3$ but the trans-Cr(CO)$_4$PPh$_3$(cyclohexane) complex. A UV/visible difference spectrum of the first transient species is shown in Figure 3.2.3.1.1 and has a $\lambda_{max}$ at 480nm, the same maximum as the trans-Cr(CO)$_4$PPh$_3$(cyclohexane) species proposed on 355nm excitation. The reaction kinetics of this species with CO was the same as for the second transient species compared to the 355nm laser photolysis of Cr(CO)$_5$PPh$_3$ yielding a second order rate constant of $1.9 \times 10^6 \pm 2.0 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 298K ($k_{[CO]}$ 355nm = $1.9 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 298K). Therefore this species was identified as trans-Cr(CO)$_4$PPh$_3$(cyclohexane).

3.2.3.2 Second transient species

The characteristics of the second transient species were the same as those observed for the third transient species on 355nm excitation. A UV/visible difference spectrum of this complex is shown in Figure 3.2.3.2.1 and has a $\lambda_{max}$ at 460nm, the same as that observed for the 355nm third species. The reaction kinetics of this species were also consistent with the 355nm observations demonstrating that this photocomplex decayed independent of CO concentration.

Weak transients were observed on the timebase of the fourth species on 355nm excitation indicating that this species was formed but that its yield had been affected. An obvious conclusion from this was that this species was a dinuclear complex formed from the reaction of a primary photoproduct with parent. The difference in yield of the dinuclear complexes between 355 and 266nm excitation could be accounted for by the relative extinction coefficients between 355 and 266nm, i.e., 355nm ($\varepsilon = 1223$ dm$^3$ mol$^{-1}$ cm$^{-1}$), 266nm ($\varepsilon = 14220$ dm$^3$ mol$^{-1}$ cm$^{-1}$). The difference in magnitude of the extinction coefficients of -10 corresponds to a difference of -10 in the concentration of Cr(CO)$_5$PPh$_3$ at 355nm and 266nm excitation. Therefore, the concentration of parent...
at 266nm was 10 times less than at 355nm and so preventing the formation of a dinuclear species. The overall scheme for the photolysis reactions of Cr(CO)$_5$PPh$_3$ on 355nm and 266nm excitation is given in Scheme 3.5.1

**Figure 3.2.3.1.1** A UV/visible difference spectrum of trans-Cr(CO)$_4$PPh$_3$ taken 10μs after the laser pulse
Figure 3.2.3 2.1 A UV/visible difference spectrum of the second transient species taken 2500μs after the laser pulse
3.3 Photolysis of Mo(CO)$_5$PPh$_3$

3.3.1 Infra red monitored photolysis of Mo(CO)$_5$PPh$_3$

355nm photolysis, using an Nd YAG laser of room temperature argon degassed cyclohexane solutions of Mo(CO)$_5$PPh$_3$, was carried out to determine which ligands were lost on photolysis at this wavelength. An infra red spectrum of the photolysis result is given in Figure 3.3.1.1. The bands at 2074 and 1952 cm$^{-1}$ correspond to the A$_1$ and E modes respectively of the parent complex. The A$_2$ mode at 1988 cm$^{-1}$ usually observed was masked by the photolysis products. The parent bands were depleted to produce five new bands at 2024, 1988, 1931, 1907 and 1868 cm$^{-1}$. The band at 1988 cm$^{-1}$ was indicative of the T$_{1u}$ band of the Mo(CO)$_6$ complex. Therefore a tris(triphenylphosphine) ligand was lost on photolysis. As the experiment was carried out in a sealed system the source of CO must have come from the photoejection of a CO from the parent complex. This result was not unexpected as 366nm photolysis of Mo(CO)$_5$PPh$_3$ in tetrahydrofuran solution also revealed the loss of a tris(triphenylphosphine) ligand with a quantum yield of 0.115. The CO stretching frequencies at 2024 and 1907 cm$^{-1}$ suggested the formation of a trans complex. The most likely explanation for this observation was that a Mo(CO)$_4$PPh$_3$ intermediate produced on photolysis of Mo(CO)$_5$PPh$_3$ reacted with the free tris(triphenylphosphine) generated from unique ligand loss from the parent. The intensity of the 1907 cm$^{-1}$ band indicated that this may be the major photoproduct. The bands at 1931 and 1868 cm$^{-1}$ point to the formation of a cis complex, probably Mo(CO)$_4$(PPh$_3$)$_2$. Four bands are usually observed for cis-M(CO)$_4$L$_2$ complexes however overlapping of $\nu$CO bands prevented the 1945 and 2020 cm$^{-1}$ bands being observed. To investigate the reactions further and prevent the formation of Mo(CO)$_6$ excess tris(triphenylphosphine) was added to a solution of argon degassed cyclohexane and Mo(CO)$_5$PPh$_3$ and subsequently photolysed at 355nm as before. The photolysis result is shown in Figure 3.3.1.2.
Figure 3.3.1.1 The infra red carbonyl region following 355nm photolysis of Mo(CO)$_5$PPh$_3$ in argon degassed cyclohexane solution
Figure 3.3 1.2 The infra red carbonyl region following the 355nm photolysis of Mo(CO)$_3$PPh$_3$ with excess triphenylphosphine in argon degassed cyclohexane solution
The infrared spectrum was identical to that obtained for the photolysis of Mo(CO)$_4$PPh$_3$ in the absence of added ligand except the band indicating the formation of Mo(CO)$_6$ at 1988 cm$^{-1}$ was no longer observable presumably because of reaction of any pentacarbonyl produced on photolysis with free trphenylphosphine. Again the dominant photoproduct appeared to be the trans-Mo(CO)$_4$(PPh$_3$)$_2$ complex with a strong absorption at 1907 cm$^{-1}$ cis configuration Mo(CO)$_4$(PPh$_3$)$_2$ was also observed at 1932 and 1876 cm$^{-1}$. These observations were in contrast to those observed in tetrahydrofuran solutions by Darensbourg et al. The dominant photoproduct in this system was the cis-Mo(CO)$_4$(PPh$_3$)$_2$ complex. The difference in the photolysis products may be because of the solvents used in the reactions. Tetrahydrofuran is a good $\sigma$-donor solvent while cyclohexane has little $\sigma$-donating capacity. Therefore, the intermediates produced on photolysis would have very different lifetimes. The Mo(CO)$_4$PPh$_3$(THF) (THF = tetrahydrofuran) intermediate produced on photolysis would be much longer lived than the corresponding cyclohexane intermediate because of a greater capacity of THF to stabilise the intermediate and a significantly higher activation barrier to the displacement of the solvent molecule. As a consequence of this longer lifetime the possibility of a rearrangement to the thermodynamically more stable cis configuration increases. Photolysis experiments carried out by Darensbourg and Murphy on trans-Mo(CO)$_4$(PPh$_3$)$_2$ in the presence of trphenylphosphine afforded the cis-Mo(CO)$_4$(PPh$_3$)$_2$ product. They observed that cis-Mo(CO)$_4$(PPh$_3$)$_2$ undergoes thermal rearrangement to trans-Mo(CO)$_4$(PPh$_3$)$_2$ at elevated temperatures. Therefore the cis product was the thermodynamically more stable configuration. In cyclohexane solution the cyclohexane solvated intermediates produced would have less time to rearrange to the cis form and trap an incoming ligand more quickly than the corresponding tetrahydrofuran intermediates. Therefore it is possible that initial loss position of a CO ligand may be trans to a trphenylphosphine ligand.

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3.3.2 355nm laser flash photolysis of Mo(CO)$_5$PPh$_3$ with UV/visible monitoring

The 355nm laser flash photolysis of Mo(CO)$_5$PPh$_3$ produced evidence for the formation of five transient species. One of these species was identified as the primary photoproduct, \textit{cis}-Mo(CO)$_4$PPh$_3$. The identities of the other species are unknown. Tentative assignment of two of these species to possibly \textit{trans}-Mo(CO)$_4$PPh$_3$(cyclohexane) and Mo(CO)$_5$(cyclohexane) is proposed. It was likely that the long-lived transients were dinuclear species formed from the reaction of the primary photoproducts with parent complex.

3.3.2.1 First transient species

This species was identified as \textit{cis}-Mo(CO)$_4$PPh$_3$ on the basis of its reactivity with CO and to a lesser extent on its UV/visible difference spectrum. A typical transient obtained for this species is shown in Figure 3.3.2.1.1. The fast portion of the transient corresponded to the decay of \textit{cis}-Mo(CO)$_4$PPh$_3$ complex. The slower part of the decay corresponded to the second transient species. The difference in reactivity of \textit{cis} and \textit{trans} phosphine substituted molydenum tetracarbonyl intermediates has been reported by Dobson and coworkers on work carried out on Mo(CO)$_4$(NP) where NP = 1-(diethylamino)-2-(diphenylphosphino)ethane$^{17}$. The chelating ligand NP contained both nitrogen and phosphorus coordinated moieties. Laser flash photolysis ($\lambda = 355$nm) of this complex in chlorobenzene produced both \textit{cis} and \textit{trans} intermediates from the photocleavage of the nitrogen coordinated ligand site and rearrangement of the intermediate to form a mixture of \textit{cis} and \textit{trans}-Mo(CO)$_4$(\textit{η}$^1$-NP)(chlorobenzene) isomers. The \textit{cis} isomer reacted with added ligand L (L = phosphines and phosphites) two orders of magnitude faster than the corresponding \textit{trans} intermediate to form the \textit{cis} and \textit{trans}-Mo(CO)$_4$(\textit{η}$^1$-NP)L products. In other systems such as \textit{cis}-W(CO)$_4$(PPh$_3$)(pip)$^{18}$ and W(CO)$_5$PPh$_3$$^{10}$ studied by laser flash photolysis, the \textit{cis} solvated intermediates formed have been the most reactive.
Figure 3.3.2.1.1 A typical transient obtained for the fast species in the 355nm laser flash photolysis of Mo(CO)₅Ph₃ under 0.5 atmospheres of CO monitored at 420nm. The fast portion of the curve corresponds to the ciss-Mo(CO)₄PPh₃ species.

A UV/visible difference spectrum of ciss-Mo(CO)₄PPh₃ can be seen in Figure 3.3.2.1.2. A UV/visible difference spectrum of Mo(CO)₅(cyclohexane) obtained from the 355nm photolysis of Mo(CO)₆ is displayed in Figure 3.3.2.1.3. These spectra were different with maxima at 420nm and 480nm for ciss-Mo(CO)₄PPh₃ and a single maximum for Mo(CO)₅(cyclohexane) at 420nm. In order to demonstrate conclusively that this species was not Mo(CO)₅(cyclohexane) a study was carried out by varying the concentration of CO in the cyclohexane solution to calculate the second order rate constant for the reaction of ciss-Mo(CO)₄PPh₃ with CO. A graph of the concentration of CO against the observed rate constant is shown in Figure 3.3.2.1.4. The slope of this graph corresponded to the second order rate constant and was calculated as 1.51 x 10⁸ dm³ mol⁻¹ s⁻¹. This experiment demonstrated that this species was not...
Figure 3.3.2.1.2 A UV/visible difference spectrum of cis-Mo(CO)$_4$PPh$_3$ obtained from the 355nm laser flash photolysis of Mo(CO)$_5$PPh$_3$ 2μs after the laser pulse

Figure 3.3.2.1.3 A spectrum of Mo(CO)$_5$(cyclohexane) obtained from the 355nm photolysis of Mo(CO)$_6$ in cyclohexane 0.2μs after the laser pulse
Figure 3.3.2.1 4 A plot of $k_{obs}$ (s$^{-1}$) against concentration of CO (mol dm$^{-3}$) for the reaction of $\text{cis-Mo(CO)}_4\text{PPh}_3$ with CO at 298K.

$k_{[CO]} = 1.51 \times 10^8 \pm 2.16 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$

Intercept = $4.88 \times 10^{-4} \pm 1.45 \times 10^5$ s$^{-1}$

Corr Coeff = 0.98
Mo\((CO)\)_5\((cyclohexane)\) as the second order rate constant for the reaction of Mo\((CO)\)_6\((cyclohexane)\) with CO was calculated as 2.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} from the 355nm photolysis of Mo\((CO)\)_6 in a CO saturated cyclohexane solution. The second order rate constant for \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) was very fast for a reaction in cyclohexane solution and indicates that perhaps the intermediate was not solvated on the timescale of the experiment. Therefore as in the case of the chromium analogue the bulky triphenylphosphine ligand may be preventing coordination of a solvent molecule to the metal centre. The formation of this species indicates that it may be a primary photoproduct. In order to prove that \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) was indeed a primary photoproduct the transients obtained at various concentrations of CO were fitted with a double exponential curve. The parameter corresponding to the intercept of the decay of the \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) component and hence the initial absorbance of this species was plotted against CO concentration (Figure 3 3 2 1 5). The initial absorbance of \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) and therefore its concentration did not change with varying CO concentration after 0.5 atmospheres of added CO. This demonstrated that the yield of \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) was unaffected by changing CO concentration indicating that it was a primary photoproduct. The loss in yield indicated in the graph for a CO concentration of 0.003 \text{ mol dm}^{-3} may be because of an isomensation process from \textit{cis} to \textit{trans}\(-\)Mo\((CO)\)_4\(PPh_3\) which could have taken place on the timescale of the reaction of the \textit{cis}\(-\)Mo\((CO)\)_4\(PPh_3\) intermediate with CO. The addition of CO would prevent the isomensation process and therefore increase the yield of Mo\((CO)\)_5\(PPh_3\) produced from a \textit{cis} derivative.
Figure 3.3.2.1.5 A plot of the initial absorbance of \textit{cis}-Mo(CO)_4PPh_3 against concentration of CO in cyclohexane solution.

3.3.2.2 Second transient species

The second transient species could not be unambiguously assigned but could be Mo(CO)_5(cyclohexane). A UV/visible difference spectrum of this intermediate obtained after 50 µs is presented in Figure 3.3.2.2.1. The spectral feature of this species was similar to those observed for Mo(CO)_5(cyclohexane) i.e., \( \lambda_{\text{max}} \approx 420\text{nm} \). A typical transient of this species is depicted in Figure 3.3.2.2.2. Its decay follows pseudo first order reaction kinetics. A plot of the observed rate constant against different concentrations of CO gave a straight line with a slope of \( 3.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). This second order rate constant was not very different to that obtained for Mo(CO)_5(cyclohexane) at \( 2.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and therefore it was possible that this species was Mo(CO)_5(cyclohexane). A graph of initial absorbance against concentration of CO in solution, shown in Figure 3.3.2.2.4, indicated that the yield of this species increased with increasing CO concentration. This observation was
consistent with loss of unique ligand from the parent complex because in the presence of CO, any Mo(CO)\(_5\)(cyclohexane) formed would react with CO to form Mo(CO)\(_6\).

Since a flow through sample cell was not used in the experiments the concentration of Mo(CO)\(_6\) in the sample cell would increase with increasing laser photolysis. This would increase the concentration of Mo(CO)\(_5\)(cyclohexane) in the sample solution as both Mo(CO)\(_6\) and Mo(CO)\(_3\)PPh\(_3\) would be photolysed in subsequent laser pulses.

The inclusion of a liquid pumping phase did not affect the formation of transient species so it was not produced from the reaction of a transient intermediate with water in the solvent.
Figure 3.3.2.2.1 A UV/visible difference spectrum obtained 50μs after the laser pulse for the second transient species

![Absorbance vs Wavelength](image)

10 mU/div

Figure 3.3 2.2.2 A typical transient obtained for the second transient species obtained under 10 atmosphere of CO monitored at 420nm

20 us/div
Figure 3.3.2.3 A plot of the observed rate constant (s^{-1}) for the second transient species against the concentration of CO (mol dm^{-3}) in solution at 298K.
Figure 3.3.2.2.4 A plot of initial absorbance of the second transient species against concentration of CO in cyclohexane solution

3.3 2.3 Third transient species

The identity of this species was unknown but it reacts with parent complex and therefore it appears that it is a primary photoproduct possibly \textit{trans}-\textit{Mo(CO)}_4PPh_3. A UV/visible difference spectrum of this intermediate is shown in Figure 3.3.2.3.1 and consists of a single broad band with a $\lambda_{\text{max}}$ at 410nm not unlike the spectra of the other species. A typical transient of this species is depicted in Figure 3.3.2.3.2 with the fast part of the decay corresponding to the third transient species. This species showed dependence on CO concentration and a plot of the observed rate constant against CO concentration is shown in Figure 3.3.2.3.3. The slope of this graph yielded a second order rate constant of \(4.0 \times 10^5\) dm$^{-3}$ mol$^{-1}$ s$^{-1}$. The decay of this species at 420nm was accompanied by the grow in of a band at 360nm. The rate of this grow in was dependent on the concentration of Mo(CO)$_3$PPh$_3$ in the solution.
Figure 3.3.2.3.1 A UV/visible difference spectrum obtained for the third transient species 600μs after the laser pulse

Figure 3.3.2.3.2 A typical transient for the third species obtained from the 355nm photolysis of Mo(CO)₅PPh₃ in cyclohexane containing 0.25 atmospheres of CO monitored at 420nm
$k_{\text{obs}} = 4.00 \times 10^5 \pm 3.49 \times 10^4 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

$\text{Intercept} = 5.30 \times 10^2 \pm 2.48 \times 10^2 \text{s}^{-1}$

$\text{Corr Coeff} = 0.993$

Figure 3.3.2.3.3 A plot of the observed rate constant (s$^{-1}$) for the third transient species against the concentration of CO (mol dm$^{-3}$) in cyclohexane solution at 298K
Figure 3.3.2.3.4 A plot of concentration of parent complex (mol dm$^{-3}$) against the observed rate constants (s$^{-1}$) for the reaction of the third transient species at 298K.
Absorbance

Figure 3.3.2.3.5 A plot of initial absorbance of the third transient species against concentration of CO in cyclohexane solution

A plot of concentration of parent against the observed rate constant (Figure 3.3.2.3.4) gave a second order rate constant of $6.95 \times 10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ This indicates that perhaps this species is a primary photoproduct which was reacting with parent to form a dinuclear species in solution A plot of the initial absorbance of this species against the concentration of CO in cyclohexane shows that the initial absorbance of this species decreased by a small amount as the CO concentration increased This observation may be because of the isomisation process which was proposed for the drop in yield of the $\textit{cis}$-Mo(CO)$_4$PPh$_3$ intermediate The prevention of the $\textit{cis}$ intermediate from isomising to the $\textit{trans}$ configuration would decrease the yield of $\textit{trans}$ in the solution Another possibility which may not be overlooked is the loss of parent complex by the formation of Mo(CO)$_6$ which would also decrease the amount of $\textit{trans}$-Mo(CO)$_4$PPh$_3$ Given the lifetime and the configuration of the intermediate it was most likely that it was solvated in solution The bulky triphenylphosphine ligand, in a $\textit{trans}$ configuration, would be in an axial position at the furthest point from the
vacant coordination site. Therefore, like Mo(CO)₅(cyclohexane) this intermediate was probably solvated. The transient species was not the result of the reaction with water in the solvent as it was present with or without a liquid pumping stage in the sample preparation.

3.3.2.4 Fourth transient species

The fourth transient species was most probably a dinuclear species produced from the reaction of one of the primary photoproducts with an unphotolysed parent complex. A UV/visible difference spectrum of this complex is presented in Figure 3.3.2.4.1 and has a λmax of 400 nm unlike the other species. A typical transient for this species is depicted in Figure 3.3.2.4.2. This species reacted with CO and a graph of the observed rate constant against the concentration of CO in cyclohexane solution is shown in Figure 3.3.2.4.3 and yielded a second order rate constant of 6.0 x 10⁵ dm³ mol⁻¹ s⁻¹. The yield of this product was sensitive to the presence of CO in the solution and a graph of initial absorbance against concentration of CO (Figure 3.3.2.4.4) shows the loss in yield as the concentration of CO increased. Therefore this species was a secondary photoproduct.
Figure 3.3.2.4.1 A UV/visible difference spectrum obtained for the fourth transient species under 10 atmospheres of argon at 20000µs after the laser pulse.

10 mV/div

20000 µs/div

Figure 3.3.2.4.2 A typical transient of the fourth species obtained at 420nm under 0.25 atmospheres CO.
Figure 3.3.2.4.3 A plot and the experimental data of the observed rate constant (s⁻¹) for the fourth transient species against the concentration of CO (mol dm⁻³) in solution at 298K

\[ k_{[\text{CO}]} = 5.79 \times 10^3 \pm 1.06 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

Intercept = 27.2 ± 7.12 s⁻¹

Corr Coeff = 0.967
Figure 3.3.2.4 A plot of initial absorbance for the fourth transient species against the concentration of CO in cyclohexane solution

3.3.2.5 Fifth transient species

The presence of a fifth transient species suggested that the trans-Mo(CO)$_4$PPh$_3$(cyclohexane) and the Mo(CO)$_5$(cyclohexane) intermediates were formed on photolysis and reacted with the parent to produce two dinuclear species the fourth and the fifth transients. This is because both these intermediates were presumed to adopt a square planar configuration in solution. This type of orientation would be the most sterically favourable for dinuclear species formation. A UV/visible difference spectrum of the fifth transient species is shown in Figure 3.3.2.5.1 and has a maximum at 400nm. In the typical transient presented in Figure 3.3.2.5.2 the fast portion of the decay represents the fourth transient species while one can clearly see that the fifth transient species was decaying at a slower rate. In line with the other species in this system this transient reacted with CO added to the cyclohexane solution.
Figure 3.3.2.5.1 A UV/visible spectrum of the fifth transient species obtained 50000 μs after the laser pulse under 1.0 atmosphere of CO.

Figure 3.3.2.5.2 A typical transient obtained for the fifth transient species monitored at 420 nm under 0.5 atmospheres of CO.
Figure 3.3.2.5.3 A plot of the observed rate constant (s\(^{-1}\)) for the fifth transient species against the concentration of CO (mol dm\(^{-3}\)) in cyclohexane solution at 298K.
A graph of the observed rate constant of this species against CO concentration, as shown in Figure 3.3.2.5.3, yielded a second order rate constant of \(908 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). Again the presence or absence of a liquid pumping phase did not affect formation of this transient species. The graphical representation in Figure 3.3.4.5.4 of the yield of the photoproduct as a function of concentration of CO shows that the yield of this product is dependent on the concentration of CO and therefore is a secondary photoproduct.

3.3.3 266nm laser flash photolysis of Mo(CO)\(_5\)PPh\(_3\) with UV/visible monitoring

The 266nm laser flash photolysis of Mo(CO)\(_5\)PPh\(_3\) produced evidence for the production of two transient species. These species were the same as those produced on 355nm photolysis of Mo(CO)\(_5\)PPh\(_3\) and were the primary photoproducts. Significantly the third, fourth and fifth transients observed on 355nm photolysis were only present as weak transients. For the fourth and fifth transient species this is presumably because
of the difference in concentration of $\text{Mo(}CO\text{)}_5\text{PPh}_3$ between the 355nm and 266nm photolysis experiments as these were assigned to dinuclear species on 355nm photolysis. Room temperature infrared studies were not possible because of the strong absorption of sodium chloride plates in the UV region.

3.3.3.1 First transient species

The first transient species was identified as $\text{cis-Mo(}CO\text{)}_4\text{PPh}_3$ as in the 355nm analysis. A UV/visible difference spectrum of this species is shown in Figure 3.3.3.1.1 and has the same absorption characteristics as the spectrum obtained for the 355nm excitation of $\text{Mo(}CO\text{)}_5\text{PPh}_3$ i.e. $\lambda_{\text{max}} = 420\text{nm and } 480\text{nm}$. The reaction kinetics of this species with CO indicate that this species was the same as that obtained at 355nm excitation. The second order rate constant for the reaction of the first transient species with CO ($1.2 \times 10^7 \pm 2.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) on 266nm excitation was similar to that

![Figure 3.3.3.1.1](image)

Figure 3.3.3.1.1 A UV/visible difference spectrum of $\text{cis-Mo(}CO\text{)}_4\text{PPh}_3$ obtained 1µs after the pulse
obtained for the first transient species on 355nm excitation

3.3.3.2 Second transient species

The results obtained for the second transient species were similar to those for the second transient species observed for 355nm excitation. Therefore, it was presumably the same species proposed on 355nm excitation. i.e. Mo(CO)₅(cyclohexane). The UV visible spectrum shown in Figure 3.3.2.1 was identical to that obtained for the second species in the 355nm excitation. The reaction kinetics of this species with CO suggests that these species were the same. The second order rate constant obtained for the reaction of this species with CO was $4.2 \times 10^6 \pm 9.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and compared favourably with the rate constant obtained at 355nm of $3.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

![Absorbance vs Wavelength](image)

Figure 3.3.2.1 A UV/visible difference spectrum of the second transient species obtained 20µs after the laser pulse
The absence of the other transients indicated that they may have been dependent on the parent concentration. Constraints on the absorbance values of the sample solution at the excitation wavelengths i.e. between 0.5 and 2.0 absorbance units, means that because of the differences in extinction coefficients for \( \text{Mo(CO)}_5\text{PPh}_3 \) at 355nm and 266nm the concentration of \( \text{Mo(CO)}_5\text{PPh}_3 \) at 266nm is \(-10\) less than at 355nm. Therefore the probability of formation of a dinuclear species at 266nm is less than at 355nm. The presence of a weak transient at the timescale of the third transient was interesting because this species, on 355nm excitation, reacted with \( \text{Mo(CO)}_5\text{PPh}_3 \). This may point to wavelength dependency for the production of the third transient species. It was suggested that this species may have been \( \text{trans-} \text{Mo(CO)}_5\text{PPh}_3(\text{cyclohexane}) \) and so this points to a change in the labilisation along the z axes for 355nm and 266nm excitation where the 266nm excitation favoured loss of a triphenylphosphine ligand. A full reaction scheme of the photolysis products formed on 355nm and 266nm excitation is given in Figure 3.5.2.
3.4 Photolysis of W(CO)$_5$PPh$_3$

3.4.1 Infra red monitored photolysis of W(CO)$_5$PPh$_3$

An argon degassed cyclohexane solution of W(CO)$_5$PPh$_3$ was photolysed using the 355nm laser line of an Nd YAG laser in 0.1mm pathlength sodium chloride cells. The resultant infra red spectrum of the carbonyl region is displayed in Figure 3.4.1.1. The parent complex carbonyl bands were at 2073, 1981 and 1942 cm$^{-1}$ and corresponded to the $A_1$, $A_2$, $E$ modes respectively of W(CO)$_5$PPh$_3$. The bands at 2073 and 1942 cm$^{-1}$ were depleted on photolysis while the band at 1981 cm$^{-1}$ increased in intensity and moved to 1983 cm$^{-1}$. This increase was because of the formation of W(CO)$_6$ arising from the loss of a triphenylphosphine ligand from the parent and its subsequent reaction with a CO molecule photochemically lost from another parent complex. The band at 1983 cm$^{-1}$ corresponds to the $T_{1u}$ mode of W(CO)$_6$. Other new bands were formed at 2021, 1926, 1903 and 1870 cm$^{-1}$. The most intense of these new bands was the $\nu$CO at 1903 cm$^{-1}$. This band suggests the formation of a trans complex as complexes of the type trans-$M$(CO)$_4$L$_2$ have a very strong absorption at ~1890 cm$^{-1}$. This complex could have been formed from the reaction of photochemically produced W(CO)$_4$PPh$_3$ with free triphenylphosphine ligands lost from the parent complex. The $\nu$CO at 2010 cm$^{-1}$ could arise from the $A_{1g}$ band observed in trans complexes or the 2010 cm$^{-1}$ band observed in cis complexes. The band at 1926 cm$^{-1}$ also indicates the formation of some cis complex. This complex may have been formed from the reaction of cis-W(CO)$_4$PPh$_3$ with triphenylphosphine or the isomerisation of the trans complex to the cis complex. To investigate if the products were triphenylphosphine disubstituted tetracarbonyl complexes, the photolysis was carried out in excess triphenylphosphine. The infra red spectrum of the carbonyl region from the photolysis is shown in Figure 3.4.1.2. The band arising from the W(CO)$_6$ complex was absent presumably because of efficient reformation of the parent complex by the
Figure 3.4.1.1 The infra red carbonyl region after the 355nm photolysis of W(CO)$_3$PPh$_3$. 

Wavenumbers (cm$^{-1}$)
Figure 3.4.1.2 The infra red carbonyl region following the 355nm photolysis of \( \text{W(CO)}_2\text{PPh}_3 \) with an excess of \( \text{PPh}_3 \)
reaction of the pentacarbonyl intermediate with the excess ligand. All other bands were present as in the previous experiment leading to the conclusion that cis and trans complexes were formed from one or more W(CO)$_4$PPh$_3$ intermediates. The trans vCO band at 1903 cm$^{-1}$ was again the most intense indicating that this was perhaps the major product of the photoreaction.

3.4.2 355 nm laser flash photolysis of W(CO)$_5$PPh$_3$ with UV/Visible monitoring

The 355 nm laser flash photolysis of W(CO)$_5$PPh$_3$ produced evidence for the existence of five transient species of which three were identified as primary photoproducts. One was identified as cis-W(CO)$_4$PPh$_3$ and the others were tentatively assigned as W(CO)$_5$(cyclohexane) and trans-W(CO)$_4$PPh$_3$(cyclohexane). The identities of the other two species were unknown but were presumed to be dinuclear species as a result of the reactions of the primary photoproducts with parent complex.

3.4.2.1 First transient species

The first transient species was identified as cis-W(CO)$_4$PPh$_3$ primarily on the basis of its reaction kinetics as spectral data were ambiguous. The UV/visible difference spectrum of the first transient species is shown in Figure 3.4.2.1.1. The spectrum consisted of a broad band with a maximum at ~425 nm. The UV/visible difference spectrum of W(CO)$_5$(cyclohexane) obtained from the 355 nm laser flash photolysis of W(CO)$_6$ is presented in Figure 3.4.2.1.2 and has a $\lambda_{max}$ at 430 nm. Therefore given the close agreement of the spectra of the two transient intermediates it is difficult to exclude the possibility that this species is W(CO)$_5$(cyclohexane). The laser flash photolysis of W(CO)$_5$PPh$_3$ in a cyclohexane solution containing different concentrations of carbon monoxide was used to determine if the reacting species was W(CO)$_5$(cyclohexane) or cis-W(CO)$_4$PPh$_3$. A typical transient obtained under a 0.5 atmosphere of CO is depicted in Figure 3.4.2.1.3. The reaction of cis-W(CO)$_4$PPh$_3$
with CO followed pseudo first order conditions. The kinetic data obtained from this experiment is displayed in Figure 3 4 2 1 4 and shows a linear dependence of the rate on the concentration of CO. The slope of this graph yielded a second order rate constant of $6.05 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$. Dobson and coworkers$^{10}$ carried out time resolved infra red laser flash photolysis ($\lambda = 308$ nm) on $\text{W(CO)}_5\text{PPh}_3$ in n-heptane solution and obtained a second order rate constant of $1.17 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the reaction of $\text{cis-W(CO)}_4\text{PPh}_3$(n-heptane) with CO. In photolysis experiments with n-heptane and cyclohexane, the rate constants obtained in n-heptane are normally twice as fast as those obtained in cyclohexane because of different interaction energies between the solvents and the metal centre$^{19}$. The second order rate constant obtained in this experiment indicated that the $\text{cis-W(CO)}_4\text{PPh}_3$ species may not be solvated in solution. This observation points to steric hinderance in the $\text{cis}$ position by the presence of the bulky triphenylphosphine group allowing the relatively small CO ligand to coordinate in the $\text{cis}$ position but not the larger solvent molecule. One possible solution was that the $\text{cis-W(CO)}_4\text{PPh}_3$ intermediate could fill the vacant coordination site by an 'agostic' interaction with one of the hydrogens on the triphenylphosphine ligand, most likely in an ortho position. A tungsten carbonyl complex $\text{W(CO)}_3(\text{PCy}_3)_2$ has been isolated and its structure determined where the complex, although apparently coordinately unsaturated, has an ortho hydrogen atom from one of the cyclohexyl rings filling the sixth coordination site and stabilising the complex$^8$. 
Figure 3.4.2.1.1 A UV/visible difference spectrum of $\text{cis-W(CO)}_3\text{PPH}_3$ obtained 2µs after the laser pulse from the photolysis of W(CO)$_5$PPh$_3$ in cyclohexane under 0.5 atmospheres of CO.

Figure 3.4.2.1.2 A UV/visible difference spectrum of W(CO)$_5$(cyclohexane) obtained 0.2µs after the laser pulse in the 355nm photolysis of W(CO)$_6$ under 1.0 atmospheres of CO.
Figure 3.4.2.1.3 A typical transient for the decay of $\text{cys-W(CO)}_3\text{PPh}_3$ in cyclohexane under 0.5 atmospheres of CO monitored at 440nm with a simultaneous grow in monitored at 360nm.
Figure 3.4.2.1.4 The graph and kinetic data obtained from the 355nm photolysis of W(CO)$_5$PPh$_3$ with various concentrations of CO (mol dm$^{-3}$) for the first transient species.
Figure 3.4.2.1.5 A plot of concentration of \( W(CO)_5PPh_3 \) (mol dm\(^{-3}\)) against \( k_{obs} \) (s\(^{-1}\)) for \( cis-W(CO)_5PPh_3 \) demonstrating the non-dependence of the transient species on parent concentration.

In addition, the rate of decay of the \( cis-W(CO)_4PPh_3 \) intermediate was mirrored by a concomitant grow in at ~360nm, indicating that this species was reacting to form a secondary transient photoproduct with a \( \lambda_{max} \) ~415nm. The rate of this grow in was constant regardless of the concentration of \( W(CO)_5PPh_3 \) as can be seen in Figure 3.4.2.1.5 ruling out the possibility of dinuclear complex formation. The identity of this secondary photoproduct is uncertain but could be the intramolecularly stabilised \( cis-W(CO)_4PPh_3 \) complex. It may also be the result of isomensation of the \( cis \) form of \( W(CO)_4PPh_3 \) to the \( trans \) configuration. Another possible solution was that the \( W(CO)_5PPh_3 \) intermediate could have reacted with impurities in the cyclohexane solvent even though the sample was subjected to a liquid pumping stage to remove impurities such as \( H_2O \) or \( CO_2 \) prior to photolysis. However, \( H_2O \) can be easily removed by three liquid pumping cycles prior to analysis\(^{11}\) In the absence of a liquid pumping stage in sample preparation, like the Cr and Mo analogues of this transient.
species, the first transient was absent. This may be because of fast reaction of the *cis* intermediate with water beyond the detection limit of the instrumentation or the production of a water complex from one of the other photoproducts which obscures the band arising from the *cis* complex.

A plot of initial absorbance against CO concentration showed that the yield of this species increased with increasing CO concentration (Figure 3.4.2.1.6). A possible explanation for this observation was that the *cis* intermediate was undergoing isomerisation to the *trans* form on a timescale similar to the reaction of *cis*-W(CO)₄PPh₃ with CO. Increasing the CO concentration would increase the rate of formation of W(CO)₅PPh₃ from a *cis* intermediate and so reduce the amount isomerising to *trans*-W(CO)₄PPh₃.

![Figure 3.4.2.1.6](image)

**Figure 3.4.2.1.6** A plot of initial absorbance against concentration of CO indicating an increase in yield of *cis*-W(CO)₅PPh₃ on increasing CO concentration.
3.4.2.2 Second transient species

The identification of the second transient species was tentative. A UV/visible difference spectrum is shown in Figure 3.4.2.2.1 and has a maximum at ~420 nm. Again, it was practically indistinguishable from other spectra obtained for this system. This species also reacted with CO and a plot of absorbance against time exhibited a logarithmic decay, an example of which is shown in Figure 3.4.2.2.2. Pseudo first order rate constants ($k_{obs}$) were extracted from the decay curve of this species. A plot of the observed rate constant against CO ligand concentration showed a linear dependence of the decay of this species with varying CO concentration. A graph of the observed rate constant against CO concentration is displayed in Figure 3.4.2.2.3. The second order rate constant calculated for the reaction of this species with CO was $6.6 \times 10^5 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. This value was close to that observed in an experiment carried out on W(CO)$_6$ in CO-saturated cyclohexane for the reaction of W(CO)$_3$(cyclohexane) with CO at $6 \times 10^5 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. This species did not react with the parent complex as can be seen from Figure 3.4.2.2.4. The observed rate constant remained unchanged regardless of the parent concentration. The decay of the species was mirrored by a simultaneous growth at the same rate. It may well be that the decaying species was reacting with free triphenylphosphine in solution generated from the loss of a triphenylphosphine ligand from the parent to form a cis or trans isomer of W(CO)$_4$(PPh$_3$)$_2$. Alternatively, it may be the result of a cis-trans isomerization reaction. However, Dobson and coworkers, on their experiments with W(CO)$_4$L(pip) ($L = \text{phosphines, phosphites, pip} = \text{pipendine}$), reported that the interconversion of the intermediates was not as fast as their bimolecular reactions. In contrast to this, these workers report that in the photolysis of Mo(CO)$_4$(NP)$_3$ (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane) a single primary photoproduct was formed from the cleavage of the nitrogen coordinated atom in the chelate followed by rearrangement of...
Figure 3.4.2.2.1 A UV/visible difference spectrum of the second transient species obtained 50 $\mu$s after the laser pulse under 0.5 atmospheres of CO

Figure 3.4.2.2.2 A typical transient signal obtained for the second transient species showing a decay at 440 nm and a concomitant growth at 360 nm
Figure 3.4.2.2.3 The graph and data of the observed rate constants (s\(^{-1}\)) and the corresponding concentrations of CO (mol dm\(^{-3}\)) for the reaction of the second transient species with CO.
the intermediate, prior to solvation, to form a mixture of cis and trans solvatocomplexes. Another possible solution was a recombination reaction of a photochemically generated W(CO)$_5$(cyclohexane) moiety with triphenylphosphine. The triphenylphosphine ligand is large and bulky and may not have diffused sufficiently far from the other photofragment produced from photolysis of W(CO)$_5$PPh$_3$, i.e., W(CO)$_5$(cyclohexane). Photolysis at 355nm at room temperature of W(CO)$_5$PPh$_3$ in infra red cells demonstrated that loss of a triphenylphosphine occurred *vide infra*.

![Graph](image)

**Figure 3.4.2.2.4** A plot of $k_{obs}$ $(s^{-1})$ against W(CO)$_5$PPh$_3$ concentration $(mol dm^{-3})$ monitored at 360nm.
Additionally, Dalgren and Zink calculated the quantum yield for unique ligand loss as 0.29 for the 366 nm excitation of W(CO)$_5$PPh$_3$ in cyclohexane solution$^{13}$ As the experiments to calculate the second order rate constant of this species were carried out on the same sample the loss of a triphenylphosphine ligand from W(CO)$_5$PPh$_3$ would be expected to produce W(CO)$_6$ in solution. The presence of W(CO)$_6$ would increase the concentration of W(CO)$_5$(cyclohexane) formed in solution as the laser pulse would photolyse both W(CO)$_6$ and W(CO)$_5$PPh$_3$. Deconvolution of the kinetic decays at various concentrations of CO showed that the yield of this transient species increased with increasing CO concentration (Figure 3.4.2.25). Time resolved infra red experiments carried out by Dobson et al on W(CO)$_5$PPh$_3$ in n-heptane solution yielded a second order rate constant of $3 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the reaction of trans-W(CO)$_4$PPh$_3$(n-heptane) with CO$^{10}$. Given the different interaction energies of cyclohexane and n-heptane with the coordinately unsaturated intermediates produced in photolysis experiments, reactions of n-heptane solvated complexes tends to be faster by a factor of two compared to the corresponding cyclohexane solvated species. Therefore the second order reaction rate of trans-W(CO)$_4$PPh$_3$(cyclohexane) with CO would be expected to be $1.5 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, twice the rate constant obtained in this experiment. Given the above data this species can be tentatively assigned as W(CO)$_5$(cyclohexane).
Figure 3.4.2.5 A plot of initial absorbance against concentration of CO for the second transient species

3.4.2.3 Third transient species

The identity of this third transient species was unknown. A UV/visible difference spectrum of this species is shown in Figure 3.4.2.3.1 and contains a broad band with a maximum at ~430 nm. A typical transient representing the decay profile of this species is depicted in Figure 3.4.2.3.2. The decay of this species was dependent on the concentration of CO in solution. A graph of the concentration of CO against the observed rate constant is displayed in Figure 3.4.2.3.3. The second order rate constant for the reaction of this species with CO was calculated from the slope of the line as $1.27 \times 10^4 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$. This second order rate constant was slow in comparison to the rates observed for primary photoproducts in cyclohexane solution which are usually of the order of $10^6 \text{s}^{-1}$. Figure 3.4.2.3.4 shows the dependence of the yield of this photoproduct on CO concentration and indicates that this intermediate is not a primary photoproduct.
Figure 34.2.3.1. A UV/visible difference spectrum obtained for the third transient species 800 µs after the laser pulse

Figure 34.2.3.2 A typical transient obtained for the third transient species under 0.25 atmospheres of CO at 420 nm
The loss in yield may be explained by the isomerisation process implied for the \textit{cis}-\text{W(CO)}_{4}\text{PPh}_3 \text{ intermediate} However, the rate of disappearance of this transient species at 430nm was echoed by a simultaneous grow in monitored at 360nm when measured under an argon atmosphere The formation of this photoproduct was dependent on the concentration of the parent Therefore this species must be reacting with \text{W(CO)}_{5}\text{PPh}_3 \text{ in solution to yield a dinuclear species} A graph of the observed rate constant against the parent concentration is displayed in Figure 3 4 2 3 5 The second order rate constant for the formation of this species was $3.0 \times 10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ The reactive intermediate may be \textit{trans}-\text{W(CO)}_{4}\text{PPh}_3(\text{cyclohexane}) The presence of the electronegative phosphorus group \textit{trans} to the vacant coordination site would be better able to stabilise a solvated intermediate than an intermediate with the vacant site \textit{trans} to a CO ligand \textsuperscript{17}. In addition, the square planar intermediate with a PPh\textsubscript{3} in the axial position would facilitate attack on a parent complex because of less steric hindrance compared to a square planar intermediate with the relatively large PPh\textsubscript{3} ligand in an equatorial position. As stated before intermediates generated in n-heptane solution tend to react twice as fast as those in cyclohexane solution In Dobson and coworkers time resolved infra red (TRIR) 308nm excitation of \text{W(CO)}_{5}\text{PPh}_3 \text{ the second order rate constant for the reaction of } \textit{trans}-\text{W(CO)}_{4}\text{PPh}_3(\text{n-heptane}) \text{ with CO was } 3 \times 10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \text{10 On this basis the reactivity of } \textit{trans}-\text{W(CO)}_{4}\text{PPh}_3(\text{cyclohexane}) \text{ would be } 1.5 \times 10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \text{ Therefore, given that TRIR is a better method for the elucidation of structure than time resolved UV, this species may not be } \textit{trans}-\text{W(CO)}_{4}\text{PPh}_3(\text{cyclohexane})
$k_{(CO)} = 1.27 \times 10^4 \pm 7.93 \times 10^2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

Intercept $= 103 \pm 53 \text{ s}^{-1}$

Corr Coeff $= 0.996$

Figure 3.4.2.3.3 A plot of the observed rate constants (s$^{-1}$) for the decay of the third transient species with different concentrations of CO (mol dm$^{-3}$) at 298K
Figure 3.4.2.3.4 A plot of initial absorbance of the third transient species against concentration of CO
$k_{obs} = 10^{-3}$ s$^{-1}$

$[W(CO)\$_5PPh\textsubscript{3}] \times 10^{-4}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>$[W(CO)$_5PPh\textsubscript{3}] \times 10^4$ mol dm$^{-3}$</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.89</td>
<td>221</td>
</tr>
<tr>
<td>5.24</td>
<td>511</td>
</tr>
<tr>
<td>6.92</td>
<td>1303</td>
</tr>
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<td>8.72</td>
<td>1593</td>
</tr>
</tbody>
</table>

$k[W(CO)\$_5PPh\textsubscript{3}]= 3.04 \times 10^6 \pm 4.3 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$

Intercept = -969 ± 156 s$^{-1}$

Corr Coeff = 0.980

Figure 3.4 2.3.5 A plot of concentration of $W(CO)\$_5PPh\textsubscript{3}$ (mol dm$^{-3}$) against the observed rate constants (s$^{-1}$) obtained for the third transient species at 298K.
3.4.2.4 Fourth transient species

A UV/visible difference of the fourth transient species observed in the 355nm laser flash photolysis of W(CO)$_5$PPh$_3$ is shown in Figure 3.4.2.4.1 and had a broad band with a $\lambda_{\text{max}}$ at ~430nm. The nature of this species was unknown but it may be the decay of the dinuclear species formed from the third transient species and the parent complex or the decay of the intramolecularly stabilised complex described for the first transient. The first option was the most likely solution given the reactivity of the $\text{cis}$-W(CO)$_4$PPh$_3$ to CO. A typical transient for the decay of this species can be seen in Figure 3.4.2.4.2. This photoproduct like the others appeared to react with CO and yielded a second order rate constant of $1.14 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ A graph of the dependence on CO concentration is shown in Figure 3.4.2.4.3. As expected the yield of this product depended on the concentration of CO. The plot in Figure 3.4.2.4.4 of the initial absorbance of the species against CO concentration shows the decrease in yield with increasing CO concentration. This therefore indicates that the fourth transient species is a secondary photoproduct.
Figure 3.4.2.4.1 A UV/visible difference spectrum of the fourth transient species obtained 20000μs after the laser pulse

10 mV/div

Figure 3.4.2.4.2 A typical transient signal obtained for the fourth transient species under 10 atmospheres of CO monitored at 420nm
Figure 3.4.2.43 The experimental data obtained for the graph of the observed rate constants (s\(^{-1}\)) for the fourth transient species with concentration of CO (mol dm\(^{-3}\)) at 298K.

<table>
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<tr>
<th>[CO] mol dm(^{-3})</th>
<th>(k_{\text{obs}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>6.99</td>
</tr>
<tr>
<td>0.006</td>
<td>12.6</td>
</tr>
<tr>
<td>0.009</td>
<td>15.26</td>
</tr>
<tr>
<td>0.012</td>
<td>17.51</td>
</tr>
</tbody>
</table>

\[ k_{[\text{CO}]} = 1.14 \times 10^3 \pm 1.86 \times 10^2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \]

Intercept = 4.53 ± 1.52 s\(^{-1}\)

Corr Coeff = 0.974
Figure 3.4.2.4 A plot of the initial absorbance of the fourth transient species against CO concentration showing the dependence of the yield on concentration of CO.

3.4.2.5 Fifth transient species

A UV/visible difference spectrum of the fifth transient species is shown in Figure 3.4.2.5.1 and it can be seen that, like the other transient species, it has $\lambda_{\text{max}}$ at ~400nm. A typical transient signal obtained for this species is shown in Figure 3.4.2.5.2. This species appears to be stable even under a CO atmosphere. However, kinetic measurements at long timescales is difficult because of the effect of diffusion of product from the monitoring beam. This species was affected by the presence of CO in the sample solution. A plot of initial absorbance against CO is given in Figure 3.4.2.5.3 and shows a drop in yield of this photoproduct with increasing CO concentration. This species was not the result of reaction with water in the cyclohexane solution as it was present with and without a liquid pumping phase in the sample preparation and so therefore it probably is a dinuclear complex.
Figure 3.4.2.5.1 A UV/visible difference spectrum of the fifth transient species obtained 0.3 s after the laser pulse.

Figure 3.4.2.5.2 A typical transient obtained for the fifth transient species under 0.25 atmospheres of CO.
Figure 3.4.2.5.3 A plot of initial absorbance against CO concentration for the fifth transient species.

3.4.3 266nm laser flash photolysis of W(CO)$_5$PPh$_3$ with UV/visible monitoring

Laser flash photolysis of W(CO)$_5$PPh$_3$ at 266nm produced evidence for the formation of three photoproducts. Room temperature infra red experiments were not possible because of significant absorption by the sodium chloride plates and the large extinction coefficient of W(CO)$_5$PPh$_3$ at 266nm ($\varepsilon = 20040$ cm mol dm$^{-3}$). Identities for these photoproducts were suggested primarily on the basis of their reaction kinetics. UV/visible difference spectra were also used to aid in the identification of the photoproducts. The species produced on 266nm photolysis of W(CO)$_5$PPh$_3$ were cis-W(CO)$_4$PPh$_3$, W(CO)$_5$(cyclohexane) and trans-W(CO)$_4$PPh$_3$(cyclohexane).

3.4.3.1 First transient species

A UV/visible difference spectrum of the first transient species is shown in Figure 3.4.3.1.1 and contains a broad band with a $\lambda_{\text{max}}$ at ~430nm commonplace in
these tungsten carbonyl photoproducts. No significant conclusions could be drawn from this spectrum. The reaction of this intermediate with CO was extremely important in determining the identity of this species. A plot of the observed pseudo first order rate constant against differing CO concentrations in cyclohexane solution revealed that the change in $k_{obs}$ with CO concentration was linear. The bimolecular rate constant was obtained from the slope and calculated as $3.2 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ ± $1.9 \times 10^6$. This rate was half that observed for the cis-$W$(CO)$_4$PPh$_3$ intermediate on 355 nm excitation. The reason for this change was unknown but it may be because of discrete changes in the transient profile as 266 nm irradiation was prone to shock waves. The reaction rate of the first species in the 266 nm photolysis was significantly faster than the corresponding rate for W(CO)$_5$(cyclohexane) at $6.6 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ and therefore was not W(CO)$_5$(cyclohexane). Alternatively, the species could be trans-$W$(CO)$_4$PPh$_3$. However, trans-$W$(CO)$_4$PPh$_3$(n-heptane) reacted significantly slower than the corresponding cis-$W$(CO)$_4$PPh$_3$(n-heptane) in Dobson and coworkers TRIR 308 nm excitation of W(CO)$_5$PPh$_3$ ($cis$ $1.4 \times 10^5$ s$^{-1}$, $trans$ $3.5 \times 10^4$ s$^{-1}$)$^{10}$ Knowing that photolysis of metal carbonyl species in cyclohexane slows down the rate of decay of the species produced relative to n-heptane because of different interaction energies of the solvent with the metal centre, this species could not be assigned to trans-$W$(CO)$_4$PPh$_3$(cyclohexane). In addition, the positioning of the triphenylphosphine trans to the vacant site would facilitate solvation and stabilise the trans species for a longer period of time relative to a non-solvated intermediate. It was therefore concluded that this species was the cis-$W$(CO)$_4$PPh$_3$ intermediate.

3.4.3.2 Second transient species

The second transient species had a lifetime of approximately 500 μs under one atmosphere of CO. A UV/visible difference spectrum of this transient is shown in Figure 3.4.3.2.1. As expected, the intermediate exhibited a broad band with a $\lambda_{max}$ at
-430nm typical of these photocomplexes. Photolysis of this species under varying concentrations of CO revealed a linear dependence of the observed rate constant with CO. The second order rate constant for the reaction of this species with CO was \(4.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \pm 1.5 \times 10^5\) and was in agreement with the second transient observed in the 355nm photolysis of \(\text{W(CO)}_5\text{PPh}_3\). Therefore it may be assumed that this species was present in both 355nm and 266nm photolysis of \(\text{W(CO)}_5\text{PPh}_3\). In the 355nm photolysis experiments this species was assigned to \(\text{W(CO)}_5(\text{cyclohexane})\).

![Figure 3.4.3.1.1](image)

**Figure 3.4.3.1.1** A UV/visible difference spectrum of \(\text{cis- W(CO)}_4\text{PPh}_3\) obtained 5μs after the laser pulse.
Figure 3.4.3.2.1 A UV/visible difference spectrum of the second transient species obtained 50μs after the laser pulse

Figure 3.4.3.3.1 A UV/visible difference spectrum of the third transient species obtained 2500μs after the laser pulse
34.3.3 Third transient species

A third transient species was observed and had a \( \lambda_{\text{max}} \) at 430 nm. A UV/visible difference spectrum of this species can be seen in Figure 34.3.3.1. The second order rate constant for the reaction of this species with CO was calculated as \( 1.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \pm 1.8 \times 10^3 \) and indicates that this species was the same as that observed on 355 nm photolysis. In the 355 nm experiments, this species was tentatively assigned as \textit{trans-}W(CO)_{5}\text{PPh}_{3}(\text{cyclohexane}).

Weak transients were observed for the last species presumably because of the lower concentration of W(CO)\textsubscript{5}PPh\textsubscript{3} in solution compared to the experiments at 355 nm. This demonstrates that this species was a dinuclear species as the lower parent concentration would decrease the chance of a primary photoproduct reacting with parent.
3.5 Conclusions

The possibility of three primary photoproducts on photolysis of compounds of the type \( \text{M(CO)}_5\text{PPh}_3 \) (M = Cr, Mo or W) can lead to the production of many photoproducts, both primary and secondary. The reaction kinetics of the intermediates formed in the photolysis can help in identifying the nature of the transient species. A summary of the second order rate constants for the transient species obtained upon 355nm photolysis of \( \text{M(CO)}_5\text{PPh}_3 \) complexes is presented in Table 3.5.1. It can be seen that the reactivity of the transient species was dependent on the type of metal and the metal radii, i.e., steric and electronic requirements. For the first transient species, the \( \text{cis-M(CO)}_4\text{PPh}_3 \) analogue, the reactivity of the intermediates was in the order Cr > Mo > W. This order is consistent with the relative atomic radii of the metal atoms and indicates a steric requirement as generally molybdenum carbonyl complexes tend to react faster than chromium and tungsten complexes. The first transient species in each case was presumed to be non-solvated on the basis that the second order rate constants obtained for the reaction of the \( \text{cis} \) intermediate with CO were two orders of magnitude faster than the rates for the corresponding \( \text{M(CO)}_5\text{(cyclohexane)} \) intermediates and thereby indicating that the metal centre did not coordinate a solvent molecule on photolysis. Steric effects arising from the triphenylphosphine ligand were believed to cause this difference in reactivity; i.e., the larger solvent molecule could not coordinate to the metal because of the triphenylphosphine ligand but the smaller CO molecule could. The intermediates may have been stabilised by intramolecular reaction with the triphenylphosphine ligand possibly an ortho metallation type interaction. The \( \text{cis} \) species may be isomsembling to the \textit{trans} configuration although the evidence is not conclusive. Dobson \textit{et al.} reported that the solvation of the \( \text{LW(CO)}_4 \) species inhibits the isomensation process. Therefore if the \( \text{cis} \) species is not solvated then the isomensation process may be favourable.
In the case of the second transient species the results do not conclusively identify if this species was $\text{M(CO)}_5$ (cyclohexane). The reactivity of the second transient species was in the order $\text{Mo} > \text{W}$. This series reflects the relative reactivities of the metal hexacarbonyls; i.e., molybdenum tends to be the most reactive.\(^\text{20}\) The reactivity of $\text{trans-Cr(CO)}_4\text{PPh}_3$ indicates that it may in fact be $\text{Cr(CO)}_5$ (cyclohexane) even though spectral data indicate otherwise. If one includes the $\text{trans-Cr(CO)}_4\text{PPh}_3$ (cyclohexane) second order rate constant in the $\text{M(CO)}_5$ (alkane) series, the relative rates i.e., $\text{Mo} > \text{Cr} > \text{W}$ fit the reactivity series for the $\text{M(CO)}_5$ (alkane) solvato complexes.\(^\text{21}\) The third transient species $\text{trans-M(CO)}_4\text{PPh}_3$ (cyclohexane) also reflected this trend if the rate for the $\text{trans-Cr(CO)}_4\text{PPh}_3$ (cyclohexane) complex was omitted from the series. $\text{trans-Cr(CO)}_4\text{PPh}_3$ (cyclohexane) appeared to react faster than the other species by an order of magnitude. This species however was not observed to react with parent complex.

<table>
<thead>
<tr>
<th>Transient Species</th>
<th>$\text{Cr} \ \text{k}_{[\text{CO}]}^a$</th>
<th>$\text{Mo} \ \text{k}_{[\text{CO}]}^a$</th>
<th>$\text{W} \ \text{k}_{[\text{CO}]}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{cis-M(CO)}_4\text{PPh}_3$</td>
<td>$2.04 \times 10^8$</td>
<td>$1.51 \times 10^8$</td>
<td>$0.60 \times 10^8$</td>
</tr>
<tr>
<td>$\text{M(CO)}_5$ (cyclohexane)</td>
<td>Absent</td>
<td>$3.83 \times 10^6$</td>
<td>$0.66 \times 10^6$</td>
</tr>
<tr>
<td>$\text{trans-M(CO)}_4\text{PPh}_3$ (cyclohexane)</td>
<td>$1.92 \times 10^6$</td>
<td>$4.00 \times 10^5$</td>
<td>$1.27 \times 10^4$</td>
</tr>
<tr>
<td>dinuclear</td>
<td>No reaction</td>
<td>$6.0 \times 10^3$</td>
<td>$1.14 \times 10^3$</td>
</tr>
<tr>
<td>dinuclear</td>
<td></td>
<td>$489$</td>
<td>$908$</td>
</tr>
</tbody>
</table>

Table 3.5.1 A table showing the second order rate constants for the reaction of the transient species produced on 355nm laser flash photolysis of $\text{M(CO)}_5\text{PPh}_3$ ($\text{M} = \text{Cr}$, $\text{Mo}$ or $\text{W}$) with CO $^a \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, $^b$ estimated from the observed rate constant under 1 atm CO
The other intermediates reacted with both CO and parent which suggested that they were primary photoproducts even though the yield of the intermediates dropped on addition of CO to the sample solutions. The absence of a fourth transient species for the chromium analogue implied that the photochemical processes for \( \text{Cr(CO)}_5\text{PPh}_3 \) were simpler than the corresponding molybdenum and tungsten complexes. It may reflect a smaller number of photoproducts on 355nm excitation producing perhaps a \( \text{cis} \) and \( \text{trans} \)-\( \text{Cr(CO)}_4\text{PPh}_3 \) intermediate with a low quantum yield for loss of the unique ligand as was observed in the photochemistry of \( \text{Cr(CO)}_4\text{PMe}_3 \). The lifetimes of these transient species suggested that they were dinuclear species. The lifetimes of the fifth transient species were of the order of seconds again indicating that they were dinuclear complexes. The molybdenum intermediate was again the most reactive. The absence of a value for the tungsten analogue may reflect the thermal stability of tungsten complexes in general. There was a decay for a fifth transient species but its lifetime was longer than the instrumentation could measure accurately. In addition, diffusion of the photoproducts from the monitoring beam path can induce errors in kinetic measurements at long timescales. An estimate for the decay of this species under 1 atmosphere of CO gives a second order rate constant of 200 dm\(^3\) mol\(^{-1}\) s\(^{-1}\). This fits in the reactivity series for the Group VIB metal carbonyl complexes.

It was difficult to perceive any wavelength dependency on the 355nm and 266nm photolysis of these complexes. The first transient species \( \text{cis-M(CO)}_4\text{PPh}_3 \) was present for \( M = \text{Mo, W} \) but absent for \( M = \text{Cr} \). This indicated that the higher energy excitation of \( \text{Cr(CO)}_5\text{PPh}_3 \) does not induce the loss of a CO ligand in the \( \text{cis} \) position. The reduction in quantum yield could be the result of a different non-radiative pathway for the \( \text{cis-Cr(CO)}_4\text{PPh}_3 \) intermediate arising from the higher energy excitation. The second transient species was present for all complexes and was identified, in all cases, as the same species present on 355nm excitation. The quantum yield of this species may have increased with the move to higher energy excitation.
third species was present for chromium and tungsten but in a low yield for molybdenum. This suggests that there may be wavelength dependency for ligand loss in Mo(CO)$_2$PPh$_3$. This third species was shown to react with parent and CO on 355 nm excitation which suggests it may have been a primary photoproduct. The low yield of this species on irradiation at 266 nm may have reflected a change in the photochemistry of Mo(CO)$_2$PPh$_3$. The overall reaction schemes are shown Schemes 3.5.1, 3.5.2 and 3.5.3 for chromium, molybdenum and tungsten respectively.
Scheme 3.5.1 The reaction scheme for the photochemical and subsequent thermal reactions on the laser flash photolysis of Cr(CO)$_5$PPh$_3$.

S = cyclohexane
P = Cr(CO)$_5$PPh$_3$
Scheme 3.5.2 The reaction scheme for the photochemical and subsequent thermal reactions on the laser flash photolysis of Mo(CO)$_5$PPh$_3$
Scheme 3.5.3 The reaction scheme for the photochemical and subsequent thermal reactions on the laser flash photolysis of $\text{W(CO)}_5\text{PPh}_3$. 

$S = \text{cyclohexane}$  
$P = \text{W(CO)}_5\text{PPh}_3$
REFERENCES

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CHAPTER 4

THE CRYSTAL STRUCTURES OF $(\eta^5$-$\text{C}_6\text{H}_7)$Mn(CO)$_2$(C$_5$H$_5$N) AND

$(\eta^5$-$\text{C}_6\text{H}_7)$Mn(CO)$_2$(cis-$\text{C}_8\text{H}_{14}$)
4.1 Introduction

X-ray crystallography has become a very important technique in the elucidation of the structure of molecules. X-rays with wavelengths of less than 2 Å are used for the determination of the relative positions of atoms in crystals because their wavelengths are comparable to the spacings of atoms in a molecule. X-rays interact with crystals in what can be described as a diffraction phenomenon. Crystals themselves are characterized by periodicities in three dimensions, i.e., the atomic grouping is repeated by symmetry elements so as to build up a crystal. The regularity of the 3-D structure of crystals acts to reinforce the diffraction caused by any molecule in the crystal. The nature of the diffraction provides a method where the molecular structure and crystal structure may be determined.

The crystal structures of two manganese complexes were determined. The complexes were of the type \((\eta^5-C_5H_4CH_3)Mn(CO)_2L\) where \(L =\) pyridine and \(\text{cis-cyclooctene}\). These compounds were examined to see if the presence of two distinctly different ligands \((L)\) had an effect on the \((\eta^5-C_5H_4CH_3)Mn(CO)_2\) unit, i.e., the strong \(\sigma\) donating capacity of the pyridine ligand and the strong \(\pi\) accepting capacity of the \(\text{cis-cyclooctene}\) ligand. The structures were solved by the Patterson heavy atom method. The heavy atom method can give a trial structure which can then be refined. This method involves location of the heaviest atom(s) in the molecule by calculating an electron density map (Patterson map) from the collected reflection data. Refinement takes place in four stages:

1. A crude model of the structure is calculated from the first calculated electron density functions and the observed structure factors with the observed phases.
2. A set of structure factors is calculated allowing for thermal effects. A new electron density map and structure is calculated from the observed structure factors and calculated phases. This procedure is repeated until a reproducible model is obtained (cyclic Fourier refinement).
3. A difference Fourier synthesis produces a
difference Fourier map which allows for further refinement to produce more precise locations of atoms, identification of missing atoms and refinement of thermal parameters. Steps (2) and (3) are repeated as necessary until the discrepancy under $R$ (see Equation 4.11) is reduced. (4) A statistical model of the structure is obtained using least squares refinement which represents the best fit with the observed data. Three positional and six thermal parameters are fitted to each atom. The final result is an electron density map which correlates with the true structure. At each stage an $R$ value is calculated. This value indicates the correlation of the calculated structure to the actual structure and is computed from the following equation:

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$  

Equation 4.11

where $|F_o|$ is the observed structure factor and $|F_c|$ is the calculated structure factor.

The reflection data were collected on a four circle diffractometer. Using a four circle diffractometer allows for total freedom of rotation about three mutually perpendicular axes so that the crystal can be placed in any orientation. The fourth circle is the position of the counter and the incident beam which can only be moved in the horizontal plane (Figure 4.11).
Figure 4.1.1 A schematic diagram of the geometry of a four circle diffractometer
<table>
<thead>
<tr>
<th>compound</th>
<th>((\eta^5-C_6H_7)\text{Mn(CO)}_2(C_2H_4N))</th>
<th>((\eta^5-C_6H_7)\text{Mn(CO)}<em>2(cis-C_8H</em>{14}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>F a m u</td>
<td>269.18</td>
<td>300.28</td>
</tr>
<tr>
<td>space group</td>
<td>P2(_1)/c</td>
<td>P2(_1)/a</td>
</tr>
<tr>
<td>crystal</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>(a) Å</td>
<td>7.761(5)</td>
<td>6.198(5)</td>
</tr>
<tr>
<td>(b) Å</td>
<td>20.578(10)</td>
<td>19.476(13)</td>
</tr>
<tr>
<td>(c) Å</td>
<td>15.634(11)</td>
<td>12.273(10)</td>
</tr>
<tr>
<td>(\beta) deg</td>
<td>103.10(6)</td>
<td>94.21(6)</td>
</tr>
<tr>
<td>(V) Å(^3)</td>
<td>2432(3)</td>
<td>1477.6(2)</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>density g cm(^{-3})</td>
<td>1.45(5) (meas), 1.47 (calc)</td>
<td>1.35(5) (meas), 1.394 (calc)</td>
</tr>
<tr>
<td>radiation</td>
<td>Mo K(_\alpha) ((\lambda = 0.710692,\text{Å})) monochromated graphite</td>
<td>Mo K(_\alpha) ((\lambda = 0.710692,\text{Å})) monochromated graphite</td>
</tr>
<tr>
<td>(\mu) cm(^{-1})</td>
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<td>8.53</td>
</tr>
<tr>
<td>(F(000))</td>
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</tr>
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<td>reflections</td>
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<td>4801</td>
</tr>
<tr>
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<td>3774</td>
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<tr>
<td>unique reflections</td>
<td>3286</td>
<td>3191</td>
</tr>
<tr>
<td>(I &gt; 2\sigma(I))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R)</td>
<td>0.056</td>
<td>0.049</td>
</tr>
<tr>
<td>(R_w)</td>
<td>0.055</td>
<td>0.0546</td>
</tr>
</tbody>
</table>

\[w = \frac{1.7056}{(\sigma^2(F) + 0.001F^2)}\]

\[w = \frac{0.4794}{(\sigma^2(F) + 0.001F^2)}\]

Table 4.1.1 A summary of the crystallographic data for the complexes \((\eta^5-C_6H_7)\text{Mn(CO)}_2L\) where \(L\) = pyridine and \(cis\)-cyclooctene
4.2 Data collection for \((\eta^5-C_6H_7)\text{Mn(CO)}_2(C_5H_5N)\)

The synthesis of \((\eta^5-C_6H_7)\text{Mn(CO)}_2(C_5H_5N)\) is described in the experimental section. The crystallographic data was collected by Dr R A Howie at the University of Aberdeen. A rectangular prismatic crystal of dimensions 0.3 x 0.3 x 0.5 mm\(^3\) was selected for crystal structure determination. The crystal was mounted on a Nicolet P3 four circle diffractometer. Mo K\(\alpha\) radiation (0 71069 Å) was used in the analysis of the complex in which a total of 6196 reflections were measured in the range \(h -10\) to 10, \(k 0\) to 23, \(l 0\) to 20 out to \(2\theta = 55^\circ\) using a \(\theta/2\theta\) scan technique. Of these reflections 5628 were unique of which 3286, with \(I/\sigma(I)\), were considered observed. No absorption correction was applied to the data \((\mu = 10.3\text{cm}^{-1})\). At an interval of 50 measurements standard reflections 4 0, 2 and 0 12, 0 were measured and their intensity decreased by 25\% during the data collection. The data was corrected by linear interpolation between the standard intensity values. The density measurement was carried out by using the density gradient tube method.

The structure was solved using SHELXS86 by the Patterson heavy atom method followed by partial structure expansion to calculate the positions of the non-hydrogen atoms. The atomic coordinates were refined by least squares refinement using SHELX76. Hydrogen atom positions were calculated from the positions of the non-hydrogen atoms to which they were attached. Standard isothermal parameters \(U_{eq}\) of 0.05 Å\(^2\) for the aromatic hydrogens and 0.13 Å\(^2\) for the methyl hydrogens were used. In the final refinement stages the methyl unit was treated as a rigid body. The final calculated R values were \(R = 0.056\) and \(wR = 0.055\) \((w = 1.7056/(\sigma^2(F) + 0.001F^2))\). The maximum and minimum values for \(\Delta\rho\) in the final electron density map were 0.529 and -0.370 Å\(^3\) respectively. The maximum least shift to squares error \((\Delta/\sigma_{max})\) in the final cycle was 0.163 for non-hydrogen atoms. Atomic scattering factors for manganese were taken from the International Tables for X-ray Crystallography Vol IV. The final atomic
coordinates are given in Appendix A for all non-hydrogen atoms. A full listing of the bond distances and angles can be found in Appendix A. A view of the molecular structure of two atoms of the asymmetric unit is given in Figure 4.2.1. Figure 4.2.2 shows a diagram of the unit cell. A summary of the crystallographic data can be found in Table 4.1.1.

4.3 Crystal structure of \((\eta^5-C_6H_{17})Mn(CO)_2(C_5H_5N)\)

The structure contained two independent and structurally distinct molecules per asymmetric unit. The two molecules of this unit can be seen in Figure 4.2.1. This crystallographic independence has been seen in other molecules of the type \(CpMn(CO)_2L\) where \(Cp = \) cyclopentadienyl and \(L = CMe_2\left(\eta^2-\text{CH}_2-\text{CPh}-(\text{OCOMe})\right)_2\) and \(\eta^2-1\)-diethylphosphonato-2-phenyl ethylene. The principal differences between the structures of the two independent molecules in the title complex were firstly that the dihedral angle \(C(10)-cCp-Mn(1)-N(1)\) (\(cCp = \) the centroid of the cyclopentadienyl ring) was \(16(2)\)° in molecule 1 and \(62(2)\)° in molecule 2 and secondly that the angle between the mean planes of the cyclopentadienyl and pyridine rings was \(24.7(2)\)° in molecule 1 and \(44.9(2)\)° in molecule 2. The Mn-N distances were also different at \(2.023(4)\)Å for molecule one and \(2.038(4)\)Å for molecule 2. No significant interactions were observed between the two molecules. The pyridine rings were planar in both molecules. The maximum deviation from the plane was \(0.0183\) Å for \(N(1)\) in molecule 1 and \(0.0068\) Å for \(N(1A)\) in molecule 2. The carbon-carbon and the carbon-nitrogen distances were normal within the pyridine ring.

The orientation of the methyl group was \(\text{cis}\) to the pyridine ligand. This orientation causes the mean plane of the cyclopentadienyl ring to tilt slightly from orthogonality to the Mn ring-centroid vector (92.6(3)° for molecule 1 and 93.2(2)° for molecule 2). As a result, the mean Mn-Cp(π) distances were not equivalent ranging in molecule 1 from Mn(1)-C(10) at \(2.201(5)\)Å to Mn(1)-C(8) at \(2.117(6)\)Å. The equivalent
values for molecule 2 were 2.209(5)Å to 2.119(6)Å. This was in contrast to other compounds of the type MeCpMn(CO)₂L (L = PPh₃ 2.132(9)-2.162(8)Å, L = menthylmethoxycarbene 2.14(2)-2.16(2)Å, L = norbornadiene 2.17(2)-2.19(2)Å; L = SO₂ 2.07(2)-2.11(1)Å). The differences in the Mn-Cp(π) may not be exclusively the result of steric factors and may be because of the increased electron density on the central metal atom. This increased electron density results from the good σ-donating but poor π-accepting capacity of the pyridine ligand. Carbonyl stretching frequencies are a good indicator of electron density on a metal atom. The greater the electron density on a metal in a carbonyl complex lowers the carbonyl stretching frequencies. The values for pyridine were 1943 and 1886cm⁻¹ compared to 2032 and 1945cm⁻¹ for MeCpMn(CO)₃ (vide infra). This tilting of the cyclopentadienyl ring may give an indication of the early stages of a η⁵ to η³ ring slippage. The η³ complex [η³-MeCpMn(CO)₃]²⁻ with a negatively charged manganese centre has been observed in the infrared region. Therefore ring slippage may be a function of charge on the manganese centre. The five ring carbons are coplanar. The maximum deviation from the mean plane was 0.002(5)Å for C(8) in molecule 1 and 0.011(5)Å for C(10) in molecule 2. The distance between the ring carbons was normal for a coordinated cyclopentadienyl ring at 1.415(9)Å for molecule 1 and 1.410(7)Å for molecule 2. The methyl carbon was displaced from the mean plane of the cyclopentadienyl ring by 0.075(5)Å in molecule 1 and 0.057(6)Å in molecule 2. This deviation from the mean plane is normal in η³ coordinated methylcyclopentadienyl complexes.

The metal to carbon monoxide bond distances and angles were as expected for this type of complex. No significant increase in CO bond length was noted for the increased electron density arising from coordination of the pyridine ligand. The angles within the Mn(CO)₂L tripod were 91.7(2)° for C(13)-Mn(1)-C(12), 93.4(2)° for C(13)-Mn(1)-N(1), and 97.3(2)° for C(12)-Mn(1)-N(1). The equivalent values in molecule 2.
were 91.6(2), 95.0(2) and 93.2(2). The angles in the tetrahedron cCp, C(13), C(12) and N(1) show distortion from ideal tetrahedral geometry.
Figure 4.2.1 A SCHAKAL$^{16}$ drawing of the two molecules of the asymmetric unit in the crystal structure of $(\eta^5$-$C_6H_7)\text{Mn(CO)}_2(C_5H_5N)$.
Figure 4.2.2 The unit cell of \((\eta^5-C_6H_7)Mn(CO)_2(C_7H_5N)\) \((Z = 8)\) as represented by a SCHAKAL\textsuperscript{16} drawing.
The synthesis of \((\eta^5-C_6H_7)Mn(CO)_2(cis-C_8H_{14})\) is described in the experimental section. The X-ray data were collected by Dr R A Howie at the University of Aberdeen. A yellow crystal of dimensions 0.34 x 0.6 x 0.56 mm was selected for crystal structure analysis. A Nicolet P3 four-circle diffractometer was used for the determination. Mo Kα radiation (0.71069 Å) was used to determine 4801 reflections of which 583 were rejected by having \(I < 2\sigma(I)\) and 3191 were considered observed. The data was obtained by omega scan for \(2θ\) in the range 0-60°. Scan rates were in the range 1.0 to 29.3 deg min\(^{-1}\). The scan width was 0.6 deg at all times. Background counts were taken at ±1.0 deg. The indices were in the range \(h 0\) to 9, \(k 0\) to 28, \(l -18\) to 15. Internal standards at 2,9,0 and 2,4,5 were stable to ±1.99 and ±2.11% (1 x σ) respectively. No correction was applied for absorption (\(μ = 8.53 \text{cm}^{-1}\)). Density measurements were carried out using the gradient tube method.

The structure was solved by the Patterson heavy atom method with partial structure expansion to find all non-hydrogen atoms using SHELXS86. The atomic coordinates were refined with full matrix least squares refinement using SHELX76. Hydrogen atoms were located in their calculated positions and refined using the non-hydrogen atoms to which they were attached. Standard isothermal parameters (\(U_\text{iso}\)) of 0.5 Å\(^2\) for non-aromatic hydrogens and 0.13 Å\(^2\) for aromatic hydrogens were used. In the final stages of refinement, the methyl group was treated as a rigid body. R values were calculated to be \(R = 0.049\) and \(wR = 0.0546\) where \(w = 0.4794/σ^2(F) + 0.001F^2\). The maximum and minimum values in the electron density difference map were 0.427 Å\(^3\) and -0.452 Å\(^3\) respectively. The maximum least shift to error ratio (\(Δ/σ_{\text{max}}\)) was calculated as 0.330 for all non-hydrogen atoms. Atomic scattering factors for manganese were taken from the International Tables for X-ray Crystallography Vol IV. A full set of bond distances, angles and atomic coordinates can be found in Appendix B. Figure
4.4.1 shows the structure of \((\eta^5-C_6H_7)\text{Mn}(CO)_2(\text{cis-C}_8\text{H}_{14})\) Figure 4.4.2 shows a representation of the unit cell A summary of the crystallographic data can be found in Table 4.1.1

4.5 Crystal structure of \((\eta^5-C_6H_7)\text{Mn}(CO)_2(\text{cis-C}_8\text{H}_{14})\)

The \((\eta^5-C_6H_7)\text{Mn}(CO)_2(\text{cis-C}_8\text{H}_{14})\) complex contains one molecule per asymmetric unit as represented in Figure 4.4.1 The \textit{cis}-cyclooctene ring is \(\eta^2\) coordinated to the \(\text{MeCpMn(CO)}_2\) moiety via the ring double bond The distance between the carbon atoms of the double bond and the central manganese atom were 2.193(2)Å and 2.201(3)Å Similar distances were found for \(\text{CpMn(CO)}_2(\eta^2\text{-cyclooctatetraene})\) of 2.193(2)Å and 2.202(2)Å Other complexes with asymmetric \(\eta^2\) coordinated ligands show unequivalent bond distances arising from either a bulky group on one of the ring carbons as in the case of \(\eta^2\)-anthronylketene \((1.976(6)\text{Å and }2.242(6)\text{Å})\) or from inductive effects from groups on one of the carbons as with \(\eta^2\)-methylvinylacetone \((2.149(8)\text{Å and }2.175(7)\text{Å})\) The length of the double bond serves as an indicator of the strength of interaction between the metal and the \(\eta^2\) coordinated ligand The length of a normal carbon-carbon double bond is 1.34Å On coordination, backdonation from the metal d orbitals into the ligand \(\pi^*\) orbitals increases the length of the double bond The \(\eta^2\) \textit{cis}-cyclooctene bond length was 1.376(4)Å This was shorter than other similar manganese complexes with \(\eta^2\) ligands e.g anthronylketene \((1.448(8)\text{Å}), \text{norbornadiene}^{21} 1.404(4)\text{Å}, \text{cyclooctatetraene}^{17} 1.398(2)\text{Å} \) and methylvinylacetone \((1.390(12)\text{Å})\) The shorter bond length indicates that the \textit{cis}-cyclooctene ligand may not be as tightly bound as in other complexes with \(\eta^2\) ligands It may be because of inductive effects from the groups bound to the carbons in the double bond as these are known to affect bond distances in alkene compounds This difference was also noted in the bond angle between the metal and the double bond carbon atoms e.g \(\text{C(1)-Mn(1)-C(8)}\) in the title compound was
Figure 4.4.1 A SCHAKAL\textsuperscript{16} drawing of the crystal structure of ($\eta^5$-C\textsubscript{6}H\textsubscript{7})Mn(CO)\textsubscript{2} (\textit{cis} -C\textsubscript{8}H\textsubscript{14})
Figure 4.4.2 A SCHAKAL$^{16}$ representation of the unit cell of \((\eta^5-C_6H_7)Mn(CO)_2(\text{cis-}C_8H_{14})\) \((Z = 4)\)
36 $5(1)^\circ$, methylvinylacetone$^{19}$ $37$ $5(0.3)^\circ$, norbornadiene$^{21}$ $38$ $0(1)^\circ$ and anthronylketene$^{18}$ $39$ $5(2)^\circ$ Disorder was noted in the cyclooctene ring system where C(4) and C(5) could be represented by two positions within the structure i.e. C(4A) and C(5A). This disruption was presumably because of chair and boat-like conformations as observed in cyclohexane. The cyclooctene carbon-carbon single bond distances were on average $1.528(9)\text{Å}$ for one orientation and $1.556(13)$ for the second orientation (C(4A), C(5A)). These were normal for C-C single bond distances ($1.54\text{Å}$)$^{20}$

The cyclopentadienyl ring carbons were an average of $2.149(6)\text{Å}$ from the central manganese atom. This value was typical of the average Mn-C($\pi$) bond lengths as can be seen in Table 4.5.1. Some disorder may be noted in the ring where the maximum and the minimum deviations from the mean plane were $0.139$ and $-0.139\text{Å}$ respectively for C(11) and C(12). The average bond length between ring carbons was $1.394(6)\text{Å}$. This distance was usual for carbon-carbon bonds in cyclopentadienyl rings.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Mn-C (Cyclopentadienyl) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-methylvinylketone)</td>
<td>$2.137(8)$</td>
<td>$^{19}$</td>
</tr>
<tr>
<td>$(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-cyclooctatetraene)</td>
<td>$2.156(2)$</td>
<td>$^{17}$</td>
</tr>
<tr>
<td>$[(\eta_5$-$C_6H_7)Mn(CO)_2]_2N_2$</td>
<td>$2.144(7)$</td>
<td>$^{22}$</td>
</tr>
<tr>
<td>$[(\eta_5$-$C_6H_7)Mn(CO)_2S(CH_3)_2C_2H_3]PF_6$</td>
<td>$2.141(4)$</td>
<td>$^{23}$</td>
</tr>
<tr>
<td>$(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-norbornadiene)</td>
<td>$2.166(9)$</td>
<td>$^{11}$</td>
</tr>
<tr>
<td>$(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-anthronylketene)</td>
<td>$2.155(7)$</td>
<td>$^{18}$</td>
</tr>
<tr>
<td>$(\eta^5$-$C_6H_7)Mn(CO)_2(\eta^2$-cis-cyclooctene)</td>
<td>$2.149(6)$</td>
<td>$^*$</td>
</tr>
</tbody>
</table>

Table 4.5.1 The Mn-C($\pi$) cyclopentadienyl average bond distances (Å) for manganese complexes with cyclopentadienyl ligands *this work
The Mn(l)-(CO) distances 1 775(3)Å and 1 762(3)Å were within the expected ranges for this type of complex, PPh₃ 1 76(1)Å, 1 77(1)Å⁹ The Mn-(CO) angles were 177.2(3) for Mn(1)-C(15)-O(1) and 176 1(3) for Mn(1)-C(16)-O(1) The angles in the tripod Mn(CO)₃(cis-cyclooctene) using the centre of the double bond (CDB) as the reference point for the cis-cyclooctene ligand were 94 5(1)° for C(16)-Mn(1)-CDB, 95 8(1)° for C(15)-Mn(1)-CDB and 90.0(2)° for C(16)-Mn(1)-C(15) The angles involving the cis-cyclooctene ligand show distortion in the tetrahedral geometry of the manganese complex (fourth reference point = centroid of the cyclopentadienyl ring) caused by coordination of the ligand to manganese These types of distortions have been noted in other η² coordinated complexes involving the CpMn(CO)₂ component e.g. cyclooctetraene¹⁷, norbornadiene²¹ and methylvinylacetone¹⁹

4.6 A comparison of the crystal structures of (η⁵-C₆H₇)Mn(CO)₂(pyridine) and (η⁵-C₆H₇)Mn(CO)₂(η²-cis-cyclooctene)

In the comparison of the title complexes, which are of the type (η⁵-C₆H₇)Mn(CO)₂L, the only difference between the two compounds is the unique ligand L (where L = pyridine and cis-cyclooctene). These ligands are different in that the pyridine is a good σ donating ligand by virtue of the lone pair on the ring nitrogen but a poor π accepting ligand because of the lack of antibonding π* orbitals to accept electron density from the low valent manganese atom In contrast, the cis-cyclooctene ligand is a poor σ donor because the electrons required in the σ bond to the metal are mainly involved in the ligand π system but a good π acceptor because the metal can donate electron density into the empty ligand π* orbitals In terms of stability this means that the pyridine complex was extremely air sensitive and decomposed rapidly in aerated solvents In the solid form a layer of manganese oxide was present on the surface of the crystal and so prevented air oxidation of the complex In contrast, the cis-
cyclooctene complex was more stable surviving for approximately 1 hr in non-degassed solvent and for a period of weeks before air oxidation decomposed the crystals. The effect of the pyridine ligand was to leave more electron density on the manganese atom relative to the cis-cyclooctene ligand. This effect can be clearly seen in the orientation of the methyl group of the cyclopentadienyl ring in the complexes. In the cis-cyclooctene complex, the methyl group was cis to a carbonyl ligand. This orientation was the preferred position in all the complexes of the type (η^5-C_6H_6)Mn(CO)_2L when L was a relatively good π accepting ligand. Although the methyl group was not necessarily cis to a carbonyl in these complexes, the orientation of the methyl group was always trans to the unique ligand L. In contrast, the location of the methyl group in the pyridine complex was cis to the pyridine ligand. This feature appears to be common to all compounds containing a nitrogen donor ligand bound to a (η^5-C_5H_4R)Mn(CO)_2 fragment. Examples of this type of interaction were [(η^5-C_5H_4R)Mn(CO)]_2N_2 (R = H)^22 and the chelate complex (η^5-C_5H_4R)Mn(CO)_2 (R = CH_2CH(CH_3)N(CH_3)(C_3H_5))_2^24 where the coordinating nitrogen atom was cis to the methyl group of the cyclopentadienyl ring. The reason for the differing orientation may lie in the amount of electron density on the central manganese atoms in the complexes. Pyridine is a relatively strong base and on coordination to the manganese atom, the electron density from the non-bonding electrons from the nitrogen atom would reside mainly on the metal. In cis-cyclooctene, the σ bonding electrons come from the π orbitals of the double bond and therefore would not impart as much electron density on the atom relative to the pyridine. In addition, the metal could remove some of the electron density into the π* antibonding orbitals of the cis-cyclooctene ligand. This would not be the case in the pyridine complex where the poor π accepting ability of the pyridine ligand would leave a significant amount of the electron density on the metal atom. An added effect of this increased electron density on the complex was to tilt the cyclopentadienyl ring. This tilting may be the result of steric interaction of the methyl group with the...
pyridine ligand or as a result of the increased electron density on the manganese inducing the initial stages of a $\eta^3$ ring slippage. All other aspects of these complexes were typical. The metal-cyclopentadienyl ring carbon bond distances on the cis-cyclooctene complex were normal for these types of compounds (see Table 4.5.1) and the Mn-(CO) bond distances were also in the normal ranges.
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CHAPTER 5

PROGRAM FOR TRANSIENT ANALYSIS
5.0 Computer program for transient analysis

5.1 Introduction

The advent of computers has greatly enhanced the speed and accuracy of data acquisition in fast kinetic experiments. The original method for the analysis of transient data involved taking a picture of the recorded transient on the oscilloscope. This picture was then traced onto paper, enlarged and subsequently analysed by tedious mathematical calculations to determine the order and the observed rate for the reaction. Computer interfacing with modern oscilloscopes has greatly reduced the workload with the analysis times for recorded transients having been reduced from hours to seconds. Commercial programs have been developed for transient analysis but they usually contain more sub programs than are actually required by the user and therefore they are more complicated to use. What follows is an explanation of a GW-BASIC program developed specifically for the analysis of transient data. The menu-driven program allowed for the collection, accumulation, viewing, analysis and storage of transient waveforms. The acquired data could be manipulated to create files compatible with other commercial analysing and graphics packages and with other developed programs. The system consisted of an Olivetti PCS 286 interfaced via a GPIB-IEEE-488 card to a Philips PM 3311 oscilloscope. The laser system has been described (vide infra). A modified version of this program was written to enable it to be used with a Hewlett-Packard HP54510A oscilloscope. The program could be run directly from a batch file which initiated the interface card drivers and the graphics drivers. A full listing of the PM 3311 program can be found in Appendix C.
5.2 Computer program

The main menu for the program was as follows,

1. New Measurement
2. Decay Analysis
3. Create STATIS File
4. View Files
5. Absorbance Calculations
6. DOS Functions
7. Exit

The first section of the program was used for transient acquisition. A sub-menu was used for this part of the program as the options were usually needed many times during a typical experiment. Before the sub-menu appeared on the screen, the program asked for the title of the experiment to be performed. This prevented tedious re-entering of an experiment title during data file creation. The sub-menu listing was as follows,

1. Io Measurement
2. Transient Measurement
3. Exit

The Io measurement is a very important parameter which must be calculated prior to the capture of a kinetic trace. It corresponds to the amount of light passing through the solution prior to photolysis by the laser pulse. It is measured by getting the difference in mV of the amount of light transmitted by the solution when the shutter on the monitoring beam is closed and then opened. From the Beer-Lambert law (Equation 5.2.1), the absorbance of a reactant or product is linearly proportional to its concentration in solution provided the absorbance value is within the limits of optical linearity.

\[ A = \varepsilon c l \]  

(5.2.1)

where \( A \) is the absorbance, \( \varepsilon \) is the molar extinction coefficient (dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)), \( c \) is the concentration of the reactant or product (mol dm\(^{-3}\)) and \( l \) is the pathlength (cm).
The change in millivolts on the oscilloscope produced by a transient species is also a function of the light transmitted by a solution per unit time (It). Therefore one can calculate the absorbance value from It/Io. The photomultiplier was normally adjusted to the maximum linear working range of 200mV. To speed up the process of acquiring the data for the Io measurement only the first 25 channels, of the 256 channels available to store data in the oscilloscope, were averaged to obtain the values (in mV) when the shutter was closed and opened. For the HP54560A scope, the data in the first 50 of the 500 available channels were transmitted. The value of the voltage scale on the scopes was also sent to enable calculation of the mV values.

The transient measurement function recorded transient data and wrote the data to a file. The program prompted for a filename, for the wavelength of the monochromator and for Io if it had not previously been measured. If Io had been measured, its value was retained to enable measurement of transients of different timebases at the same analysis wavelength. It also displayed the previous filename (if any) to prevent confusion if sequential filenames were entered. Pressing return (CR) recorded the data from the oscilloscope. The display consisted of two halves, one which contained the averaged transient and the other containing the current transient on the oscilloscope (Figure 5.21). This aided enormously in the judging of the number of laser shots required to obtain good quality transient waveforms. In the first acquisition, the program asked for the front panel settings from the scope: i.e., the voltage scale, the timebase. After each acquisition, the averaged data was automatically stored on disk along with the title, timebase, number of shots, voltage scale, wavelength and the Io measurement. This prevented data loss as a result of oscilloscope 'crashing'. The data were averaged by summing the channel numbers sent from the oscilloscope (0-255) after each shot and dividing the total by the number of shots. This had the added effect of reducing the noise level in the traces.
Part two of the program was concerned with data analysis. The program prompted for a filename and searched by default the for the file from floppy disk. This could be changed to search in other drives. The called file was displayed on one half of the screen and the user was asked if curve smoothing was required.

![File c crhl trs](image)

**Shot No. 10**  
Cr(CO)$_6$ in hexane + 1 atm CO  

$I_0 = 196.45$ mV  
Scale = 10 mV/div  
Timebase = 10 us/div  
Wavelength = 500 nm

Press return for another shot measurement  
Enter any character to return to menu?

Figure 5.2.1 The split screen showing the current transient and the averaged transient in the 355nm flash photolysis of Cr(CO)$_6$ under 1 atm atmosphere of CO in hexane.
The procedure used was a Savitzky-Golay 5 point moving least squares method\(^2\) and the equation is shown in Equation 5.2.2

\[
z(i) = \frac{(-3z(i-2) + 12z(i-1) + 17z(i) + 12z(i+1) - 3z(i+2))}{35} \tag{5.2.2}
\]

where \(z\) was greater than 2 and less than \(n-2\) (\(n=\) number of data points) This technique was ideally suited for the transient data as one of the requirements for the smoothing is that each data point must be obtained at the same time interval from each preceding point. This is a feature of fast transient digitizers. The effect of this smoothing procedure was to reduce noise in the transients without degrading the quality of the data. The next step in the analysis process was to set a baseline where the change in slope of the transient decay was at a minimum. This was extremely important as this line set the value of absorbance at infinity (\(A_{inf}\)) which was used in the first and second order rate constant calculations. Next the channel numbers had to be selected, corresponding to the channel numbers on the oscilloscope, to identify the portion of the curve for analysis. The typical starting channel was 32 (50 using the HP54510A oscilloscope) as in the recording of the transient data, the first portion of the trace was usually given to the millivolt reading before the photolysis of the sample by the laser pulse. A typical trace is shown in Figure 5.2.2. An option then prompted the user to choose a first or second order analysis. The first order analysis used Equation 5.2.3 which is derived from basic first order kinetics and the Beer-Lambert law\(^3\)

\[
k_r t = \ln (A_0 - A_{inf}) - (A_t - A_{inf}) \tag{5.2.3}
\]

Where \(k_r\) is the rate constant, \(t\) is the time, \(A_0\) is the absorbance at time zero, \(A_{inf}\) is the absorbance at time infinity (calculated from the baseline) and \(A_t\) is the absorbance at time \(t\). A plot of \(\ln(A_t-A_{inf})\) versus \(t\) is linear for a first order process with a slope equal
to \(-k_t\). The second order rate constants were calculated from second order kinetics rate equation incorporating the Beer-Lambert law\(^3\) (Equation 5.2.4)

\[
k_{t,t} = \frac{1}{(A_t - A_{inf})} - \frac{1}{(A_0 - A_{inf})}
\]

(5.2.4)

The symbols are the same as for the first order equation. A plot of \(1/(A_t-A_{inf})\) versus \(t\) yields a straight line with a slope of \(k_t\).

On the unused half of the screen the data points were displayed on a graph of the calculated absorbance values from the rate equations versus time (Figure 5.2.3). The best line of fit was drawn through the points. This was calculated using simple linear regression. The observed rate constant, and its linear regression coefficient were displayed on the screen. The rate constant could be recalculated by choosing a different portion of the curve.

Part three of the program created files in a format which could be used with STATIS3 a data analysis program. The program prompted for a filename of the file to be converted. The data was then read in to the computer and the equation of the line for the first 20 points of the data was calculated. The standard deviation calculated for this line was used to compute the channel number where the laser fired as the data in the file from channel numbers 1 to 20 consisted of the mV reading from the photomultiplier before the laser photolysis pulse hit the sample solution and was therefore not part of the transient decay. The data after the calculated fire channel was written to the file in the form of absorbance and time so that accurate rate constants could be determined. An option was given to export the file to the STATIS3 directory or to write it to disk. A second option was given whether the user wished to run STATIS3 or to return to main menu.
Figure 5.2.2 A typical trace of a transient species where the initial portion of the curve corresponds to the absorbance of the sample prior to the photolysis pulse.

The STATIS3 package could be used to perform statistical calculations on any data set in the form required by the program. The main use of this program in the analysis of transient data was in one and two exponential curve fitting. These functions acted as a complement to the previously described transient analysis methods. The advantages of this form of analysis over the linear regression method were that the data was not transformed, as in the linear method, and that it enabled the calculation of the intercepts on the decay curves which could be used to estimate the relative amounts of each component produced in the photolysis experiments.

The fourth part of the program was used to view files. An option appeared at the beginning of this function which enabled the user to examine the files contained on disk for their content. This helps to find specific files but was not thought as a replacement for recording the file details on paper. A requirement to use this feature.
Figure 5.2.3 The analysis profile of a transient with the transient displayed on the lefthand side. The arrows correspond to the analysis portion of the curve. The right hand side of the screen shows a plot of the first order fit to a set of datapoints from the analysis portion of the curve against time with the line of best fit drawn though the points. The file details, calculated rate constant and correlation coefficient are displayed under the graphs.
was that the recalled files had to be in numerical sequence. The next prompt asked for a specific filename. The view files choice permitted the user to display, overlay and clear the specified files from the screen. An example of this screen is shown in Figure 5.2.4. A screen dump could be carried out by pressing the print screen option on the keyboard which ran DOS graphics which was originally initiated in the laser batch file. This applied to any screen in the program.

The fifth section of the program was concerned with outputing data to a file which was compatible with HARVARD GRAPHICS, a program which could produce excellent spectral plots of transient species. The user was prompted by a request for a common file string and the starting and ending file number and an increment to identify a certain series of filenames. A maximum of four time delays could be entered. An option was also displayed so the calculated absorbances could be output to a printer or to a working file for the graphics package. The program systematically calculated the fire channel of the laser for each of the files and then used this channel number as time zero for the subsequent absorbance value calculations.

There were many constraints on this part of the program. The files had to be sequential in order for the file search loop to execute and the entered times for the absorbance calculations could not exceed the limit of the transient timescale. The created file could be directly imported into HARVARD GRAPHICS. A crude approximation of the spectrum could be viewed at the end of the absorbance calculation and this aided in determining if there were inconsistencies in the calculations because of incorrect fire channel selection. With channel numbers greater than 35 and less than 26, the program automatically entered a fire channel number of 30. The existence of this inserted number was denoted by an asterisk. A complementary program was written which plots the data in a 3-D spectrum of
absorbance against time (µs) against wavelength (nm)\(^4\). This program more clearly demonstrated the existence or non-existence of any produced transient species.

The final part of the program was a simple SHELL command. This enabled the use of the DOS functions available on the computer. The most important of these was the file editor EDLIN which was used to correct incorrectly entered data, e.g., wavelength, during the data acquisition. Other uses involved the execution of other programs or packages compatible with DOS.

The `exit` command was used to exit the program. An option was given whether to exit to DOS or to GWBASIC. On exiting to DOS the program returns to the default C\ directory. Exiting to GWBASIC enabled the loading and executing of other basic programs.
Figure 5.2.4 An example of the View Files screen with overlayed transients from the photolysis of MeCpMn(CO)$_2$PPh$_3$ under various pressures of CO. The display shows that the transient produced was not a primary photoproduct.
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CHAPTER 6

EXPERIMENTAL SECTION
6.0 Experimental Section

6.1 Introduction

The photosubstitution reactions of metal carbonyl compounds are well known (Reaction 6.1.1)\(^1\). Reactions usually involve the photolysis of the metal carbonyl complex in a donor solvent e.g. an alcohol, ether, cyanoalkane or in 'inert' alkane solvents. The function of the donor solvent is to coordinate loosely to the site left by photolytic loss of a carbon monoxide ligand (Reaction 6.1.2) and in some cases prevent further CO loss. The addition of a stronger ligand i.e. a good σ donor to the solution can displace the donor solvent thermally to produce the appropriate compound. The solvent can alternatively be removed under reduced pressure and so drive the reaction (Reaction 6.1.3) to completion.

\[
\text{M(CO)}_x \xrightarrow{h\nu} \text{M(CO)}_{x-1} + \text{CO} \quad (6.1.1)
\]

\[
\text{M(CO)}_{x-1} + S \xrightarrow{} \text{M(CO)}_{x-1}S \quad (6.1.2)
\]

\[
\text{M(CO)}S + L \xrightarrow{} \text{M(CO)}_{x-1}L + S \quad (6.1.3)
\]

S = donor solvent   L = ligand

If the coordinating ligand is sufficiently strong so as not to afford higher substitution products then an alkane solvent e.g. cyclohexane can be used. Usually in these reactions it is necessary to remove oxygen as the reactive intermediates formed could coordinate to the oxygen molecules and subsequently decompose into the corresponding metal oxides. This is usually performed by bubbling an inert gas through the photolysis solution and also has the added effect of removing any CO liberated in the reaction, preventing backreactions and so shortening the photolysis time.
6.2 Photolysis apparatus

All the prepared photolyses were carried out in a photoreactor as in Figure 6.2.1. The double walled pyrex glass vessel contained a medium pressure mercury lamp (400W) cooled by running water. The external vessel contained the solution to be irradiated. Air and carbon monoxide (liberated during the reactions) were removed by bubbling nitrogen or argon through the solution. The products were isolated by removing the solvent under reduced pressure and purifying by ambient or low temperature recrystallisation and/or classical chromatography depending on the air sensitivity of the compounds.
Air sensitive solutions for IR or UV/visible spectroscopy were filled in a nitrogen atmosphere glove box

6.3 Materials

MeCpMn(CO)₃ (Strem chemicals), Cr(CO)₆ (Strem chemicals), Mo(CO)₆ (Strem chemicals), W(CO)₆ (Strem chemicals), pyridine (Aldrich Chemical Co.), \textit{cis}-cyclooctene (Aldrich Chemical Co.), triphenylphosphine (BDH), and n-pentane (Reidel de Haen) were used without further purification. Cyclohexane was stored under size 4A molecular sieve. Argon (IIG), carbon monoxide (IIG), and oxygen free nitrogen (IIG) were used without further purification. MeCpMn(CO)₃ for laser flash photolysis studies was vacuum distilled and stored under argon at -30°C.

6.4 Equipment.

Infra red spectra were recorded on a Perkin Elmer 983-G IR spectrophotometer using sodium chloride solution cells (pathlength 0.1 mm) or in KBr pellets. UV/visible spectra were obtained on Hewlett Packard 8425a spectrophotometer using quartz cells (pathlength 1.0 cm).

6.5 Synthesis of manganese complexes

6.5.1 Preparation of \( \eta^5 \)-methylcyclopentadienylmanganese(I)dicarbonyltriphenylphosphine

The yellow MeCpMn(CO)₂PPh₃ complex was prepared by UV irradiation with a 400W medium pressure mercury lamp of a continuously N₂ purged n-pentane solution (150mls) that contained 2.3mmoles of MeCpMn(CO)₃ and an equimolar equivalent of PPh₃. Nitrogen purging was maintained throughout the reaction to avoid oxidation of the complex. The photolysis time was 3hrs. Following irradiation the solvent was removed under reduced pressure avoiding exposure to the air in the...
transferring process. The resultant orange residue was dissolved in a minimum of hot ethanol and on cooling the MeCpMn(CO)₂PPh₃ complex recrystallised as yellow crystals. IR νCO n-hexane 1938, 1879 cm⁻¹

6.5.2 Preparation of η²-methylcyclopentadienylmanganese(I)dicarbonylpyridine

2.3 mmoles of MeCpMn(CO)₃ were dissolved in 150 ml of tetrahydrofuran and photolysed by UV irradiation using a 400 W medium pressure mercury lamp for 3 hrs. The solution was continuously purged throughout the reaction by a stream of nitrogen. The resultant burgundy coloured solution was transferred under argon to a 250 ml flask which contained an equimolar amount of pyridine. The solvent was removed under reduced pressure and the residue was redissolved in 2 ml of argon degassed ethanol and filtered through cotton wool. The solution was stored for 2 weeks at -30°C. Brown crystals of MeCpMn(CO)₂(pyridine) were isolated by alternate washings with 40-60 pet-ether at -70°C and water. The crystals were covered in an opaque layer of presumably MnO₂ which prevented decomposition of the complex. IR νCO n-hexane 1930, 1863 cm⁻¹. X-ray structure see Chapter 5.

6.5.3 Preparation of η²-methylcyclopentadienylmanganese(I)dicarbonyl η²-cis-cyclooctene

The MeCpMn(CO)₂(cis-cyclooctene) complex was prepared by prior photochemical generation of the tetrahydrofuran adduct MeCpMn(CO)₂(THF) as in the previous complex preparation. When the irradiation was complete a 20 molar excess of cis-cyclooctene was added to the solution. The THF was removed under reduced pressure and the resultant yellow oily product was placed in a low temperature circulator for 3 days at -80°C. On returning to room temperature a yellow precipitate formed. This was subsequently recrystallised from methanol at -30°C. The
product was identified as MeCpMn(CO)$_2$(cys-cyclooctene) IR $\nu$CO n-hexane 1959, 1900 cm$^{-1}$ X-ray structure see Chapter 5

6.6 Synthesis of Group VIB monosubstituted triphenylphosphine pentacarbonyl complexes

6.6.1 Preparation of Cr(CO)$_5$PPh$_3$

A 200 mL solution of tetrahydrofuran (THF) and parent hexacarbonyl Cr(CO)$_6$ (0.5g) was degassed for 15 minutes and then irradiated with a 400W medium pressure mercury lamp for 3hrs. The solution was continuously purged with nitrogen throughout the irradiation to avoid oxidation of the metal. After irradiation a stoichiometric amount of ligand was added to the solution and the solvent was removed using a rotary evaporator. The pale yellow Cr(CO)$_5$PPh$_3$ complex was purified by repeated recrystallisation from hexane and washing with methanol to remove unreacted PPh$_3$. Purity was confirmed by TLC and infra red spectroscopy IR $\nu$CO cyclohexane, 2066 (m), 1989 (w), 1945 (vs) cm$^{-1}$

6.6.2 Preparation of Mo(CO)$_5$PPh$_3$

A THF solution of parent hexacarbonyl W(CO)$_6$ (0.5g) was irradiated as in the previous synthesis. An equimolar amount of PPh$_3$ was added to the resultant solution and the solvent removed by rotary evaporation. The remaining green residue was dissolved in a minimum amount of chloroform and chromatographed on a 15cm alumina column with a 5:95 ethyl acetate:pet-ether eluent. The complex was purified by recrystallisation from n-hexane at -30$^\circ$C to give white crystals of Mo(CO)$_5$PPh$_3$ IR $\nu$CO cyclohexane, 2072 (m), 1989 (w), 1945 (vs) cm$^{-1}$

6.6.3 Preparation of W(CO)$_5$PPh$_3$
The complex was prepared as for the synthesis of the corresponding chromium compound. The complex was recrystallised from ethanol to give yellow crystals of WCO)₅PPh₃. IR νCO cyclohexane, 2074(m), 1988(w), 1945(vs) cm⁻¹

6.7 Laser flash photolysis

6.7.1 Introduction

Laser flash photolysis has become a very important technique in the study of photoreaction intermediates. In principle flash photolysis involves the generation of a high concentration of short-lived intermediate using a very high intensity pulse of radiation of very short duration. A short time interval after the generating pulse the system is analysed by observing its emission or absorption characteristics. The process can be followed by photographing the emission spectrum using a spectrograph or the absorption spectrum by triggering an analytical beam passing through the reaction cell to flash at a predetermined time interval after the initial flash. Alternatively the process may be followed kinetically by monitoring the emission or absorption at a particular wavelength using a detector coupled to an oscilloscope with a time-based sweep. The latter process is used here. Typical traces for transient absorption and decay are given in Figure 6.7.1. The polychromatic nature of the radiation from conventional discharge tubes increases the possibility of generating more than one emitting or absorbing species. Lasers overcome this problem because their radiation is monochromatic. Other advantages are that the pulse from a laser is of very short duration (Q-switching) and highly reproducible. Frequency doubling can be employed to increase the range of the laser source from its fundamental harmonic. Oscilloscope traces of the decay of the intermediate can be obtained if a high intensity monitoring beam is used to overcome problems caused by background noise with lower intensity sources. Background noise can further be reduced by repeating the measurement many times and averaging the results. Spectra of the decay of an intermediate can be obtained point by point on the
monitoring monochromator and recording a series of readings at a fixed time interval after the flash.

6.7.2 Preparation of samples for flash photolysis

All the photolysis solutions were prepared in cyclohexane. Solutions of the metal carbonyl complexes were adjusted until the absorbance readings were between 0.5 and 2.0 absorbance units. Absorbance measurements were taken on a Hewlett-Packard 8452a UV/visible spectrophotometer. Concentrations of the metal carbonyl compounds in solution were calculated from previously determined extinction coefficients. The solutions were degassed by three cycles of a freeze pump thaw method. Argon or carbon monoxide was added to prevent boiling of the solutions and to check the reversibility of the photochemical reactions observed. The concentration of carbon monoxide in cyclohexane solution was calculated from reference 2 and was equal to $1.2 \times 10^{-2}$ mol dm$^{-3}$ under 1.0 atmosphere of CO at 298K.

6.7.3 Laser flash photolysis system with UV/visible monitoring

Flash photolysis studies were carried out using a Spectron Laser Systems Q-switched Nd YAG laser with a fundamental frequency at 1064 nm. This frequency can be doubled, tripled or quadrupled to generate a second (532 nm), third (355 nm) or fourth (266 nm) harmonic. The energy of the pulse can be varied by altering the voltage across the amplifier flash tube. At the frequencies employed, 355 nm and 266 nm, the energies were typically 30 mJ per pulse and 40 mJ per pulse respectively. The UV/visible monitoring source was an Applied Photophysics 40804 250W Xenon arc lamp. The laser beam and UV light source were placed in a cross beam arrangement with the sample holder at the intersection. The laser beam was directed onto the sample holder by two Pellin-Broca prisms. The monitoring beam was focused onto an Applied Photophysics f3.4 monochromator using a lens. Optical filters were used to cut...
Figure 6.7.1 Typical traces obtained from an oscilloscope for transient absorption (a) and decay (b)
off the monitoring beam in order to minimise unnecessary photolysis from the Xenon arc lamp at wavelengths >345nm and >400nm. At the exit slit of the monochromator a Hamamatsu five stage photomultiplier, operating at 850V, detected absorbance changes and relayed the output to a transient digitizer via a variable load resistor. The digitizer, a Philips PM3311 storage oscilloscope, was interfaced through an IEEE card to an Olivetti 286PCS microcomputer. The resultant data were stored on floppy disk. A schematic diagram of the laser system is shown in Figure 6.7.31. House programs were used to analyse the data. The resultant transients were analysed by first order kinetics. All errors on the second order rate constants are one standard deviation on the scatter of the graphical points.

6.8 Transient deconvolution

Transient decays exhibiting characteristics of two first order decays can be difficult to separate in terms of their kinetic data. The transient is however a linear combination of two exponential decays. Therefore by fitting a double exponential curve (Equation 6.8.1) to the transient it should be possible to separate the transients into their individual components

\[ Y = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \]  

(6.8.1)

The \( A_1 \) and \( A_2 \) terms in Equation 6.8.1 are constants, \( k_1 \) and \( k_2 \) refer to the decay constants for each of the components in the decay profile, \( t \) refers to the time and \( Y \) to the value on the resultant decay curve. For a single exponential decay as in Equation 6.8.2 the inverse log of the equation (Equation 6.8.3) can be used to obtain a linear plot of \( \ln Y \) against time (\( t \)) to yield a slope of \(-k\) and an intercept \( \ln A \)

\[ Y = A e^{-kt} \]  

(6.8.2)

\[ \ln Y = \ln A -kt \]  

(6.8.3)
Figure 6.7.3 A schematic diagram of the laser system used in the laser flash experiments.
Rearranging Equation 6.8.3 to give Equation 6.8.4 produces an equation which is similar in form to the spectroscopic equation for first order decay analysis\(^3\) (Equation 6.8.5),

\[
kt = \ln(A_0 - A_{\infty}) - \ln(A_t - A_{\infty}) \tag{6.8.4}
\]

where \(A_0\) is the absorbance at time zero, \(A_t\) is the absorbance at time \(t\), \(A_{\infty}\) is the absorbance at time infinity, \(t\) is the time and \(k\) is the observed rate constant. Therefore using a linear combination of the exponential decay curves it is possible to calculate the initial absorbances of the transient species and therefore the relative yields at different concentrations of CO from the \(A_1\) and the \(A_2\) terms for each decaying species.

### 6.9 Activation parameter measurements

Activation parameters for the metal carbonyl complexes were calculated from the Arrhenius (Equation 6.9.1) and Eynng (Equation 6.9.2) equations

\[
\ln k = \ln A - \frac{E_{\text{act}}}{RT} \tag{6.9.1}
\]

\[
\ln \frac{k_{\text{obs}}}{T} = \ln \frac{k}{R} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \tag{6.9.2}
\]

In the Arrhenius equation \(A\) is the frequency factor related to the number of collisions between the reactant molecules, \(E_{\text{act}}\) is the activation energy, \(R\) is the universal gas constant, \(T\) is the absolute temperature and \(k_{\text{obs}}\) is the observed rate constant. A plot of \(\ln k_{\text{obs}}\) against \(\frac{1}{T}\) should yield a straight line of slope \(-\frac{E_{\text{act}}}{RT}\) from which the activation energy can be determined. In the Eynng equation \(k\) is the Boltzmann constant, \(h\) is Planck's constant, \(R\) is the universal gas constant, \(\Delta H^*\) is the enthalpy change of activation, \(\Delta S^*\) is the entropy change of activation, \(T\) is the absolute temperature and \(k_{\text{obs}}\) is the observed rate constant. A plot of \(\ln \frac{k_{\text{obs}}}{R}\) against \(\frac{1}{T}\) yields a slope of \(-\frac{\Delta H^*}{R}\) and an
intercept equal to \( \ln \frac{k}{\Delta S^*} + \frac{\Delta S^*}{R} \Delta H^* \) and \( \Delta S^* \) can be determined from the slope and the intercept respectively. Temperature changes for the sample were achieved by immersing the sample cell in a temperature controlled water bath for a fixed period of time to attain equilibrium between the sample solution and the water. Transient signals at this temperature were obtained and the sample was again immersed in the water bath at a different temperature. Experiments were performed usually at increments of 5°C.
REFERENCES

1  Strohmeier, W., Agnew Chem Int Ed Engl., 1964, 3(11), 730
Further Work

The effect of a triphenylphosphine ligand on the ability of the various metal centres to coordinate to a solvent has been observed in this thesis. Therefore, as a natural progression, the effects of other phosphine ligands such as trimethylphosphine, tricyclohexylphosphine etc should be investigated. In addition, phosphites should be considered as the additional oxygen atom on phosphite ligands should decrease the ring strain on agostic interaction with the ligand C-H bonds. The effect of different solvents should also be considered as some of these reactive intermediates appear non-solvated in cyclohexane but solvated in n-heptane solution.
APPENDIX A
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Atomic coordinates $x \times 10^4$ for non-hydrogen atoms with s d's in parentheses for ($\eta^5-C_5H_4CH_3$)-

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211
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A complete listing of bond lengths (Å) for (γ²-C₅H₅CH₃)Mn(CO)₂(pyridine)
A complete listing of bond angles (°) for \(^{\circ}$-C\(\text{C}_5\text{H}_4\text{CH}_3\)Mn(CO)\(_2\)pyridme) (P T O)

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A complete listing of bond angles (°) for \((\eta^2-C_5H_4CH_3)\text{Mn(CO)}_2(\text{pyridine})\) (continued)

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<td>H14c</td>
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Coordinates $\times 10^4$ for hydrogen atoms in $(\eta^8$-C$_8$H$_8$CH$_3$)Mn(CO)$_2$(a-cyclooctene)
<table>
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<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
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Anisotropic temperature factors x 10^3 with e s d’s in parentheses for (η^5-C_5H_4CH_3)Mn(CO)_2(α-cyclooctene)
10 REM Program for transient capture and analysis
20 KEY OFF
30 REM commands to set up GPIB-IEEE card
40 DEF SEG=0
50 DRIVER1=PEEK(&H4F0)+256*PEEK(&H4F1)
60 DRIVER2=PEEK(&H4F4)+256*PEEK(&H4F5)
70 DEF SEG=DRIVER1 REM SELECT CARD #1
80 INIT=3 ABORTIO=6 DEVCLEAR=9 LOCAL=12
90 LOCALLOCKOUT=15 REMOTE=18 IRESUME=21 TRIGGER=24
100 OUTPUT=27 ENTER=30 STATUS=33 SETTERMINATOR=36
110 SETTIMEOUT=39 SERIALPOLL=42 SRQCHECK=45 ERRCHECK=48
120 SETEOI=51 SETTERM=54 PARALLELPOLL=57 SRVREQ=60
130 NCINIT=63 BLOCKOUT=66 BLOCKIN=69 BYTESWAP=72
140 TRANSFER=75 TALK=78 UNTALK=81 LISTEN=84
150 UNLISTEN=87 ATTN=90 MTA=93 MLA=96
160 DIM AB(56) DIM Y%(257) DIM W%(257) DIM S <  257) DIM AB1(56) DIM V$(257)
170 DIM AB2(56) DIM DE<4) DIM DE$(4)
180 DIM SI(256) DIM OD(256) DIM X(256) DIM WL(56) DIM A(50) DIM B(50)
190 REM command to initialise the GPIB-IEEE card
200 CALL INIT
210 OSC=8 PI=3.14159
220 CLS D=0
230 SCREEN 0 WIDTH 80
240 REM Menus
250 LOCATE 8,34 COLOR 4 PRINT " MENU"
260 LOCATE 9,30 COLOR 7 PRINT "New Measurement [1]"
270 LOCATE 10,30 PRINT "Io measurement [1]"
280 LOCATE 11,30 PRINT "Transient measurement [2]"
290 LOCATE 12,30 PRINT "Exit [3]"
300 IF D>3 OR D<1 THEN 480
310 IF D=3 THEN 220
320 IF D=2 THEN GOSUB 3470 DRAW MEASURED TRANSIENTS
330 IF D=1 THEN GOSUB 3220 IO MEASUREMENT
340 GOTO 250
350 REM -------------------------Decay Analysis------------------
360 CLS D=0
370 LOCATE 11,30 PRINT "Enter Filename " FILE$
380 INPUT#1,DT$
390 ON ERROR GOTO 6720
400 OPEN FILE$ FOR INPUT AS #1
410 IF D=3 OR D<1 THEN 480
420 IF D<3 THEN 480
430 IF D<2 THEN GOSUB 5140 CLEAR ARRAYS AND CONSTANTS
440 IF D=2 THEN GOSUB 3220 IO MEASUREMENT
450 IF D<2 THEN GOSUB 3470 DRAW MEASURED TRANSIENTS
460 GOTO 410
470 REM -------------------------Decay Analysis------------------
480 CLS D=0
490 LOCATE 11,30 PRINT "Enter Filename " FILE$
500 INPUT#1,DT$
510 ON ERROR GOTO 6720
520 OPEN FILE$ FOR INPUT AS #1
530 INPUT#1,DT$
540 INPUT#1,MB
670 INPUT#1,W%(257)
680 INPUT#1,SCL
690 INPUT#1, WL
700 INPUT#1, INUL
710 FOR I%=1 TO 256
720 INPUT#1, S(I%)
730 NEXT I%
740 CLOSE#1
750 SCREEN 3
760 IF L=1 THEN VIEW(21,26)-(275,190) CLS
770 VIEW
780 LINE(20,25)-(276,191), B
790 X1=20+1 Y1=191-S(1)*648
800 FOR I=1 TO 256
810 X=20+I Y=191-S(I)*648
820 PSET (X,Y),1
830 LINE (X1,Y1)-(X,Y),1
840 X1=X Y1=Y
850 NEXT I
860 FOR I=1 TO 10
870 REM LINE (20+25+6*I,25)-(20+25+6*I,191),&HAAAA
880 REM LINE (20,25+16*1)-(276,25+16*1),&HAAAA
890 NEXT I
900 LOCATE 1,1 PRINT "mV" "Div"
910 LOCATE 14,15 PRINT TMB,"us/Div"
920 REM LOCATE 15,20 PRINT DT$,INUL,TMB,W%(257)
930 IF B$="y" THEN LOCATE 17,43 PRINT " 
940 LOCATE 17,20 INPUT "Curve Smoothing (y/n)",B$
950 IF B$<>"y" AND B$<>"n" THEN 940
960 IF B$="n" THEN 1050
970 FOR I=3 TO 254
980 S(I)=(-3*S(I-2)+12*S(I-1)+17*S(I)+12*S(I+1)-3*S(I+2))/35
990 NEXT I L*1
1000 GOTO 760
1010 GOTO 1050
1020 LINE (21,BL)-(275,BL),0
1030 VIEW PRINT 16 TO 22
1040 CLS
1050 LOCATE 17,5 PRINT "Use arrow up and arrow down keys to set baseline and present "
1060 VIEW PRINT
1070 WHILE EXIT$=
1080 UPDN$=INKEY$ REM LINE (20+25+6*I,25)-(20+25+6*I,191),&HAAAA
1090 IF UPDN$="" THEN 1080
1100 UPDN=ASC(RIGHT$(UPDN$,1))
1110 IF UPDN=72 THEN Z=Z-1
1120 IF UPDN=80 THEN Z=Z+1
1130 IF UPDN=CHR$(13) THEN 1180
1140 IF Z=0 THEN Z=256
1150 IF Z=166 THEN Z=0
1160 GOSUB 4900 BASELINE ARROW
1170 WEND
1180 BL=25+Z
1190 LINE (20,BL)-(276,BL)
1200 VIEW PRINT 16 TO 22
1210 ULS
1220 LOCATE 17,20 INPUT *Is the baseline correct y/n *,B$
1230 IF B$<>"y" AND B$<>"n" THEN 1220
1240 IF B$="n" THEN 1020
1250 VIEW PRINT
1260 GOTO 1290
1270 LOCATE 17,56 PRINT *
1280 LOCATE 19,53 PRINT *
1290 IF VP>0 THEN VIEW PRINT 16 TO 24 CLS
1300 IF VP=0 THEN VIEW PRINT
1310 LOCATE 17,20 INPUT *Enter starting channel for analysis *,ST

225
LOCATE 19,20 INPUT "Enter stop channel for analysis ", SP
1340 IF ST<0 OR SP>256 THEN 1270
1350 C=1 GOSUB 5010 REM Positioning arrow
1360 FOR I=ST TO 256
1370 S1(I)=(255-1543*BL-25)-S(I))*SCL*10)/256
1380 NEXT I
1390 FOR I=ST TO SP
1400 OD(I)=ABS(LOG(INUL)/(INUL+S1(I))))/2 303)
1410 NEXT I
1420 LOCATE 21,20 PRINT "First or Second order analysis ", RO
1430 IF RO<1 OR RO>2 THEN 1420
1440 IF RO=1 THEN 1450 ELSE 1530
1450 LOCATE 22,20 PRINT "First order 
1460 XMAX=-10 XMIN=0
1470 FOR I=ST TO SP
1480 X(I)=LOG(OD(I))
1490 IF XMAX<X(I) THEN XMAX=X(I)
1500 IF XMIN<X(I) THEN XMIN=X(I)
1510 NEXT I
1520 GOTO 1600
1530 LOCATE 22,20 PRINT "Second order"
1540 XMAX=0 XMIN=10
1550 FOR I=ST TO SP
1560 X(I)=1/OD(I)
1570 IF XMAX<X(I) THEN XMAX=X(I)
1580 IF XMIN<X(I) THEN XMIN=X(I)
1590 NEXT I
1600 XX=(XMAX-XMIN)
1610 IF VP>0 THEN VIEW (300,10)-(639,220) CLS
1620 VIEW
1630 FOR I=ST TO SP
1640 R=R+1
1650 YY=256/(SP-ST)
1660 XXI=(XMAX-X(I))/XX
1670 IF I=ST THEN R=0
1680 G=369+(R)*YY H=26+XX1*164
1690 PSET(G,H),1
1700 NEXT I
1710 SUM=0 SUMX=0 SUMY=0 SUMXY=0 SIGMA=0 CORR=1
1720 GOSUB 4690 REM statistical analysis
1730 XXI=TAU*ST+ICP XX2=TAU*SP+ICP
1740 Gl=369 H1=26+((XMAX-XX1)/(XMAX-XMIN))*164
1750 G2=369+(R)*YY H2=26+((XMAX-XX2)/(XMAX-XMIN))*164
1760 H3=191-H2
1770 LINE (G1,H1) -(G2,H2)
1780 IF RO=2 THEN LINE (G1-(G1* 05),26)-(G1-(G1* 05),H2+H3)
1790 LINE (G1-(G1* 05),26)-(G1-(G1* 05),H2+H3)
1800 LINE (G1-(G1* 05),H2+H3)-(G2,H2+H3)
1810 IF RO=1 THEN 1820 ELSE 1850
1820 LOCATE 2,37 PRINT USING "#### ##",XX1
1830 LOCATE 12,37 PRINT USING"#### ##",XX2
1840 GOTO 1870
1850 LOCATE 2,37 PRINT USING "#### ##",XX2
1860 LOCATE 12 37 PRINT USING"#### ##",XX1
1870 A=TMBA/25*(SP-ST)
1880 LOCATE 13,44 PRINT USING "# \\
1890 LOCATE 14,52 PRINT "time (microseconds)"
1900 VIEW PRINT 16 TO 24 CLS
1910 LOCATE 16,50 PRINT"correlation=",CORR
1920 LOCATE 19,50 PRINT "decay us=",ABS((1/TAU)*TMBA/25)
1930 RKOBS=((1/TAU)*TMBA/25)* 000001
1940 KOB=(1/RKOB)
1950 IF RO=1 THEN LOCATE 20,50 PRINT "kobs=",ABS(KOB\),"/s"
1960 IF RO=2 THEN LOCATE 20 50 PRINT kobs=",ABS(KOBS),"dm3/mol/s"
1970 LOCATE 17 50 PRINT "File ",FILES
1980 LOCATE 16,4 PRINT "DT$"
1990 LOCATE 17,4 PRINT "Io=", INUL, "mV"
2000 LOCATE 18,4 PRINT "Average of", W%(257), "shots"
2010 LOCATE 19,4 PRINT "Wavelength=", WL, "nm"
2020 IF WS = "/" THEN 2040 ELSE 220
2030 VP = 1
2040 GOTO 1250
2050 REM -----------------------------------Create STATIS Files-------------------
2060 KEY OFF
2070 CLS
2080 LOCATE 9,32 COLOR 4 PRINT "Create Statis File"
2090 LOCATE 11,29 COLOR 2 INPUT "Enter Filename", FILES
2100 LOCATE 12,29 INPUT "Enter drive specification/default A*", DR$
2110 IF DR$ = "" THEN DR$ = "A"
2120 FL$ = DR$ + " " + FILES + " tra"
2130 ON ERROR GOTO 6720
2140 OPEN FL$ FOR INPUT AS #1
2150 INPUT#1, DT$ INPUT#1, TMB INPUT#1, W%(257) INPUT#1, SCL INPUT#1, WL
2160 INPUT#1, INUL
2170 INPUT#1, IW%
2180 FOR I% = 1 TO 256
2190 INPUT #1, S(I%)
2200 X(I%) = S(I%)
2210 NEXT I%
2220 CLOSE#1
2230 ST = 10 SP = 20
2240 SUM = 0 SUMX = 0 SUMY = 0 SUMXY = 0 SIGMA = 0 CORR = 1
2250 GOSUB 4690 REM statistical analysis
2260 FOR I = ST TO 256
2270 YL = TAU * I + ICP
2280 IF X(I) > YL + 4 * SIGMA OR X(I) < YL - 4 * SIGMA THEN 2300
2290 NEXT I
2300 LF = I LOCATE 14, 29 COLOR 3 PRINT "laser fires at channel ", LF
2310 LOCATE 16, 29 INPUT "Output file to statis (y/n)", OS$
2320 IF OS$ = "y" THEN 2370
2330 SHELL "cd\statis3"
2340 SHELL "exit"
2350 FILE$ = FILE$ + " sta"
2360 GOTO 2390
2370 LOCATE 17, 29 INPUT "Enter drive specification", DR$
2380 FILES = DR$ + " +FILES+" sta"
2390 OPEN FILES FOR OUTPUT AS #1
2400 PRINT#1, DT$ 
2410 PRINT#1, 1.2, 256 - LF
2420 PRINT#1, "Time(s)"
2430 PRINT#1, "Absorbance (AU)"
2440 GOSUB 5070 REM subroutine to calculate baseline voltage
2450 FOR I = LF TO 256
2460 OD(I) = LOG(INUL / (INUL - (S(I) - AQS) * SCL * 10 / 255)) / 2.303
2470 PRINT#1, USING '#.###' (TMB / 25 * (I - LF)) * 10 - 6, OD(I)
2480 NEXT I
2490 CLOSE#1
2500LOCATE 21, 29 INPUT "Do you wish to enter statis (y/n)", ES$
2510 IF ES$ = "y" THEN 2550
2520 CLS SHELL "cd\"
2530 SHELL "cd\basic2"
2540 SHELL "cd\statis2"
2550 LOCATE 25, 30 COLOR 7 INPUT "Press return to continue", BS$
2560 IF BS$ = "" THEN 220 ELSE 2520
2570 REM -----------------------------------View Files---------------------------
2580 Q = 0 CL = 0
2590 SCREEN 0 CLS KEY OFF
2600 LOCATE 11, 34 COLOR 4 PRINT "Review Files"
2610 LOCATE 13, 30 COLOR 12 INPUT "Review file contents (y/n)", RES$
2620 IF RES$ = "y" THEN 6910 REM read file contents
2630 LOCATE 15, 30 COLOR 3 INPUT "Enter Filename ", FILES
LOCATE 16, 30 INPUT "Enter drive specification/default A",DR$  
IF DR$ = "" THEN DR$ = "A"  
IF CL = 1 THEN O = 1  
IF O = 1 THEN LOCATE 20, 1 PRINT " Enter filename", FILE$  
FILE$ = DR$ + " + FILE$ + " tra"  
ON ERROR GOTO 6720  
OPEN FILES FOR INPUT AS #1  
INPUT#1, TMB  
INPUT#1, SCL  
FOR I% = 1 TO 255  
INPUT#1, W%(I%)  
NEXT I%  
CLOSE#1  
GOSUB 4370 REM draw transient data  
LOCATE 14, 1 PRINT "<CR> to exit"  
LOCATE 16, 1 PRINT "[1] for overlay"  
LOCATE 18, 1 INPUT "[2] to clear screen", O  
IF O = 0 THEN 220  
IF O = 2 THEN 2890 ELSE 2930  
VIEW (217, 22)-(599, 276)  
CLS CL = 1  
VIEW  
GOTO 2660  
IF O = 1 THEN 2670  
REM ---------------------------EXIT---------------------  
LOCATE 17, 35 COLOR 3 INPUT "Exit to DOS (y/n)", EX$  
IF EX$ = "n" THEN SYSTEM ELSE END  
REM Subroutine for data transfer from oscilloscope  
CMD$ = "SPR 13"  
CALL OUTPUT(CMD$, OSC)  
CMD$ = "USP 47"  
CALL OUTPUT(CMD$, OSC)  
CMD$ = "WTD 30"  
CALL OUTPUT(CMD$, OSC)  
CMD$ = "UNLISTEN"  
FOR I = 1 TO 256  
VS(I) = SPACE$(20)  
NEXT I  
DELIM$ = CHR$(13)  
CALL TALK(OSC)  
CALL MLA  
CALL IRESUME  
CALL TRANSFER(VS(0), COUNT, DELIM$)  
FOR I = 1 TO COUNT  
Y%(I) = VAL(VS(I))  
NEXT I  
REM CMD$ = "FRO 0/HOR MTB/MOD REC/TRD ?"  
REM CALL OUTPUT(CMD$, OSC)  
CALL LOCAL(OSC)  
CALL LOCAL(OSC)  
RETURN  
REM Subroutine for Io measurement  
CLS  
LOCATE 11, 30 COLOR 4 PRINT " Io Measurement" COLOR 2  
LOCATE 13, 25 INPUT " Close Shutter and press return ", D$  
CALL LOCATE 13, 25 INPUT " Close Shutter and press return ", D$  
REM CMD$ = "REG 0/VER A/FCN ON/BGN 0/END 25/CNT 1/DAT ?"  
COUNT = 27  
IF D$ = "" THEN GOSUB 2970
3300 FOR I%=1 TO 26
3310 AA=AA+Y%(I%)
3320 NEXT I%
3330 AA=AA/26
3340 LOCATE 13,25 COLOR 2 INPUT " Open Shutter and press return ",D$
3350 IF D$="" THEN GOSUB 2970
3360 FOR I%=1 TO 26
3370 BB=BB+Y%(I%)
3380 NEXT I%
3390 BB=BB/26
3400 LOCATE 15,30 PRINT "'
3410 GOSUB 4170 REM front panel oscilloscope settings
3420 INUL=(AA-BB)*(ATT*10)/256
3430 LOCATE 13,25 COLOR 7 PRINT " Io=",INUL,
3440 LOCATE 15,29 COLOR 5 INPUT "Press return to continue",W$
3450 IF W$ = "" THEN 410 ELSE 3440
3460 RETURN
3470 REM Subroutine for to draw measured transients
3480 SCREEN 3 KEY OFF CLS
3490 LOCATE 11,30 PRINT "Previous file ",FILES
3500 LOCATE 13,30 INPUT "Enter filename ",FILES
3510 FILES="A " + FILES +" tra"
3520 WLI=WL
3530 LOCATE 15,30 PRINT "Enter wavelength (nm) [","WL,"] ",
3540 INPUT WL IF WL=0 THEN WL=WLI
3550 IF INUL=0 THEN LOCATE 17,30 INPUT "Enter Io",INUL
3560 LOCATE 21,30 INPUT "Press return to measure ",B$
3570 IF B$="" THEN 3580 ELSE 3560
3580 RETURN
3590 GOSUB 4170 REM front panel oscilloscope settings
3600 SCL=ATT TMB=TM
3610 FOR J=1 TO 10
3620 W%(257)=W%(257)+1
3630 IF J>1 THEN VIEW (  51,26)-(305,190) CLS
3640 IF J>1 THEN VIEW (306,25)-(561,191),B
3650 LOCATE 1,30 PRINT "File ",FILES
3660 IF J=1 THEN LINE (50,25)-(306,191),B
3670 IF J=1 THEN LINE (306,25)-(562,191),B
3680 LOCATE 13,15 PRINT"Averaged Transient"
3690 LOCATE 13,47 PRINT"Current Transient"
3700 LOCATE 15,5 PRINT "Shot No ",% (257)
3710 LOCATE 15,25 PRINT DT$
3720 IF INUL =0 THEN LOCATE 15,7 PRINT "Io not measured" GOTO 3760
3730 LOCATE 19,5 PRINT "Wavelength=" ,WL,"nm"
3740 LOCATE 16,5 PRINT "Io=",INUL,"mV 
3750 LOCATE 17,5 PRINT "Scale=",SCL,"mV/div"
3760 LOCATE 18,5 PRINT "Timebase=",TMB,"us/div"
3770 CM$="REG 0/VER A/FCN ON/BGN 0/END 255/CNT 1/DAT ?"
3780 COUNT =257
3790 GOSUB 2970 REM data transfer from oscilloscope
3800 FOR I=1 TO 256
3810 W%(I)=Y%(I)+W%(I)
3820 NEXT I
3830 VIEW
3840 XI=50+1 YI=191-(W%(I)/W%(257))* 648
3850 FOR I=1 TO 256
3860 X=50+I Y=191-(W%(I)/W%(257))* 648
3870 PSET (X,Y),1
3880 LINE (XI,YI)-(X,Y),1
3890 XI=X YI=Y
3900 NEXT I
3910 XI=306+1 YI=191-Y%(I)* 648
3920 FOR I=1 TO 256
3930 X=306+I Y=191-Y%(I)* 648
3940 PSET(X,Y),1
3950 LINE (XI,YI)-(X,Y),1
3940 X1=X Y1=Y
3970 NEXT I
3980 ON ERROR GOTO 6790
3990 OPEN FILES FOR OUTPUT AS #1
4000 PRINT#1,DT$
4010 PRINT#1,TMB
4020 PRINT#1,W%(257)
4030 PRINT#1,SCL
4040 PRINT#1,VL
4050 FOR I=1 TO 256
4060 S(I)=W%(I)/W%(257)
4070 NEXT I
4090 PRINT#1,INUL
4100 NEXT J
4100 CLOSE#1
4110 BEEP
4120 LOCATE 22,15 PRINT "Press return for another shot measurement"
4130 LOCATE 23,15 INPUT "Enter any character to return to menu ",B$
4140 IF B$="" THEN 4150 ELSE 4160
4150 NEXT J
4160 RETURN
4170 REM Subroutine to obtain oscilloscope settings
4180 CMD$="REG 0/VER A/FCN ON/ATT ?"
4190 VOLTS=SPACES$(11)
4200 CALL OUTPUT(CMD$,OSC)
4210 CALL ENTER(VOLTS,OSC)
4220 FOR I=1 TO 1000 NEXT I
4230 CALL LOCAL(OSC)
4240 CALL LOCAL(OSC)
4250 ATT$=RIGHT$(VOLTS,7)
4260 ATT=VAL(ATT$)*200
4270 CMD$="HOR ?"
4280 CALL OUTPUT(CMD$,OSC)
4290 TS=SPACES$(100)
4300 FOR I=1 TO 5000 NEXT I
4310 CALL ENTER(TS,OSC)
4320 CALL LOCAL(OSC)
4330 CALL LOCAL(OSC)
4340 TBS=MIDS(TS,21.6)
4350 TM=VAL(TBS)*10^-6
4360 RETURN
4370 REM Subroutine to draw transient data
4380 KEY OFF
4390 SCREEN 3 WIDTH 80
4400 PRINT
4410 LOCATE 2,24 PRINT "256"
4420 LOCATE 10,24 PRINT "128"
4430 LOCATE 18,26 PRINT "0"
4440 PRINT
4450 LOCATE 19,28 PRINT "Average of',W%(257),"shots"
4460 LOCATE 19,28 PRINT "Wavelength=',WL,"nm"
4470 LOCATE 19,28 PRINT "Seale=',SCL,"mV/div"
4480 FOR I=1 TO 10
4490 LINE(216+(256*I-15),21)-(216+(256*I-15),277),, &H4444
4500 LOCATE 3,1 PRINT "timebase=',TMB,"us/div"
4510 LOCATE 3,1 PRINT "File " FILES
4520 LOCATE 1,1 PRINT "Io",INUL,"mV"
4530 LOCATE 5,1 PRINT "Average of ',W%(257),"shots"
4540 LOCATE 7,1 PRINT "Wavelength=',WL,"nm"
4550 LOCATE 11,1 PRINT "Scale=',SCL,"mV/div"
4570 FOR I=1 TO 10
4580 LINE(216+(25 6*I-5),21)-(216+(25 6*I-5),277),, &H4444
4590 LINE(216,21+25 6*I),(600,21+25 6*I),, &H4444
4600 NEXT I
4610 X1=216+1 5 Y1=277-8(I)
FOR I=1 TO 256
X=216+1 5*I  Y=277-S(I)
PSET (X,Y),1
LINE (X1,Y1)-(X,Y),1
X1=X  Y1=Y
NEXT I
RETURN

REM Subroutine for statistical calculations
SUM=SP-ST+1
SUMX=SUMX+I
SUMY=SUMY+X(I)
SUMX2=SUMX2+I*I
SUMY2=SUMY2+X(I)*X(I)
SUMXY=SUMXY+X(I)*I
NEXT I
RA=(SUM*SUMXY-SUMX*SUMY)
RB=SQR(SUM*SUMX2-SUMX^2)
RC=SQR(SUM*SUMY2-SUMY^2)
CORR=RA/(RB*RC)
DELTA=(SUM*SUMX2-SUMX*SUMXY)/DELTA
ICP=(SUMX2*SUMY-SUMX*SUMXY)/DELTA
TAU=(SUM*SUMXY-SUMX*SUMY)/DELTA
FOR I=ST TO SP
SIGMA=SIGMA+(X(I)-ICP-TAU*I)^2
NEXT I
SIGMA=SIGMA/(SP-ST-1)
RETURN

REM Subroutine for baseline arrow
IF Z0Z-1 THEN LINE (277,25+Z-1)-(284,25+Z-1),0
IF Z0Z-1 THEN LINE (277,25+Z-1)-(279,28+Z-1),0
IF Z0Z-1 THEN LINE (277,25+Z-1)-(279,22+Z-1),0
IF Z0Z+1 THEN LINE (277,25+Z+1)-(284,25+Z+1),0
IF Z0Z+1 THEN LINE (277,25+Z+1)-(279,28+Z+1),0
IF Z0Z+1 THEN LINE (277,25+Z+1)-(279,22+Z+1),0
LINE (277,25+Z)-(284,25+Z)
LINE (277,25+Z)-(279,28+Z)
LINE (277,25+Z)-(279,23+Z)
RETURN

REM Subroutine for positioning arrow
IF C=0 THEN U=ST ELSE U=SP
LINE (20+U,191-S(U)*648)-(20+U,200-S(U)*648)
LINE (20+U,191-S(U)*648)-(16+U,192-S(U)*648)
LINE (20+U,191-S(U)*648)-(24+U,192-S(U)*648)
RETURN

REM Subroutine to calculate baseline voltage
QS=0
FOR I=4 TO 15
QS=QS+S(I)
NEXT I
AQS=QS/11
RETURN

REM Subroutine to clear arrays and constants
FOR I=1 TO 257
W%(I)=0
NEXT I
RETURN

--------------------Absorbance Calculation--------------------
CLS KEY OFF
N=4
LOCATE 15,25 PRINT " Enter time delay No ",I,"max=4 (/ to exit)",N
INPUT DES(I)
LOCATE 15,68 PRINT 
N=I-1
IF I=4 THEN N=4
IF DES(I)="/" THEN 5300
5280 DE(I)=VAL(DES(I))
5290 NEXT I
5300 GOSUB 5640 REM to read data from disk
5310 OPEN FILE$ FOR INPUT AS #1
5320 INPUT#1,DT$  
5330 INPUT#1,TMB  
5340 INPUT#1,W%(257)  
5350 INPUT#1,SCL  
5360 INPUT#1,WL  
5370 INPUT#1,FNUL  
5380 FOR I%=1 TO 255  
5390 INPUT#1,S(I%)  
5400 X(I%)=S(I%)  
5410 NEXT I%  
5420 CLOSE#1  
5430 ST=10 SP=20  
5440 SUM=0 SUMX=0 SUMY=0 SUMX2=0 SUMXY=0 SIGMA=0 CORR=1  
5450 GOSUB 4690 REM statistical calculations  
5460 FOR I=ST TO 256  
5470 YL=TAU*I+ICP  
5480 IF X(I)>YL+3*SIGMA OR X(I)<YL-3*SIGMA THEN 5510  
5490 YL=0  
5500 NEXT I  
5510 LF=1 IF LF>35 OR LF<26 THEN LF=30  
5520 GOSUB 5070 REM calculate baseline voltage  
5530 CH=0 CHL=0  
5540 CH1=INT((DE(1)*256)/(TMB*10))+LF  
5550 CH1=INT((DE(2)*256)/(TMB*10))+LF  
5560 CH2=INT((DE(3)*256)/(TMB*10))+LF  
5570 CH2=INT((DE(4)*256)/(TMB*10))+LF  
5580 OD(CH)=LOG(INUL/(INUL-(S(CH)-AQ)))*SCL*10/255))/2 303  
5590 OD(CH)=LOG(INUL/(INUL-(S(CH)-AQ)))*SCL*10/255))/2 303  
5600 OD(CH2)=LOG(INUL/(INUL-(S(CH2)-AQ)))*SCL*10/255))/2 303  
5610 OD(CH3)=LOG(INUL/(INUL-(S(CH3)-AQ)))*SCL*10/255))/2 303  
5620 RETURN  
5630 END  
5640 REM Subroutine to get files from disk  
5650 CLS WD=0 R=0  
5660 INPUT"Enter letter code",C$  
5670 INPUT"Enter start file no ",SF  
5680 INPUT"Enter file stop no ",FS  
5690 INPUT"Send data to printer (y/n)M,P$  
5700 IF P$<>"y" AND P$<>Mn" THEN 5700  
5710 INPUT"Write data to file (y/n)",WD$  
5720 IF WD$<>"y" THEN 5720  
5740 IF WD$="n" THEN 5780  
5750 WD=1  
5760 INPUT "Enter drive specification",DR$  
5770 FILE$="a","+C$","abs"  
5780 FOR J=0 TO FS STEP TEP  
5790 GOSUB 5100 REM read data from disk  
5800 R=R+1 IF R=1 THEN CLS  
5810 IF R=1 THEN PRINT TAB(20)"Timedelay=",DE(1),"microseconds"  
5820 PRINT TAB(20),"Wavelength Absorbance Fire cha
tnel Timebase"  
5830 IF R=1 THEN PRINT TAB(20)"Wavelength Absorbance Fire cha
tnel Timebase"  
5840 IF R=1 AND P$="y" THEN LPRINT TAB(20)"Timedelay=",DE,"microseconds"  
5850 IF R=1 THEN PRINT "Wavelength Absorbance Fire cha
tnel Timebase"  
5860 IF R=1 AND P$="y" THEN LPRINT "Wavelength Absorbance Fire cha
tnel Timebase"  
5870 PRINT USING "****###****" ',WL,OD(CH),FILE$,LF,TMB  
5880 IF P$="y" THEN LPRINT USING "****###****" ',WL,OD(CH),FILE$,LF,TMB  
5890 WL(R)=WL AB(R)=OD(CH) AB1(R)=OD(CH1) AB2(R)=OD(CH2) AB3(R)=OD(CH3)
5900 NEXT J
5910 CLOSE #1
5920 CO=(FS-SF)/TEP+1
5930 IF WD=1 THEN 5940 ELSE 6090
5940 OPEN FI$ FOR OUTPUT AS #1
5950 PRINT#1, DT$
5960 PRINT#1,
5970 IF N=1 THEN PRINT#1, DE(1)"us"
5980 IF N=2 THEN PRINT#1, DE(1)"us", DE(2)"us"
5990 IF N=3 THEN PRINT#1, DE(1)"us", DE(2)"us", DE(3)"us"
6000 IF N=4 THEN PRINT#1, DE(1)"us", DE(2)"us", DE(3)"us", DE(4)"us"
6010 CO=(FS-SF)/TEP+1
6020 FOR I=1 TO CO
6030 IF N=1 THEN PRINT#1 USING "### ### ---", WL(I), AB(I)
6040 IF N=2 THEN PRINT#1 USING "### ### --- ## ###~^~", WL(I), AB(I), AB1(I)
6050 IF N=3 THEN PRINT#1 USING "### ### --- ## ###--- ## ###~", WL(I), AB(I), AB1(I), AB2(I)
6060 IF N=4 THEN PRINT#1 USING "### ###--- ## ###--- ## ###", WL(I), AB(I), AB1(I), AB2(I), AB3(I)
6070 NEXT I
6080 CLOSE #1
6090 LOCATE 25,9 INPUT "Press return to plot spectrum (any character for menu)", W$
6100 IF W$="" THEN 6190 ELSE 220
6110 REM Subroutine to convert file numbers to strings
6120 CE$=""
6130 CE$="CE$"
6140 IF INT(J/10)>0 OR INT(J/10)<10 THEN E$=RIGHT$(STR$(J),2)
6150 IF INT(J/10)=0 THEN E$=RIGHT$(STR$(J),1)
6160 IF ABS(J/10)>999999 THEN E$=RIGHT$(STR$(J),3)
6170 CE$=CE$+E$
6180 RETURN
6190 REM Subroutine to draw line spectrum
6200 CLS
6210 SCREEN 3
6220 WIDTH 80
6230 YMAX=-10 YMIN=10
6240 XMAX=-10 XMIN=1000
6250 LINE (100,20)-(500,280),, B
6260 FOR I=1 TO CO
6270 IF WL(I)>XMAX THEN XMAX=Wl(I)
6280 IF WL(I)<XMIN THEN XMIN=Wl(I)
6290 IF AB(I)>YMAX THEN YMAX=AB(I)
6300 IF AB(I)<YMIN THEN YMIN=AB(I)
6310 IF DE(I)=0 THEN 6340
6320 IF AB1(I)>YMAX THEN YMAX=AB1(I)
6330 IF AB1(I)<YMIN THEN YMIN=AB1(I)
6340 NEXT I
6350 LOCATE 1 15 PRINT DTS
6360 LOCATE 2,7 PRINT USING"## ###", YMAX LOCATE 18,7 PRINT USING "## ###", YMIN
6370 LOCATE 19,11 PRINT XMIN LOCATE 19,61 PRINT (XMAX+XMIN)/2
6380 Y1=(YMAX-YMIN)
6390 X1=(XMAX-XMIN)
6400 IF YMIN>0 THEN 6420
6410 LINE (100,20+((YMAX-0)/Y1)*260)-(500,20+((YMAX-0)/Y1)*260)
6420 PS3=500-(YMAX-WL(I))/X1*400 PS4=20+(YMAX-AB(I))/Y1*260
6430 FOR I=1 TO CO
6440 X2=(XMAX-WL(I))/X1
6450 Y2=(YMAX-AB(I))/Y1
6460 PS1=500-X2*400 PS2=20+Y2*260
6470 PSET(PS1,PS2)
6480 LINE (PS3,PS4)-(PS1,PS2)
6490 PS3=PS1 PS4=PS2
6500 NEXT I

233
IF DEI=0 THEN 6570
FOR I=1 TO CO
SWAP AB(I),AB1(I)
NEXT I
DEI =0
GOTO 6420
GOTO 6090
END
REM ------------------------DOS Functions-------------------------------
CLS
PRINT " FUNCTION"
PRINT "A <CR> Change from hard-disk to floppy disc"
PRINT "cd\trans'<CR> Call transient directory"
PRINT "type (filename)<CR> To list the contents of the file"
PRINT "edit (filename)<CR> To edit a file"
PRINT "exit'<CR> To return to hard-disk"
PRINT "return to program"
SHELL"cd\basic2"
GOTO 220
REM Subroutine for error trapping
IF ERR=53 AND ERL=640 THEN ER=1
IF ERR=53 AND ERL=2150 THEN ER=2
IF ERR=53 AND ERL=2720 THEN ER=3
IF ER=1 THEN LOCATE 17,29 PRINT "FILE NOT FOUND SWITCH DIRECTORY?" FOR 1=
1 TO 5000 NEXT I GOSUB 6820 RESUME 220
IF ER=2 THEN LOCATE 17,37 PRINT "FILE NOT FOUND" FOR I=1 TO 5000 NEXT I GOS
1B 6820 RESUME 220
IF ER=3 THEN LOCATE 17,34 PRINT "FILE NOT FOUND" FOR I=1 TO 5000 NEXT I IF
C1=1 THEN RESUME 2660 ELSE RESUME 220
LOCATE 19,40 PRINT "INSERT DISK INTO DRIVE" FOR 1=1 TO 5000 NEXT I GOSUB 51
40 RESUME 3480
ON ERROR GOTO 0
REM Subroutine to list filenames
CLS
SHELL"A "
SHELL"dir/w"
SHELL"C "
SHELL"cd\basic2"
LOCATE 25,30 COLOR 7 INPUT "Press return to continue",B$
IF B$ ="" THEN 6900 ELSE 6880
RETURN
REM Subroutine to read and display file contents
K=0
INPUT 'Enter file string" FS
INPUT "Enter file start number",FS
INPUT "Enter file stop number",FE
FOR I=FS TO FE
K=K+1
IF K=1 THEN PRINT" FILENAME "," WAVELENGTH ","TIMEBASE ","SCALE "," DETAILS"
REM Subroutine to convert filenumbers to strings
GOSUB 7200
FILES="A "+FS+" tra"
GOTO 7270
OPEN FILES FOR INPUT AS #1
INPUT#1,DT$ 
INPUT#1,TMB 
INPUT#1,SHOT 
INPUT#1,SCL 
INPUT#1,VL 
INPUT#1,INUL
7120 CLOSE#1
7130 PRINT USING"\###
    ",FILE$,WL,TMB,SCL,DT$
7140 IF K=22 THEN GOSUB 7380
7150 NEXT I
7160 INPUT "Another go' (y/n)",AG$
7170 IF AG$="y" THEN 6910
7180 CLS GOTO 2630 END
7190 REM Subroutine to convert filenames to strings
7200 FS$=""
7210 ES$=""
7220 IF INT(I/10)>0 OR INT(I/10)<10 THEN ES$=RIGHT$(STR$(I),2)
7230 IF INT(I/10)=0 THEN ES$=RIGHT$(STR$(I),1)
7240 IF INT(I/10)>9 899999 THEN ES$=RIGHT$(STR$(I),3)
7250 FS$=FS$+ES$
7260 RETURN
7270 CLS
7280 SHELL"a "
7290 SHELL"dir/w"
7300 LOCATE 1,1 INPUT "Switch directory A \ = [1], A \TRANS = [2], no switch = [0]",SD
7310 IF SD=0 THEN 7340
7320 IF SD=2 THEN SHELL"cd\trans" GOTO 7270
7330 IF SD=1 THEN SHELL"cd\" GOTO 7270
7340 SHELL"C "
7350 SHELL"exit"
7360 GOSUB 7380
7370 RESUME 6930
7380 LOCATE 24,30 INPUT "Press return to continue",PR$
7390 IF PR$="" THEN CLS ELSE 7370
7400 K=0
7410 RETURN