

PHOTOCHEMICAL, THERMAL AND SPECTROSCOPIC STUDIES

OF METAL CARBONYL COMPLEXES

by

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DECLARATION

I hereby declare that the contents of this thesis, except where otherwise stated, are based entirely on my own work, which was carried out in Dublin City University, Trinity College Dublin, University of Nottingham, University of Aberdeen and the Max Planck Institute for Photochemistry in Mulheim.

Bernie Creaven
Bernie Creaven

Conor Long
(Supervisor)

This thesis is dedicated to my mother, Maura, and
to the memory of my father, Frank.

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Abstract

Flash photolysis of CpMn(CO)_3 , CbFe(CO)_3 and ArCr(CO)_3 in alkane solvents, resulted in the immediate formation of the solvent substituted dicarbonyl species. The reactivity of these species were investigated by uv/vis flash photolysis studies and in the case of CpMn(CO)_3 by trir flash photolysis. The rate constants for the reaction of these species with a variety of nucleophiles were determined and the thermodynamic parameters associated with these reactions were measured.

The chelation reactions of chromium carbonyl complexes, containing multidentate ligands, were investigated by uv/vis and ir spectroscopy. These chelation reaction were seen to proceed via bridging intermediates, even in those cases where the initial complex was coordinated in a monodentate fashion.

The crystal structures of a number of chromium and tungsten complexes were determined and correlated with their spectroscopic features.

Section 1
INTRODUCTION

1.1 Introduction

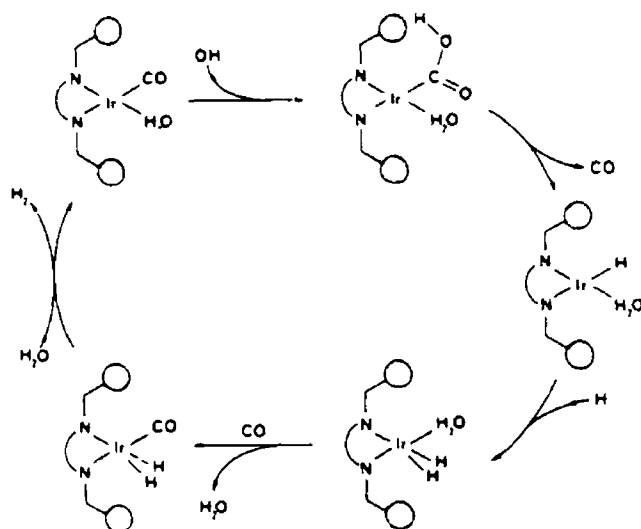
The bulk of organic chemicals produced in the world today are oxygenated compounds such as alcohols, ketones and carboxylic acids, and hydrocarbons such as ethylene, propylene and butadiene. These compounds are used as the starting materials for many other syntheses and in the case of the hydrocarbons, they may be polymerised to higher olefins such as polyethylene, polypropylene and synthetic rubbers.

The historical source of most chemical compounds was coal and coal tar products (via acetylene), but in recent years the natural gas and petroleum industries have become major sources of the organic molecules needed for industrial syntheses. Rubber was the only polymeric material of commercial value for many years, however natural rubber is not easy to process and its isolation by traditional means is labour intensive and therefore expensive. The drain on the world's natural supplies of oil, gas and rubber were felt earlier in this century and the search for alternative sources began in earnest. In recent years, synthesis gas derived methanol has increasingly become the starting point for many other bulk chemicals.

In the vast majority of modern industrial processes, which convert the simple molecules of methane, carbon dioxide, water, hydrogen, etc., to industrially useful organic molecules or polymers, transition metals or complexes of these metals are used as catalysts. A catalyst by definition speeds up the rate of a chemical reaction without losing its chemical identity. For reasons of efficiency and economy, catalysts are ideally heterogeneous on oxide, carbon and other supports though necessity may require a homogeneous catalyst. Homogeneous catalytic reactions in solution are generally very complex and the exact mechanisms of many such industrial catalysts remain ambiguous.

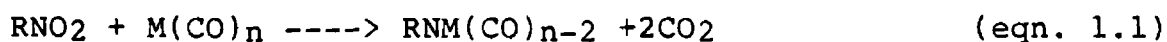
Catalytic reaction mechanisms have been extensively studied from the end of the last century. The discovery of the low pressure polymerisation of ethylene and propylene by Ziegla and Natta led not only to technical syntheses of polyalkanes and rubbers, but also to the wide use of aluminium alkyls as alkylating agents and reductants for metal complexes. Similarly, the discovery by Smidt of Palladium-catalysed oxidation of alkenes stimulated an enormous growth in the use of palladium complexes for a variety of catalytic and stoichiometric reactions of organic molecules.

One of the most important catalytic processes developed has been the synthesis gas reaction.¹ Mixtures of CO, H₂ and CO₂ may be obtained either by controlled oxidation of methane or light petroleums or by gasification of coal with oxygen and/or steam at ca. 1500°C. The synthesis gas composition can be modified by the water gas shift reaction shown in Scheme 1.1.2 Carbon dioxide can be removed by scrubber systems as are sulphur compound which act as poisons to many catalysts.

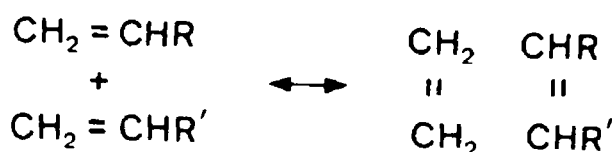


Scheme 1.1

Metal carbonyl complexes are used as industrial catalysts in a number of processes. Interaction of synthesis gas with alcohols, carboxylic acids, esters, etc., can lead to the next higher analogue. Cobalt, iron and ruthenium carbonyls, usually with iodides or phosphines as co-catalysts, have been used. Other metal carbonyls are used in the conversion of CO and H₂ to methanol, which can be converted to petroleum hydrocarbons over silica zeolites.³ Iron, ruthenium and rhenium carbonyls are used in the deoxygenation of nitro arenes by carbon monoxide (equation 1.1)⁴;



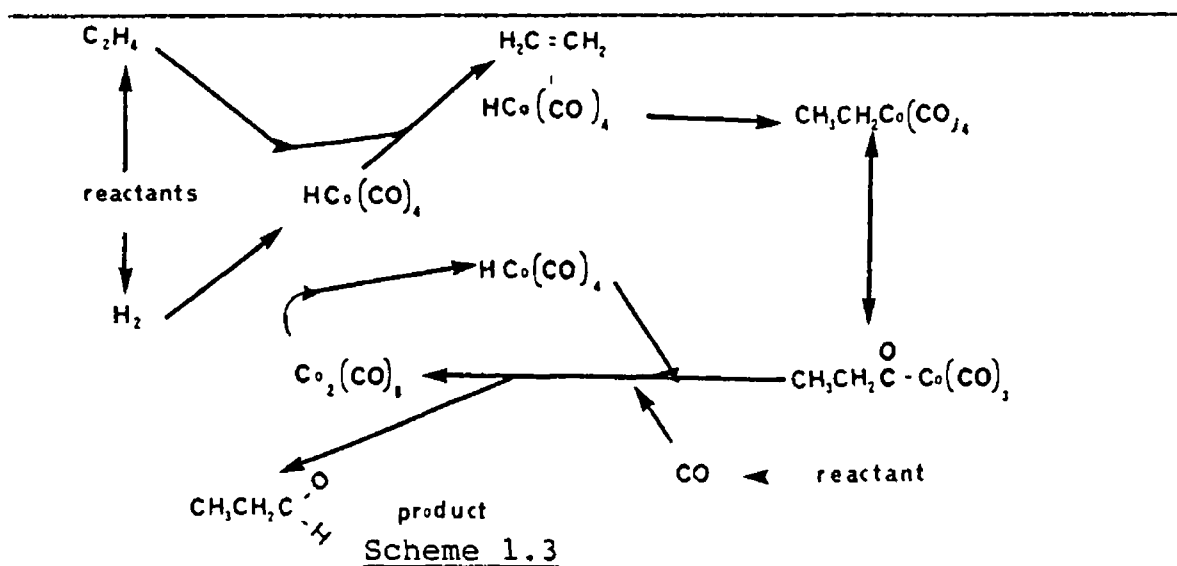
The RN moiety then undergoes further reactions such as hydrogenation to anilines, CO insertion or dimerisation. An important use of Mo(CO)₆ and W(CO)₆ is in the metathesis or dimerisation reaction of alkenes (Scheme 1.2)⁵, which occurs when olefins are passed over the metal carbonyl catalysts at 150 to 500°C deposited on Al₂O₃, silica supported metals etc.



Scheme 1.2

The catalytic activity of metal carbonyl compounds containing conjugated ring systems have also been well documented.⁶ Cais et al. have detailed the remarkable effectiveness of such complexes as catalysts in selective hydrogenation of conjugated olefins.^{6a} Non-conjugated olefins are unaffected in the reaction. In addition arene metal carbonyl complexes, as a homogeneous catalytic component of high stability, has been used in the

conversion of internal olefins.⁷ One of the first catalysts in use commercially was a cobalt carbonyl used in the "oxo" process for converting alkenes to aldehydes (Scheme 1.3).

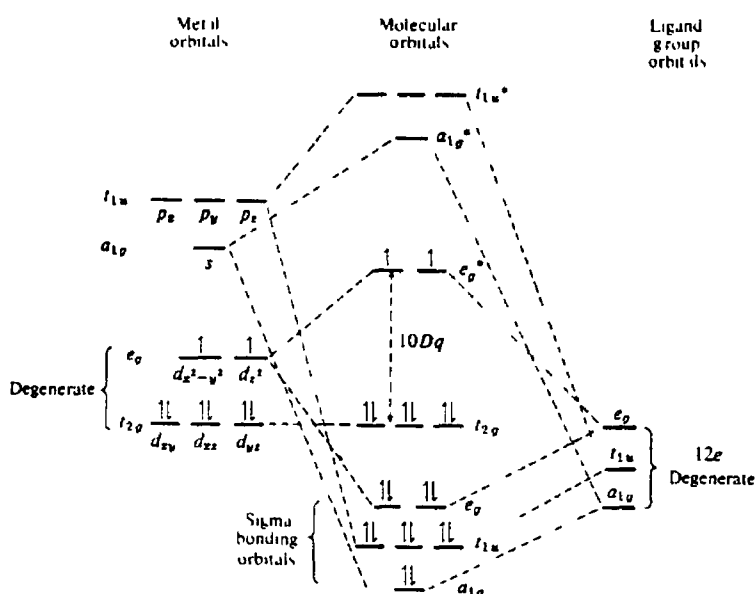


The exact mechanisms of many of these reaction are still unknown but the initial steps would seem to be the generation of a vacant co-ordination site at the metal centre which can then initiate further reactions. The generation of vacant co-ordination sites on metal carbonyl complexes and the subsequent reactions at these sites is the basis of this work.

The reactivity of metal carbonyl complexes cannot be explained without understanding the nature of the metal carbonyl bond. Figure 1.1 shows the energy level diagram depicting the interaction between ligand and metal σ -bonding orbitals in an octahedral $M(CO)_6$ complex. The carbonyl sp hybrid orbitals have the right symmetry for overlap with the s , p , d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal. Each such overlap results in the formation of a bonding molecular orbital (MO) and antibonding MO. Three of the d orbitals are nonbonding, having zero overlap with each of the ligand group orbitals. Thus interaction between each CO orbital and a metal orbital results in a net lowering in energy of the system, since the electrons enter the $M-CO$ σ -bonding orbitals. These molecular orbitals

are localised to a greater extent on the metal, which would result in a build up of charge on the molecule. However, since the CO ligands also have some empty low-lying π^* orbitals which are the correct symmetry to interact with the metal t_{2g} orbitals. Each t_{2g} orbital can interact with two π^* orbitals on CO ligands which are trans to each other. This interaction further increases the stability of the molecule since these electrons are now in a lower energy level (Figure 1.2).

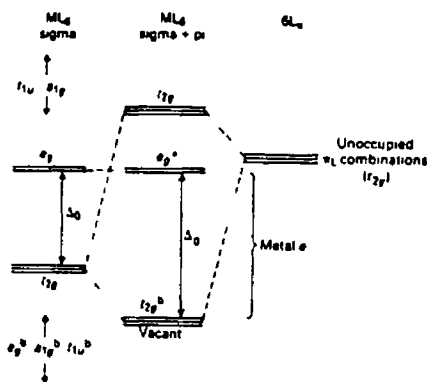
Figure 1.1: A MO energy level diagram for $M(CO)_6$ complexes, with no π -bonding.



The resulting molecular orbital has some character of the carbonyl π^* orbital. Therefore, the electronic population of this MO is effectively a population of the π^* orbital. This leads to a reduction in the bond order of the carbonyl ligand compared with free carbon monoxide (a change which can be detected by infrared spectroscopy). Thus the reactions of metal carbonyls with ligands other than CO will be reflected in the changes in the bond order of the carbonyl ligands. In addition

substitution of the carbonyl ligands changes the overall symmetry of the molecule from octahedral (O_h) to square planar (C_{4v}) leading to a corresponding change in the number and intensity of the IR absorption bands. Both of these effects were used in this work to determine the nature of the intermediates and products in the reactions of a range of carbonyl complexes.

Figure 1.2: An energy level diagram showing how π -bonding affects the value of Δ .



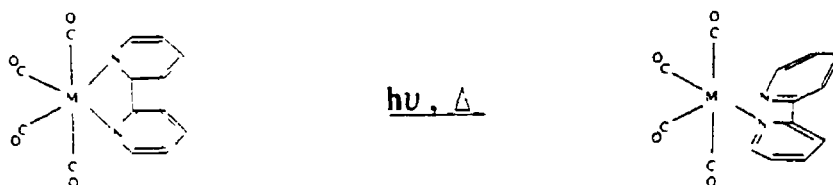
In this work, the photoinitiated reactions of carbonyl complexes of chromium, iron, and manganese complexes were studied by flash photolysis techniques. It will be shown that photoexcitation of these molecules led to dissociation of a carbonyl ligand. This excited state labilisation can be explained in the following way, taking for example the complex cyclopentadienemanganesetricarbonyl. For simplicity this complex is treated as pseudo- O_h , taking the Cp group as equivalent to three two-electron donors.

In the metal complexes it is the d orbitals that are involved in the σ and π bonding between the metal and the ligands and the effects of photochemical excitation upon the relative population of these must be considered. The d_{z^2} and the $d_{x^2-y^2}$ orbitals of e_g symmetry are antibonding (σ^*) with respect to the metal-ligand interactions whereas the d_{xy} , d_{yz} and d_{xz} orbitals of t_{2g} symmetry are weakly π -bonding between the metal and the carbonyl ligand. The lowest lying excited states in

these complexes have been assigned as ligand field states arising from $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$ transitions. These transitions involve depopulation of a metal-ligand bonding orbital and population of an orbital that is strongly antibonding between the ligands and the metal. Thus, the metal-ligand bonding is greatly weakened in the excited state, and CO loss is observed. The effect of substitution of carbonyl ligands on the ir and uv/vis spectra of carbonyl molecules will be discussed further in Section 4.1.

This work also details the study of the thermal reactions of metal carbonyl complexes bound to multidentate ligands. The generation of a vacant co-ordination site has been said to be of prime importance in catalytic cycles. This vacant site can be generated photolytically or by thermal or electrochemical means. In these complexes, breaking the bond between the metal centre and one of the co-ordination sites of the multidentate ligand would lead to a vacant co-ordination site (Figure 1.3). The energy (electrochemical, thermal or photochemical) required to break these bonds would depend on the nature of the ligand (and of course the metal centre).

Figure 1.3:



This study of the reactions of substituted metal carbonyl complexes involved determining the properties of the intermediates and transition states involved in the chelation reactions. The ultimate goal of this research is the development of heterogeneous catalysts which can be initiated by electrochemical, photochemical, or thermal means.

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Section 2

FLASH PHOTOLYSIS STUDIES OF METAL CARBONYL COMPLEXES,
CONTAINING CYCLIC LIGANDS, IN ALKANE SOLVENTS

2.1.INTRODUCTION

2.1.1 Photolytic Studies of Metal Carbonyls.

Research in organometallic photochemistry, particularly the photochemistry of metal carbonyl complexes, has expanded enormously in scope and importance in the recent past. This is because of the proven importance of such compounds as reagents for catalysing or assisting a large number of organic transformations. After the discovery of these catalysts, research began into their mode of operation. Catalysis appeared to occur via a long chain of events, initiated by the metal carbonyl, but the exact mechanisms remained uncertain. Important industrial catalysts were discovered largely by trial and error. The wastefulness of randomised research is apparent and research groups soon realised that organised investigations were required. Initiation of carbonyl catalysts via photochemical means was used to investigate the primary reactions of metal carbonyls and the reactivity of their photoproducts.

Initial studies were centred on photolysing solutions of the catalysts in industrially used solvents and analysing for any resulting products. Analysis rarely proved useful as the time scale of the experiment was so much greater than the in-situ catalysis. The products isolated were always the final products of the reaction. A method of studying the catalyst, immediately after the initiation of the catalyst (i.e. removal of a carbonyl moiety), was needed. The initial catalytic steps are of importance and must be known and understood before new and more efficient catalysts can be designed or envisioned. The greatest problem with studying these compounds was also their greatest asset as catalysts, i.e. their reactivity. In room

temperature solution catalytic intermediates were not sufficiently stable to allow ultraviolet/visible (uv/vis), infrared (ir) or nuclear magnetic resonance (nmr) spectra to be recorded and certainly not stable enough to be isolated.

The use of metal carbonyl compounds as catalysts relies on the reactivity of the co-ordinatively unsaturated fragments formed from these compounds. Such fragments can be generated via thermal or photolytic means but in general photolytic methods are more efficient and result in higher quantum yields.

The study of reactive fragments generated on the photolysis of stable molecules was greatly enhanced by the development of matrix isolation techniques.¹ This technique, first used by George Pimentell embeds the molecule of interest in an inert and transparent matrix, usually a frozen noble gas or other inert molecule at low temperatures, by vapour deposition. This allows the spectroscopic properties of intermediates produced in the matrix to be investigated. Matrix techniques have been used to generate reactive species for further catalytic reaction. Many photoproducted organometallic fragments are sufficiently reactive to activate C-H bonds in hydrocarbon compounds. The deposition of aluminium atoms in a methane matrix at 12K followed by photolysis at wavelengths below 400nm resulted in the formation of CH_3AlH .² Similar experiments with Cu atoms also indicated activation of the C-H bond in methane, in this case forming CH_3CuH .³

The matrix isolation technique has been successfully applied to the study of many metal carbonyl compounds. One of the earliest such studies was carried out by Graham et al. on the intermediates produced when $\text{Cr}(\text{CO})_6$ is photolysed in a methane matrix at 20K.⁴ They found that the primary photochemical reaction was loss of CO with a concomitant production of a $\text{Cr}(\text{CO})_5$ fragment with C_4v symmetry.

Visible absorption spectra of group 6 metal pentacarbonyls, produced upon photolysis of metal hexacarbonyls in rigid matrices, have been shown to be very sensitive to the nature of the matrix media.⁵ Mixed matrix experiments and comparison with spectra of stable species show that these shifts in spectra are due to stereospecific interactions between the $M(CO)_5$ fragment and a matrix species in the vacant co-ordination site. The frequency and intensity of ir bands of $M(CO)_5$ -matrix species indicated a change in bond angle between different $M(CO)_5$ -noble gas species in the same matrix. The shifts in visible bands from one matrix to another is because of;

- (a) the presence of a weak metal-matrix species bond,
- (b) a small change in axial-radial bond angle determined by the matrix species in the sixth co-ordination site.

The existence of such effects indicate the extreme reactivity of the co-ordinatively unsaturated metal species.

There are however limitations to the matrix isolation technique. Kinetic studies are difficult because of the restricted temperature ranges and limited diffusion. In addition the rigidity of the matrix can block pathways in photochemical reactions. For example, following the photolysis of matrix-isolated $Mn_2(CO)_{10}$ no $Mn(CO)_5$ radicals could be observed even though evidence for such radical formation in this process is available from solution studies⁶ It is likely that within the rigid structure of the matrix the highly reactive radicals quickly recombine and therefore would be undetected by conventional spectroscopic means.

Liquefied noble gases have recently proved to be very useful solvents for stabilising thermally reactive fragments Such studies have expanded on our knowledge of

primary photochemical processes of many metal carbonyl systems. Simpson et al. identified $\text{Cr}(\text{CO})_5(\text{Xe})$ as a relatively long lived species ($t_{1/2}$ ca. 2s at 193K) generated by uv photolysis of $\text{Cr}(\text{CO})_6$ dissolved in liquid Xe, or liquefied Kr doped with Xe.⁷ Studies by Jackson et al. have identified the formation of thermally labile metal carbonyl compounds co-ordinated to an alkene and either N_2 or D_2 in liquid Kr or Xe solution doped with N_2 or D_2 .⁸ These were formed upon photolysis of $\text{M}(\text{CO})_{6-x}(\text{trans-cyclooctene})_x$ ($x = 1$ or 2 , $\text{M} = \text{Cr}$ or W). Such compounds have been postulated as intermediates in photochemical hydrogenation. Liquefied noble gases allow studies of the thermodynamic parameters of reactive metal carbonyl compounds and therefore offers a great advantage over matrix isolation techniques.

Flash photolysis techniques were developed by a number of workers and have been extensively used in the study of metal carbonyl photochemistry.⁹⁻¹² Transition metal carbonyls are moderately soluble in non-polar solvents, have reasonably high uv/vis and ir extinction coefficients and have high quantum yields for their photochemical reactions. All of these properties make them ideal for study by flash photolysis techniques.

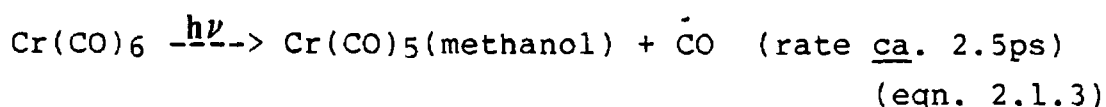
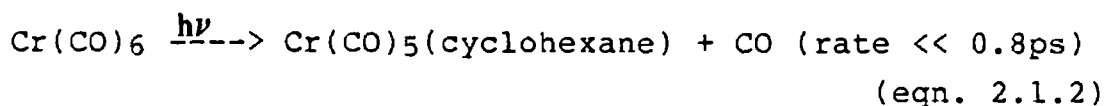


Generally photogenerated metal carbonyl fragments are easy to detect as their uv/vis spectra often vary greatly from the parent compound. The technique generally gives reliable data on the reactivity of species in solution. Such reaction rates in solution are high and good time resolution is essential for photolysis experiments. Time resolution has traditionally been limited by the pulse-time of the excitation source and the response time of the transient digitizers or oscilloscopes by which transient absorbances of reactive species are recorded. Modern

instruments with fast digitisers can have a response time of ca. 40fs. Useful solvents have negligible absorption at the wavelength of excitation of the primary species and at the wavelengths at which the transient species absorb.

Studies on an extensive series of carbonyl compounds have been recorded. In particular the group 6 metal hexacarbonyls have been studied.¹¹⁻¹⁵ One of the earliest studies carried out by Nasielski et al. reported the presence of two transient species having absorptions in the visible region of the spectrum.¹² Kelly et al. later assigned the first observable species on flash photolysis of Cr(CO)₆ in cyclohexane as a Cr(CO)₅ complex.¹³ In later studies the first observable species was identified as the solvent co-ordinated pentacarbonyl fragment, the spectroscopic features of which are dependent on the solvent.¹⁴ The kinetics of this reaction and the subsequent reactions of the solvated complex are given in Appendix 1.

At present many flash photolysis studies have been carried out on a picosecond time scale. Such studies have been centred mainly on group 6 metal hexacarbonyls and have yielded information regarding the initial reactivity of photogenerated species. In a recent study by Simon et al. the photoreaction of Cr(CO)₆ upon flash photolysis in cyclohexane and methanol was investigated.^{14b} The results can be summarised thus;



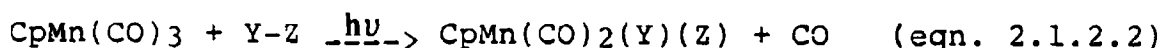
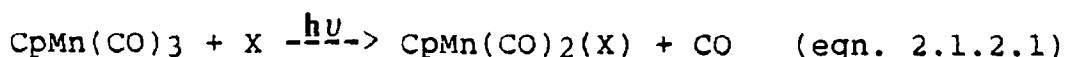
It was concluded that the slower solvation in methanol was an indication of the time needed for the solvent to restructure forming a Cr-solvent bond. These experiments

indicated that any excited state photochemistry occurs on faster time scales than indicated here.

Although uv/vis spectroscopy has many advantages for detecting intermediates generated by laser flash photolysis, it has some limitations when applied to metal carbonyl species. These limitations arise from the general broadness and lack of resolvable fine structure in the electronic absorptions of most organometallic species. Such information can be provided by transient infrared spectroscopy (trir) which can sometimes provide accurate estimates of bond angles.^{15,16} Solvent absorption is a serious problem for ir measurements even for the co region of the spectrum. Typically ir solution cells are limited to <5mm pathlength for most applications and these short pathlengths ensure greater experimental problems than equivalent uv/vis equipment. In addition faster risetimes of detectors in uv/vis measurements mean faster transient absorptions can be detected. Nevertheless trir has proven to be a very powerful technique as will be shown in this study vide infra.

2.1.2. Photolytic Studies of CpMn(CO)₃

Initial studies of the photochemistry of CpMn(CO)₃ (Cp = cyclopentadiene) centred on its characteristic photosubstitution reactions. Irradiation of CpM(CO)₃ complexes is known to result in photosubstitution of CO to yield substituted derivatives in the presence of an entering nucleophillic group, X¹⁷ or oxidative addition substrate Y-Z,¹⁸ to yield either CpM(CO)₂(X) or CpM(CO)₂(Y)(Z) (see equations 2.1.2.1 and 2.1.2.2)



In addition the former reaction is believed to occur with a quantum efficiency of unity.¹⁹ However little was known about the excited state chemistry or the reactivity of the primary photoproducts in these systems.

Herberhold et al.²⁰ studied the photochemistry of the half-sandwich carbonyl complexes of manganese, vanadium and chromium in ambient temperature solutions (hexane, tetrahydrofuran (thf), cyclooctene). Upon photolysis of CpMn(CO)_3 in thf the wine red-complex $\text{CpMn(CO)}_2(\text{thf})$ was formed and free carbon monoxide was detected (by its infrared absorption band at 2128cm^{-1}). In contrast to the photolysis in thf the assumed photoproduct $\text{CpMn(CO)}_2(\text{hexane})$ was not observed. This is because the donor solvent thf leads to stabilisation of the CpMn(CO)_2 fragment whereas the hexane molecule has little donor ability. Irradiation of the tricarbonyl species in cyclooctene also resulted in the formation of the monosubstituted derivative.

The intermediacy of CpMn(CO)_2 species has been suggested in many studies because the quantum yield of formation of $\text{CpMn(CO)}_2(\text{X})$ (X = nucleophilic ligand) is independent of the concentration of X .²¹ The photosubstitution reactions with PEt_3 (Et = ethyl) as entering ligand were studied.²⁰ The rate of disappearance of CpMn(CO)_3 upon photolysis in solution containing varying amounts of PEt_3 is not significantly influenced by the concentration of PEt_3 . However the ratio of mono- and di-substituted products depends strongly on its concentration. It appears therefore that the reactivity of the photo-excited species CpMn(CO)_3^* is relatively unaffected by the presence of PEt_3 which is only required for secondary thermal reactions. No evidence was obtained for the ejection of a cyclopentadiene ligand, even on prolonged photolysis.

These observations are characteristic of photochemical substitution reactions of metal carbonyls in solution. They

generally proceed with high quantum yields which are independent of the nature and concentration of the incoming nucleophile. The primary photochemical reaction appears to be dissociative loss of CO.

A number of low temperature studies have been carried out on CpMn(CO)_3 and related complexes. Braterman and Black^{22,23} photolysed CpMn(CO)_3 in a 3/1 methylcyclohexane/nujol mixture at 80K. They recorded the disappearance of the parent tricarbonyl peaks at 2026(A₁) and 1938(E₁)cm⁻¹ simultaneously with the appearance of two peaks at 1955(A₁) and 1886(B₁)cm⁻¹ which were assigned to the dicarbonyl species CpMn(CO)_2 .²³ Rest and co-workers conducted a series of similar experiments in frozen gas matrices at 10K.²⁴ In argon and methane matrices uv photolysis produced a CpMn(CO)_2 species characterised by ν_{CO} bands at 1972cm⁻¹ and 1903.2cm⁻¹ in an argon matrix and 1961.4cm⁻¹ and 1892.8cm⁻¹ in a methane matrix. This reaction was observed to be reversed, although not quantitatively, upon photolysis at longer wavelengths. This is because of significant production of the dicarbonyl species even following photolysis at longer wavelengths. Irradiation in ¹³CO doped (5%) CH₄ matrix gave rise to $\text{CpMn(}^{12}\text{CO)}_2(^{13}\text{CO)}$, $\text{CpMn(}^{12}\text{CO)}(^{13}\text{CO)}_2$ and ultimately $\text{CpMn(}^{13}\text{CO)}_3$. Prolonged photolysis resulted in unsaturated fragments of the above three materials

Ir spectral evidence was presented for the formation of co-ordinatively unsaturated species LM(CO)_2 (LM = ArCr, CpMn, or CbFe) on the uv photolysis of the tricarbonyl complexes in argon and methane matrices and dinitrogen complexes $\text{LM(CO)}_2(\text{N}_2)$ in nitrogen matrices at 12K. In a nitrogen matrix the bands which appear upon photolysis agree well with the positions in n-hexane for $\text{CpMn(CO)}_2(\text{N}_2)$, ν_{nn} 2169cm⁻¹ and ν_{CO} 1980 and 2923cm⁻¹.²⁹ Photoreversal does not occur in this case. $\text{CbFe(CO)}_2(\text{N}_2)$ underwent photoreversal at longer

wavelengths but $\text{ArCr}(\text{CO})_2(\text{N}_2)$ and $\text{CbFe}(\text{CO})_2(\text{N}_2)$ did not. The value of ν_{nn} was used to assess relative stabilities of the $\text{LM}(\text{CO})_2(\text{N}_2)$ complexes on the basis that the stronger the N-N bond is, the weaker will be the M-N bond (see Table 2.2.1.1). Both the chromium and manganese comolexes have ν_{nn} at 2150cm^{-1} which is near the upper limit for stable dinitrogen complexes. The iron complex has ν_{nn} at 2210cm^{-1} which is much closer to ν_{nn} for uncomplexed N_2 (ν_{nn} at 2331cm^{-1}).

TABLE 2.1.2.1: ν_{nn} (cm^{-1}) Values for $\text{LM}(\text{CO})_2(\text{N}_2)$ complexes (LM= ArCr, CpMn, or CbFe) in nitrogen matrices at 12K.

ir band	$\text{CbFe}(\text{CO})_2(\text{N}_2)$ cm^{-1}	$\text{CpMn}(\text{CO})_2(\text{N}_2)$ cm^{-1}	$\text{ArCr}(\text{CO})_2(\text{N}_2)$ cm^{-1}
A' ν_{nn}	2206.8	2175.3	2148.4
A' ν_{co}	2013.6	1978.7	1939.0
A'' ν_{co}	1961.0	1927.0	1895.8

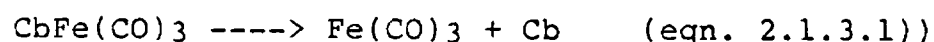
A further study of $\text{CpMn}(\text{CO})_3$ and related complexes in frozen matrix was conducted by Herbehold et al.²⁰ These workers found that photolysis of the isoelectronic compounds $\text{CpMn}(\text{CO})_3$, $\text{CpCr}(\text{CO})_2(\text{NO})$ and $\text{CpV}(\text{CO})(\text{NO})_2$ in low temperature matrices (CH_4 , Ar, CO, N_2) generally resulted in elimination of a CO ligand as the primary photoreaction. The photogenerated complexes were characterised by their ir absorptions ν_{co} , ν_{no} and by their secondary reactions in "reactive" matrices such as ^{13}CO , N_2

The most recent study on the photochemistry of $\text{CpMn}(\text{CO})_3$, by Wrighton et al.²⁵, in hydrocarbon glasses at 12K showed the primary photoproduct to be the dicarbonyl species (ν_{CO} at 1950 and 1880 cm^{-1}) with concomitant production of free carbon monoxide (ν_{CO} of 2132 cm^{-1}). The stoichiometry of the reaction, one molecule of CO appearing for each $\text{CpMn}(\text{CO})_3$ molecule disappearing, was determined using the known extinction of the two compounds. These workers also determined the activation parameters for the reaction of the dicarbonyl species with tri-substituted silanes and these will be discussed later vide infra.

2.1.3 Photolytic Studies of $\text{CbFe}(\text{CO})_3$

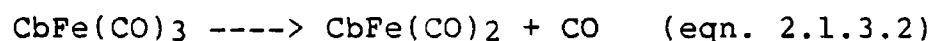
There have been several reports concerning the photochemical properties of $\text{CbFe}(\text{CO})_3$. The preparation of a number of mono-substituted $\text{CbFe}(\text{CO})_2\text{X}$ (X=ligand) compounds were reported decades ago and suggested the primary photochemical reaction was loss of CO.^{26 - 28} As with $\text{CpMn}(\text{CO})_3$ in these initial studies, the intermediate formation of the $\text{CbFe}(\text{CO})_2$ species has been suggested because the measured quantum yield of formation of $\text{CbFe}(\text{CO})_2\text{L}$ is independent of ligand concentration L, whereas if a hapticity change were occurring the photoreaction should show some dependence on the incoming ligand.

The first paper concerned with the photochemical properties of $\text{CbFe}(\text{CO})_3$ appeared in 1967. Gunning and co-workers obtained mass spectral evidence for the production of unco-ordinated Cb when $\text{CbFe}(\text{CO})_3$ was photolysed in the vapour phase.²⁹ They concluded that the primary photochemical step was that shown in equation 2.1.3.1;



It was further noted that photolysis of $\text{CbFe}(\text{CO})_3$ in diethylether solution in the presence of dimethylacetylenedicarboxylate gives a 17% yield of dimethylphthalate.²⁹ It was implied that this reaction proceeded by the thermal interaction of photochemically generated Cb with the acetylene.

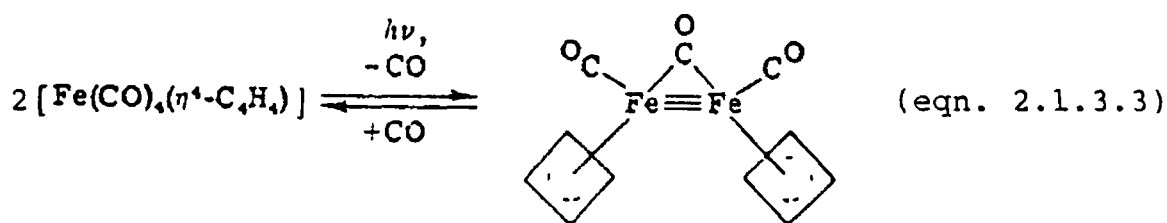
Chapman and co-workers³⁰ subsequently irradiated $\text{CbFe}(\text{CO})_3$, isolated in a krypton matrix, with $\lambda > 280\text{nm}$ and observed no evidence for the production of Cb but rather only the reaction shown in equation 2.1.3.2;



It had been previously noted that the photochemical reaction observed by Gunning et al.²⁹ between $\text{CbFe}(\text{CO})_3$ and dimethylacetylenedicarboxylate could occur following initial co-ordination of the acetylene to the photochemically generated $\text{CbFe}(\text{CO})_2$.³¹ Sodeau and co-workers described the characterisation by ir spectroscopy of a variety of species formed from $\text{CbFe}(\text{CO})_3$ in inert (argon or methane) and reactive matrices (N_2).²⁴ The ir spectroscopic evidence indicated that the initially formed photoproduct is a co-ordinatively unsaturated species $\text{CbFe}(\text{CO})_2$. This primary step is readily reversed by visible light. Pimentel et al. photolysed $\text{CbFe}(\text{CO})_3$ in a methanol/argon matrix at 20K which resulted in formation of bands which could be assigned to free CO and $\text{CbFe}(\text{CO})_2$.³² Rest and Taylor reported ir spectroscopic evidence, including ^{13}CO labelling and energy-factored force field splitting to show that photolysis of $\text{CbFe}(\text{CO})_3$ in a CO matrix at 12K leads to formation of $(\text{n}^4\text{-C}_5\text{H}_4\text{O})\text{Fe}(\text{CO})_3$.³³

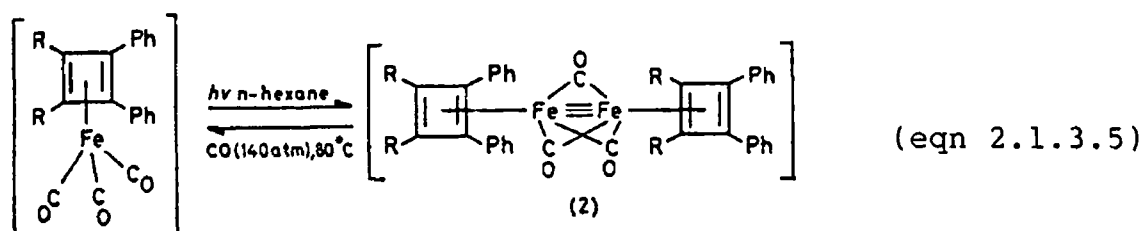
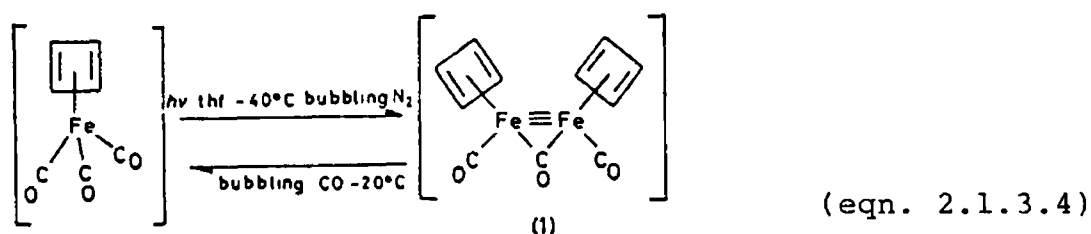
More recent results tend to suggest that loss of CO, according to equation 2.1.3.2, is the primary photochemical process for $\text{CbFe}(\text{CO})_3$.³⁴ Koerner von Gustorf and

co-workers³⁵ found that irradiation of CbFe(CO)_3 with $\lambda \geq 280\text{nm}$ in thf solution at 233K led to a product formulated as $\text{Cb}_2\text{Fe}_2(\text{CO})_3$. This reaction is only consistent with labilisation of CO since it is unlikely that free Cb would survive long enough to recombine with the iron fragments (see equation 2.1.3.3).



It was further shown by Rumin and co-workers³⁶ that irradiation of CbFe(CO)_3 in the presence of P(OMe)_3 led only to $\text{CbFe(CO)}_2(\text{P(OMe)}_3)$ and that the quantum yield of CO loss must be at least 10 times that of loss of Cb. Irradiation of $(\eta^4\text{C}_4\text{Me}_4)\text{Fe(CO)}_3$ in hexane in the presence of C_2HF_3 has been reported to lead to insertion of the olefin into the complex.³⁷ This reaction presumably arises through initial co-ordination of C_2HF_3 to photogenerated CbFe(CO)_2 fragment.

Rest et al. also reported that in contrast to MnCp(CO)_3 , attempted synthesis of $\text{CbFe(CO)}_2(\text{N}_2)$ by a low temperature synthetic route (equation 2.1.3.4) led to isolation of binuclear complex.²⁴ A related binuclear complex was obtained when photolysis was carried out in the absence of N_2 in hexane solution (equation 2.1.3.5).³⁸ The reactivity of the iron complex is reflected in the ready reversal reaction shown in equation (2.1.3.4).

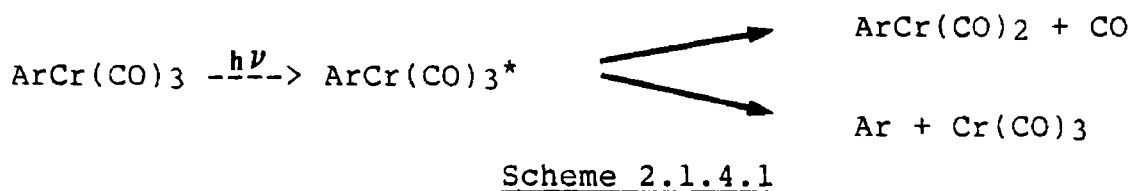


In conclusion the observation of extensive solution photochemistry of $\text{CbFe}(\text{CO})_3$ resulting in the retention of the CbFe grouping,³⁸ and also the gas matrix results suggest ejection of Cb is only a minor photoprocess.

Some recent work has been reported by Wrighton et al.^{25,39} Uv irradiation of $\text{CbFe}(\text{CO})_3$ at low temperature in alkane solvent containing Et_3SiH or in neat Et_3SiH yields CO loss to give the 16 valence-electron $\text{CbFe}(\text{CO})_2$ species as detected by ir spectroscopy. The co-ordinatively unsaturated dicarbonyl species then reacts thermally with excess Et_3SiH to give the oxidative addition product $\text{CbFe}(\text{H})(\text{SiEt}_3)(\text{CO})_3$.

2.1.4 Photolytic Studies of $\text{ArCr}(\text{CO})_3$

The earliest observations of photoreaction of $\text{ArCr}(\text{CO})_3$ were made by Strohmeier and von Hobe,⁴⁰ who proposed the reaction scheme shown below (Scheme 2.1.4.1);



These conclusions were based on experiments in which the complexes were irradiated in the presence of ^{14}C O and ^{14}C -labelled arene; in both cases incorporation of the labelled species was noted.

Yavorskii and co-workers⁴¹ and also Trembovler⁴² have described spectral changes which occurred during irradiation of $\text{ArCr}(\text{CO})_3$ in cyclohexane solution. It was concluded that the spectral data are compatible with the formation of arene and chromium hexacarbonyl during the reaction. Further, Trembovler and co-workers determined the quantum yield of photodecomposition as a function of light intensity and proposed the simultaneous occurrence of three photodecay processes, with different dependencies on light intensity. However no conclusions about the detailed photolytic reactions were drawn.

Reaction of $\text{ArCr}(\text{CO})_3$ with various substituted arene ligands has resulted in exchange of the Ar moiety.⁴³ These exchange reactions are equilibrium processes and have generally been carried out at high temperatures in sealed tubes. Addition of donor solvent such as thf or benzonitrile catalyses the arene exchange after allowing equilibrium to occur at reasonable rates and temperatures (at 140°C or below). Although both the arene and carbonyl ligands can be replaced by nucleophiles, thermal conditions generally favour arene displacement while photolysis usually leads to CO loss.

Uv irradiation of $\text{ArCr}(\text{CO})_3$ complexes in hydrocarbon solvents in the presence of suitable nucleophiles is a convenient route to an extensive range of carbonyl-substituted compounds.⁴⁴⁻⁴⁶ A number of studies have been carried out on the mechanisms of photosubstitution. For example, the quantum efficiency for the formation of $\text{ArCr}(\text{CO})_2(\text{pyridine})$ from $\text{ArCr}(\text{CO})_3$ and pyridine has been shown to be independent of the

irradiating wavelength ($\phi_{\text{CO}} = 0.72 \pm 0.007$ at 313nm, 366nm, or 436nm) and of the concentration of pyridine.⁴⁷

These results are consistent with dissociative loss of CO ligand as the primary photoprocess. Similarly, the quantum yield for the photosubstitution of a CO ligand in $(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)\text{Cr}(\text{CO})_3$ by N-dodecylmaleimide is 0.9 ± 0.09 at 313nm, and no evidence is found for the photolabilisation of the mesitylene ligand.⁵⁴ Photolysis of $\text{ArCr}(\text{CO})_3$, like the photolysis of the analogous $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$ complexes, in general leads to loss of only one carbonyl ligand. This is because the lowest ligand field involve population of σ^* states directed along the L-M-X (X=ligand) axis for $X < \text{CO}$ in LF strength.^{49,50} Disubstituted $\text{ArCr}(\text{CO})(\text{X})_2$ complexes only seem to result from the irradiation of $\text{CpMn}(\text{CO})_2(\text{X})$ when X is a reasonable π -acceptor ligand e.g. a phosphite ligand.

Gilbert et al.⁵¹ studied photoinduced CO exchange of $\text{ArCr}(\text{CO})_3$ and obtained a quantum yield in accordance with that reported by Wrighton and Haverty;⁵² furthermore, the efficiency of arene exchange was found to be approximately one-sixth the efficiency of CO loss.⁵³ Flash-photolysis in cyclohexane solution revealed the formation of a transient species which reacted within 1 ms to form a second species.⁵⁴ Both transients were strongly quenched if the solution was saturated with CO at one atmosphere pressure. It was considered that the primary species observed was $\text{ArCr}(\text{CO})_2$ and that exchange with benzene involves this intermediate and does not occur through a one-step dissociation of the excited molecule. Similar conclusions were reached from studies of $\text{ArCr}(\text{CO})_3$ in isooctane and methylmethacrylate solutions.⁵¹

Photolysis of $\text{ArCr}(\text{CO})_3$ in argon and methane matrices gives rise to bands in the ir spectrum which can be

assigned to CO and the unsaturated ArCr(CO)_2 (matrix species).²⁴ Furthermore bands assignable to $\text{ArCr(CO)}_2(\text{N}_2)$ could be identified upon photolysis of the tricarbonyl compound in an N_2 matrix. However unlike the analogous $\text{CbFe(CO)}_2(\text{N}_2)$ compound, the dinitrogen compound of ArCr(CO)_2 did not undergo reversal upon irradiation at longer wavelengths. There was no evidence in this study for photoejection of arene ligand even when ArCr(CO)_3 was photolysed in a CO matrix.

Wrighton and Hill studied the oxidative addition of trisubstituted silanes to photochemically generated co-ordinatively unsaturated species ArCr(CO)_2 .²⁵ Irradiation of ArCr(CO)_3 at low temperatures (85-157K) in inert organic solvents leads to dissociative loss of CO to form the 16 valence-electron dicarbonyl species. The unsaturated ArCr(CO)_2 moiety can be spectroscopically characterised in inert organic solvents and in the presence of R_3SiH will react to form 18 valence-electron oxidative addition products $\text{ArCr(CO)}_2(\text{H})(\text{SiR}_3)$.

In this study of the solution photochemistry of LM(CO)_3 (LM = CpMn, CbFe, or ArCr) it was hoped to identify the primary species produced upon photolysis and their subsequent reactions. We were interested in the reactivity of the photogenerated species and the thermodynamic properties governing its reactions. We have attempted the identification of the transient species involved via the following methods;

(a) the study of their spectroscopic properties, both uv/vis and ir,

(b) the study of the kinetics of the reactions of photogenerated species with various nucleophilic compounds.

2.2 RESULTS AND DISCUSSION

2.2.1 Flash Photolysis of CpMn(CO)_3 in Alkane Solvents

Abstract

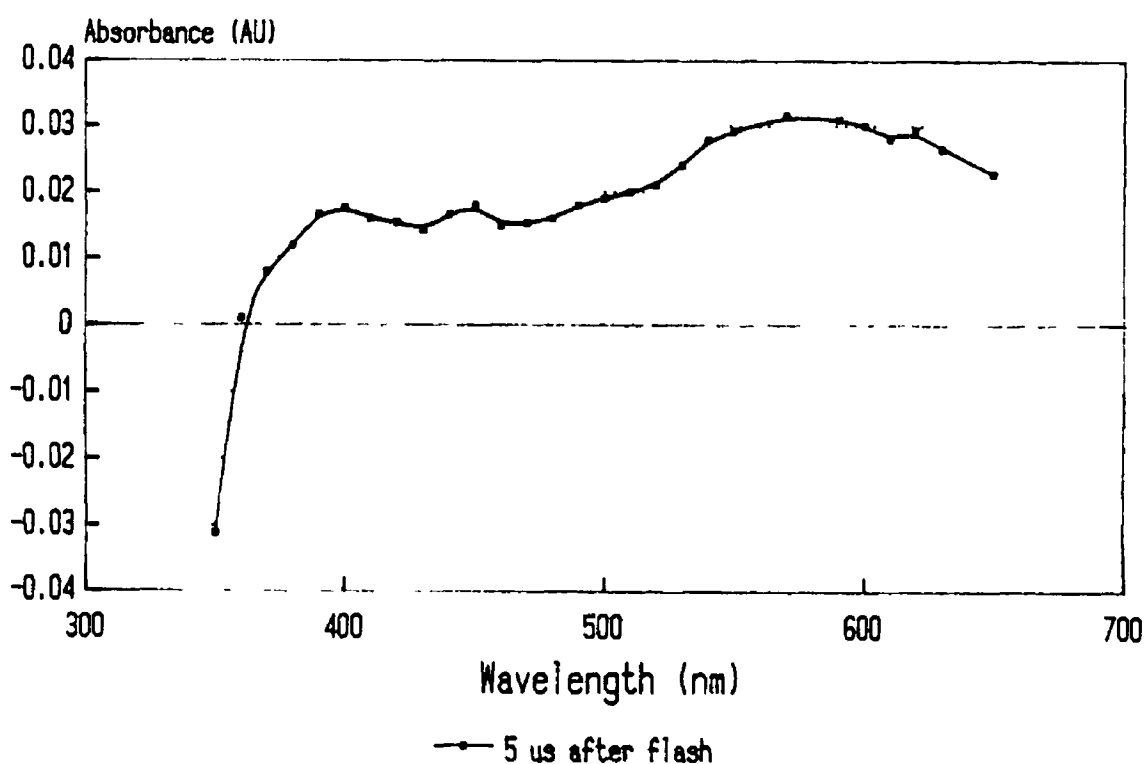
Uv laser flash photolysis (308nm,15ns) with both uv/vis and trir detection systems, has been used to characterise two transient species formed by the photolysis of CpMn(CO)_3 in alkane solution. The first species has been identified as $\text{CpMn(CO)}_2(\text{S})$ where S = cyclohexane or n-heptane, from both its kinetic behaviour and its trir spectrum. $\text{CpMn(CO)}_2(\text{S})$ reacts with CO, N_2 , PPh_3 , 1-hexene, 4-picoline and 4-vinylpyridine with bimolecular rate constants similar to those previously reported for the corresponding reactions of the group 6 metal pentacarbonyls.^{16,54,55} The second transient species $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ is formed by the reaction of $\text{CpMn(CO)}_2(\text{S})$ with unphotolysed CpMn(CO)_3 . ^{13}CO enrichment studies and trir spectroscopy were used to established that $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ has a single bridging CO group. The formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ can be suppressed by addition of nucleophilic ligands to the solution. The thermodynamic parameters for the reaction of $\text{CpMn(CO)}_2(\text{S})$ with CpMn(CO)_3 and various nucleophiles were measured.

2.2.1.1 Primary Photoproduct: Formation of $\text{CpMn(CO)}_2(\text{S})$

The uv/vis spectrum of the first observable species, recorded 5 μs after the flash showed a broad band which has a λ_{max} at about 580nm (Figure 2.2.1.1). This species was fully formed within the time resolution of the instrument (ca. 50ns). Previous workers had identified $\text{CpMn(CO)}_2(\text{S})$ (S = matrix species) as the primary

photoproduct formed upon the photolysis of the tricarbonyl in various matrices.^{21,24,34,56} The identification of the initially observed species as the dicarbonyl species was based on its kinetic behaviour and on its trir spectrum vide infra.

Figure 2.2.1.1: uv/vis Difference spectrum observed following the flash photolysis of CpMn(CO)_3 in cyclohexane solution.



2.2.1.2 Flash Photolysis of CpMn(CO)_3 in CO Saturated Cyclohexane Solution

The effect on the absorbance of the initially observed species, on saturating the alkane solvent with CO, was investigated by both uv/vis and trir detection systems. The

uv study was extensive and showed that the life time of the primary species was decreased upon addition of carbon monoxide (Table 2.2.1.1). However the addition had little effect on the yield of the primary species (Table 2.2.1.2). The variation in yield values shown in Table 2.2.1.2 was thought to be because the initially observed species has a low extinction coefficient and would therefore be greatly affected by fluctuations in I_0 (I_0 is the intensity of the incident radiation on the sample). From Table 2.2.1.2 it is difficult to say that any significant change in absorbance values of the initially formed species occurred upon addition of carbon monoxide to the system.

Table 2.2.1.1: The effect of CO on the lifetime^a of $\text{CpMn(CO)}_2(\text{S})$. The concentration of CO is $1.1 \times 10^{-2} \text{ mol dm}^{-3}$.

Measuring Wavelength (in nm)	Concentration of CpMn(CO)_3 (mol dm^{-3}) $\times 10^3$	Lifetime of $\text{CpMn(CO)}_2(\text{S})$ in absence of CO (μs)	Lifetime of $\text{CpMn(CO)}_2(\text{S})$ in presence of CO (μs)
500	2.23	355 +/- 30	200 +/- 18
390	"	340 +/- 30	180 +/- 18
390	2.01	394 +/- 30	176 +/- 12
390	2.28	280 +/- 30	143 +/- 18

^a Lifetime is given as $1/k_{\text{obs}}$

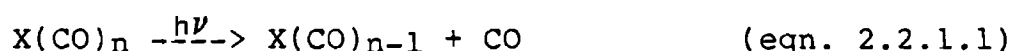
Table 2.2.1.2: The effect of CO on the yield of $\text{CpMn}(\text{CO})_2(\text{S})$ in cyclohexane solution. The concentration of CO is $1.1 \times 10^{-2} \text{ mol dm}^{-3}$.

Concentration of $\text{CpMn}(\text{CO})_3$ mol dm^{-3} ($\times 10^3$)		Absorbance (A.U. $\times 10^2$), $10 \mu\text{s}$ after the flash (wavelength in nm)				
		360	390	500	550	620
2.27	CO absent	1.20	2.45	3.70	5.60	4.63
	CO present	1.34	1.75	2.80	4.96	4.18
	% difference	+11	-28	-24	-11	-10
2.2	CO absent	6.63	8.39	1.34	1.69	1.16
	CO present	8.42	9.02	1.51	1.2	0.82
	% difference	+27	+7	+17	-29	-30
2.3	CO absent	0.89	1.04	1.09	1.87	1.50
	CO present	0.83	0.87	0.73	1.45	1.25
	% difference	-7	-16	-33	-22	-17
1.9	CO absent	0.54	0.87	1.39	1.91	1.74
	CO present	0.40	1.06	1.28	1.74	1.86
	% difference	-20	+16	-8	-9	+6

a There are at least 30% errors in the above absorbance values.

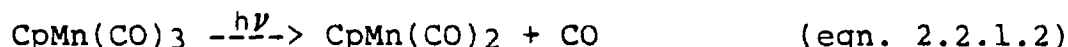
These experiments clearly illustrated a number of important facts:

(i) assuming the primary photoprocess is loss of CO, addition of carbon monoxide to the system would not affect the yield of the primary photoproduct as its formation is as a result of a physical process (equation 2.2.1.1);



(ii) the presence of CO in the solution ensures that the backreaction with the photolytically formed $X(CO)_{n-1}$ species is efficient thus reducing the lifetime of the $X(CO)_{n-1}$ species.

The primary photochemical reaction is therefore given by equation 2.2.1.2;



The lifetime of the species (at a given concentration of $CpMn(CO)_3$) was determined before and after the addition of carbon monoxide and the difference was used to calculate the rate constant for the reaction of the species with carbon monoxide. The concentration of carbon monoxide was assumed to be saturation in cyclohexane i.e. $1.1 \times 10^{-2} \text{ mol dm}^{-3}$.⁵⁷ This rate constant was found to be $3.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295K, which is an order of magnitude slower than that reported for reaction of $Cr(CO)_5$ with carbon monoxide in cyclohexane solution ($3.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).¹³

It is likely that $CpMn(CO)_2$ upon formation is co-ordinated weakly to a solvent molecule acting as a weak ligand. There are a number of reasons for thinking this:

(i) in similar studies on group 6 metal hexacarbonyls a variation in the uv/vis maximum of the pentacarbonyl fragment with solvent, was recorded. This variation was attributed to the interaction of the co-ordinatively unsaturated fragment with varying solvents;⁵

(ii) in a recent study by Simon et al. on the initial photochemical reactions of $\text{Cr}(\text{CO})_6$ in methanol they concluded that a risetime of 2.5ps recorded immediately after the flash was because of co-ordination of the pentacarbonyl fragment by methanol.¹⁴ They stated that after excitation by the laser, electronic relaxation occurs prior to solvent co-ordination and the observed risetime is a reflection of both solute isomerisation and solvent co-ordination;

(iii) Perutz et al.⁵ have deduced that the variation in C=O stretching bands in various matrices is due to the $\text{CpMn}(\text{CO})_2$ fragment co-ordinating weakly to the solvent matrix;

(iv) flash photolysis of $\text{Cr}(\text{CO})_6$ in perfluoro solvents have shown that the photogenerated $\text{Cr}(\text{CO})_5$ fragment is essentially 'naked' in solution.⁵⁸ The increased reactivity of the pentacarbonyl species in perfluoro solvents over alkane solvents indicated that the $\text{Cr}(\text{CO})_5$ fragment must be co-ordinated to the solvent molecule.

For the above reasons and from the experimental observations upon photolysis of $\text{CpMn}(\text{CO})_3$ in various matrices and in CO saturated alkane solution it can be concluded that the first observed species was $\text{CpMn}(\text{CO})_2(\text{S})$.

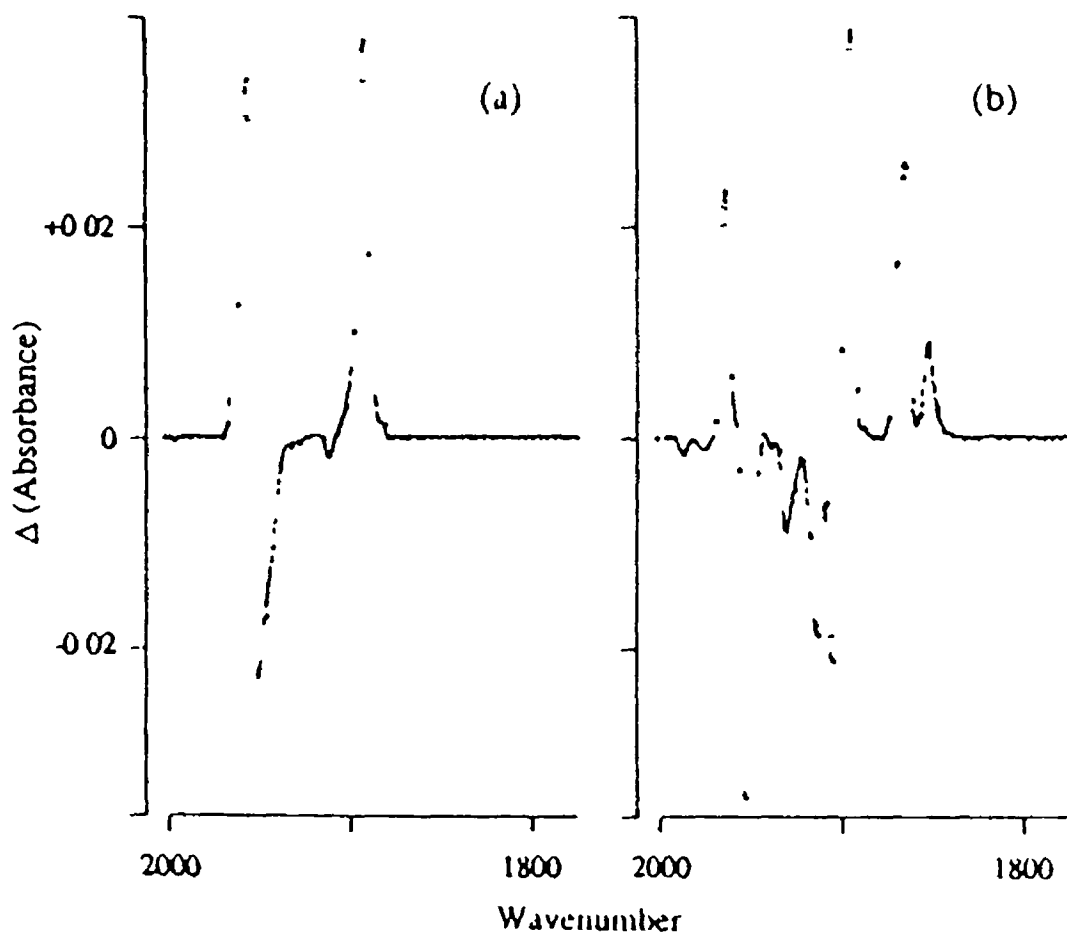
Figure 2.2.1.2 shows the trir spectrum of the first observable species also recorded $5\mu\text{s}$ after the laser pulse. The bands at 1964cm^{-1} and 1895cm^{-1} were similar to those reported for $\text{CpMn}(\text{CO})_2$ in a CH_4 matrix²⁴ and in hydrocarbon glasses^{25,34} (see Table 2.2.1.3). The differences in ν_{CO} for the $\text{CpMn}(\text{CO})_2(\text{matrix species})$ molecules are because of the different environments of the metal carbonyl fragments.

Table 2.2.1.3: Observed wavenumbers(cm^{-1}) of ir bands of $\text{CpMn}(\text{CO})_2(\text{S})$ in n-heptane solution at room temperature and in low temperature solids.

n-Heptane	CH ₄ Matrix	Hydrocarbon glasses	Assignment $\nu_{CO} \text{ cm}^{-1}$
293Ka	15Kb	77Kc 77Kd	
1964	1961	1955 1950	CpMn(12CO) ₂ S
1895	1892.8	1886 1880	CpMn(12CO) ₂ S
1886,1867e			CpMn12(CO)13(CO)S
1853,1852e			CpMn(13CO) ₂ S
			Force Const. Nm ⁻¹
1504	1501.6	1490	K _{CO}
54	53.4	53	K _{int}

e Calculated values

Figure 2.2.1.2: trir Difference spectrum observed 5 s after the flash photolysis of $\text{CpMn}(\text{CO})_3$ in n-heptane solution (a) natural abundance ^{13}CO and (b) sample 30% enriched with ^{13}CO . In both spectra the negative bands correspond to depletion of $\text{CpMn}(\text{CO})_3$. Note that the heavier points are those measured experimentally and the lighter points have been inserted by computer interpolation.



In these series of experiments, the first observable transient had C=O's of 1964 and 1895cm⁻¹ while the parent tricarbonyl exhibited ir bands at 2027 and 1947cm⁻¹. The decreasing of CO stretching frequencies in the first observable species is consistent with loss of CO being the primary photoprocess. The metal-carbon bond of the remaining 2 C=O bonds is strengthened with a corresponding decrease in C=O stretching frequency. In addition the number of ν_{CO} 's is consistent with loss of one carbonyl ligand.

It is also possible to infer the symmetry of the arrangement of the C=O groups from the number of C=O stretching bands found in the infrared spectrum⁵⁹ (see Introduction of Section 4). In these experiments the stretching vibrations of the assumed dicarbonyl species CpMn(CO)₂ were used to predict the stretching vibrations of a CpMn(CO)₂ complex which contained ¹³CO. These were then compared with a spectrum generated from ¹³CO enriched CpMn(CO)₃ sample. The results are given in Table 2.2.1.4 which shows clearly the similarity between the observed and calculated ν_{CO} for the CpMn(CO)₂ species.

Table 2.2.1.4: Comparison of calculated ¹³CO CpMn(CO)₂ carbonyl stretching frequencies(cm⁻¹) with experimental values.

	Calculated Values K _{CO} 1504 K _{int} 54		Experimental Values	
All ¹² CO freq.	1963.85	1894.55	1964	1895
All ¹³ CO freq.	1920.07	1852.33	a	1853
(¹³ CO)(¹² CO)	1867.25	1948.14	1866	a

a not observed

In addition the dicarbonyl species has C=O stretching force constants almost identical to those derived from the low temperature spectra of CpMn(CO)_2 . This experiment further proved that the first observable species was the CpMn(CO)_2 species (equation 2.2.1.2).⁵

2.2.1.4 The Reaction of $\text{CpMn(CO)}_2(\text{S})$ With Nucleophiles

The high reactivity of CpMn(CO)_2 has been demonstrated by its reaction with noble gas species to form $\text{CpMn(CO)}_2(\text{X})$ (X = noble gas molecule).²⁴ CpMn(CO)_2 has been shown to form a stable dinitrogen complex and such complexes have important consequences as far as nitrogen fixation is concerned.⁶⁰ This study measured the bimolecular rate constants for the reaction of $\text{CpMn(CO)}_2(\text{S})$ with dinitrogen and other ligands in order to determine what parameters affected the reactivity of the dicarbonyl complex. The bimolecular rate constants for the reaction of CpMn(CO)_2 with the ligands, dinitrogen, tri-methyl phosphite, 1-hexene, 4-vinylpyridine, 4-picoline and triphenylphosphine are shown in Table 2.2.1.5 and show similarities with reaction rates determined for photogenerated Cr(CO)_5 with these ligands.^{16,54,55}

The products of the former reactions e.g. $\text{CpMn(CO)}_2(\text{PPh}_3)$ have been isolated (references in Table 2.2.1.5) and characterised. The difference in reaction rates between ligands indicate that while the $\text{CpMn(CO)}_2(\text{S})$ fragment is highly reactive steric considerations do have some effect. The differences in reaction rate indicate that the rate determining step in the formation of the above products is not simply dissociation of the solvent molecule.

TABLE 2.2.1.5: Bimolecular rate constants^a
 (dm³mol⁻¹s⁻¹) for the reaction of
 CpMn(CO)₂(S) (S = n-heptane or
 cyclohexane) with various ligands at 295K.

Ligand	Rate Constant ^c x10 ⁻⁶	Solvent	Experiment ^b
CO	0.32	cyclohexane	uv/vis
N ₂ ^d	3.72	"	uv/vis
P(OMe) ₃ ^e	7.10	heptane	trir
PPh ₃ ^f	5.34	cyclohexane	uv/vis
CpMn(CO) ₃	1.16	"	"
4-vinylpyridine	3.40	"	"
4-picoline ^g	30.84	"	"
1-hexene ^h	0.30	"	"

a All rate constants have been corrected to allow for the concomitant formation of Cp₂Mn₂(CO)₅.

b See experimental section for rate determining method.

c Rate constants are accurate to +/- 15%

d Ref 22,60, e Ref. 17(b), f Ref. 61, g Ref. 21, h Ref. 62.

In summary the first observable species after the flash is the solvated dicarbonyl complex. This observation agrees with studies carried out on $\text{CpMn}(\text{CO})_3$ in low temperature matrices. The broad band observed in it's uv spectrum is probably as a result of a LF absorption within the molecule and perhaps spectra recorded in different solvents or with various substituents on the Cp ring may have yielded more information on the nature of this transition, (changing the solvent could change the strength of the $\text{CpMn}(\text{CO})_2\text{-S}$ interaction causing a corresponding change in the uv/vis spectrum). The two bands recorded in the trir studies are characteristic of a symmetrical dicarbonyl molecule. The

$\nu_{\text{C=O}}$ at 1964cm^{-1} corresponds to the antisymmetric stretch and that at 1895cm^{-1} to the symmetric stretch.

2.2.1.5 The Determination of Bond Angles in $\text{CpMn}(\text{CO})_2(\text{S})$

To a good approximation the relative intensities of different CO stretching modes can be used to calculate the angles between the carbonyls by using a simple model.⁶³ In this model, each CO oscillator is treated as a dipole vector, and the total dipole vector for the entire vibrational mode is taken to be the vector sum of these individual vectors. Since the intensities are proportional to the squares of the dipole vectors, there is a relationship between the intensities of the absorption bands and the angles between C=O bond vectors. The angle between the oscillating dipoles of these CO groups can be found from their relative absorption intensities.

For the case of two C=O groups (Figure 2.2.1.3) the ratio of the intensities of the symmetric and antisymmetric bands is given by

$$\frac{I_{\text{asym}}}{I_{\text{sym}}} = \frac{(2R \sin \theta / 2)^2}{(2R \cos \theta / 2)^2} = \tan^2(\theta / 2)$$

θ = bond angle

I_{asym} = intensity of the antisymmetric stretch

I_{sym} = intensity of the symmetric stretch

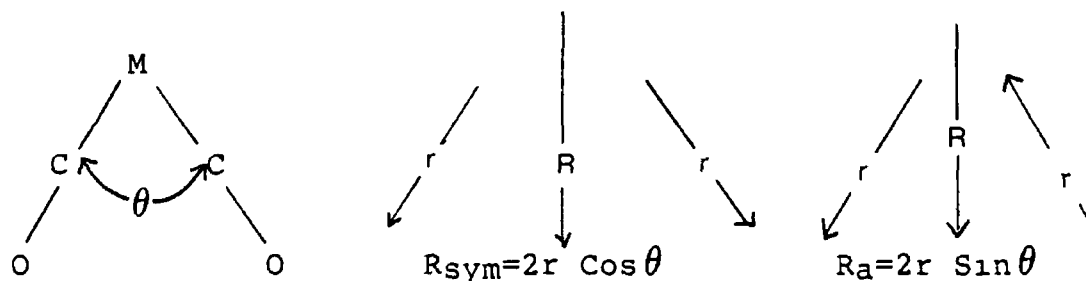


Figure 2.2.1.3: Diagram showing how the dipole vectors, r , of individual CO groups combine to give the vector R , for the symmetric and antisymmetric mode of vibration of an $M(\text{CO})_2$ moiety

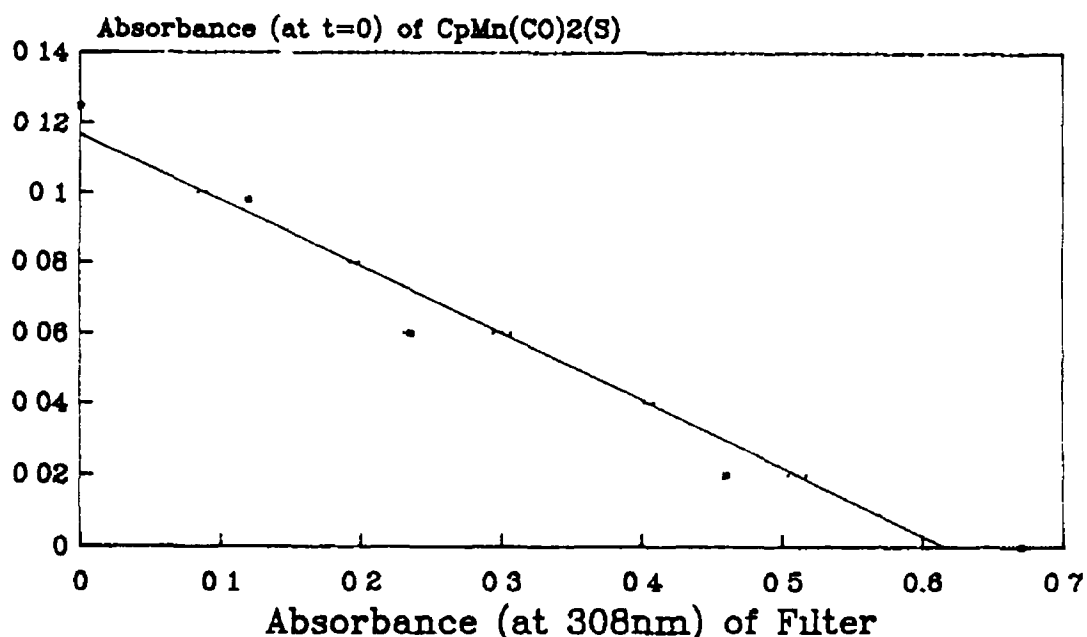
From Figure 2.2.1.3 ($I_{\text{asym}}/I_{\text{sym}}$) is found to be 1.05 $\pm$.01 and thus $\theta = 91.4 \pm 2.9^\circ$. This angle is close to those derived from crystallographic studies for the parent compound $\text{CpMn}(\text{CO})_3$ (91-94°)³⁴ and $\text{CpMn}(\text{CO})_2(\text{PPh}_3)$ (92.4°)⁶⁴ and similar to that calculated for $\text{CpMn}(\text{CO})_2$ (92.4°)²⁵ from published data on the intensity of ir bands in hydrocarbon glasses.

However the observed intensity of the symmetric stretch absorption ($\nu_{\text{CO}} = 1964\text{cm}^{-1}$) is affected by overlap with the parent tricarbonyl ($\nu_{\text{CO}} = 1947\text{cm}^{-1}$) and the calculated angle could be subject to some error, the magnitude of which is difficult to determine. It is thought however that loss of CO in this case would not significantly affect the OC-M-CO bond angle because of complexation of a solvent molecule.

2.2.1.6 A Study of the Excited State Photochemistry of CpMn(CO)_3

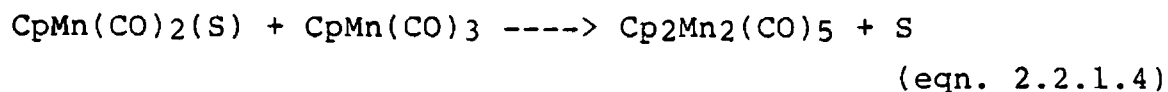
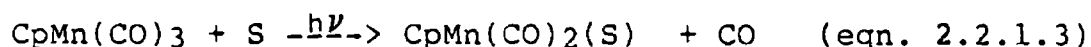
The initially observed transient has been shown to be the dicarbonyl fragment $\text{CpMn(CO)}_2(\text{S})$. Thus any excited state chemistry occurs on a faster time scale than can be measured by the detection systems used here. In order to confirm that formation of CpMn(CO)_2 was as a result of a single photon event, a study in which the intensity of the laser pulse was varied, was conducted. The absorbance of the primary species should vary linearly with the power of the laser (and in an inverse manner with the absorbance of a filter which was placed between the laser beam and the sample; see experimental section). This, as is evident from Figure 2.2.1.4, was found to be the case and the photochemical reactions observed are thus because of single photon excitation of the parent tricarbonyl.

Figure 2.2.1.4: Plot showing the variation in absorbance of $\text{CpMn(CO)}_2(\text{S})$, recorded 5 μs after the flash, with laser flash intensity.



2.2.1.7 The uv/vis Spectrum of the Second Observed Species

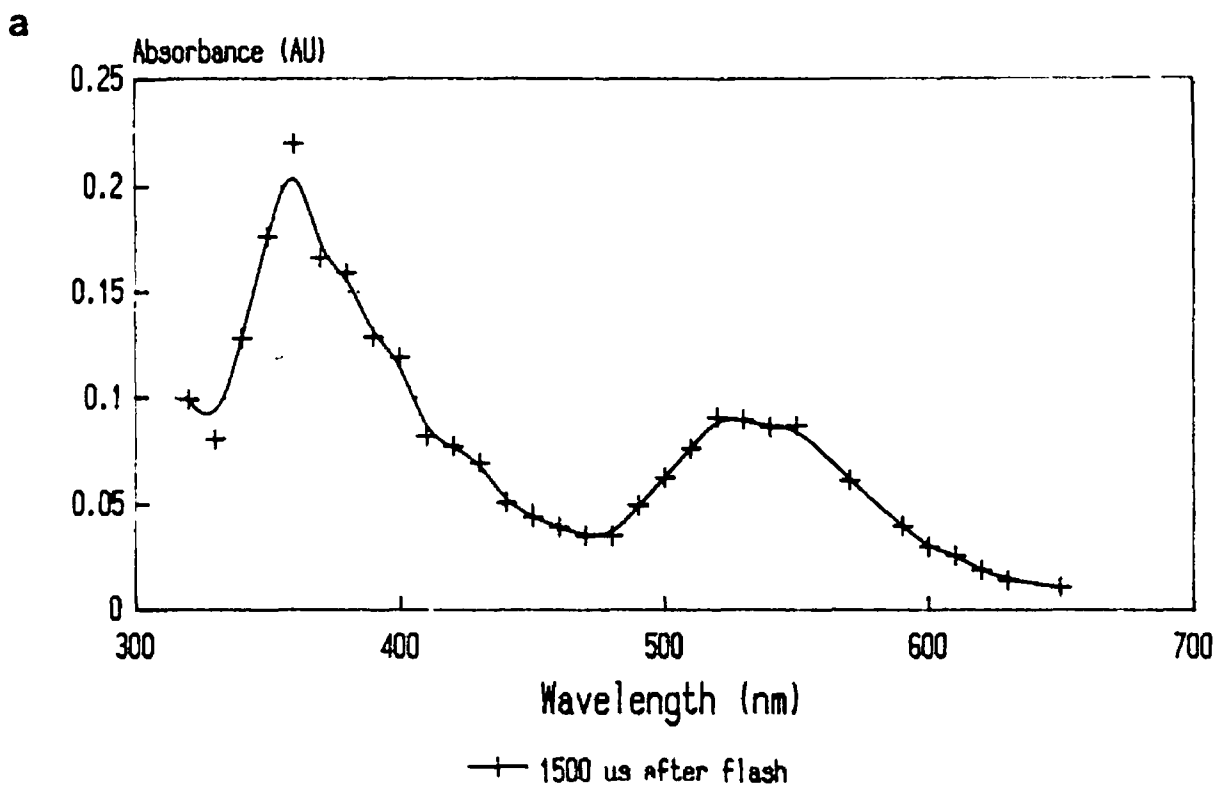
Figure 2.2.1.5 shows the transient spectrum recorded, following photolysis of CpMn(CO)_3 in alkane solvent, 500 μs after the laser flash (concentration of the CpMn(CO)_3 solution = $1 \times 10^{-3} \text{ mol dm}^{-3}$). An absorption maximum was evident in the visible region at 520nm as were two apparent maxima in the uv region at 360nm and 285nm. The uv/vis spectrum of CpMn(CO)_3 in Figure 2.2.1.5 shows an absorption maximum at 330nm. Depletion of the parent tricarbonyl upon flash photolysis is a likely cause of the apparent depression at 330nm in this Figure. The fact that this depression occurs at the uv/vis maximum absorption of the parent compound indicates this to be the case. This species is formed via the following reactions (equations 2.2.1.3 and 2.2.1.4);



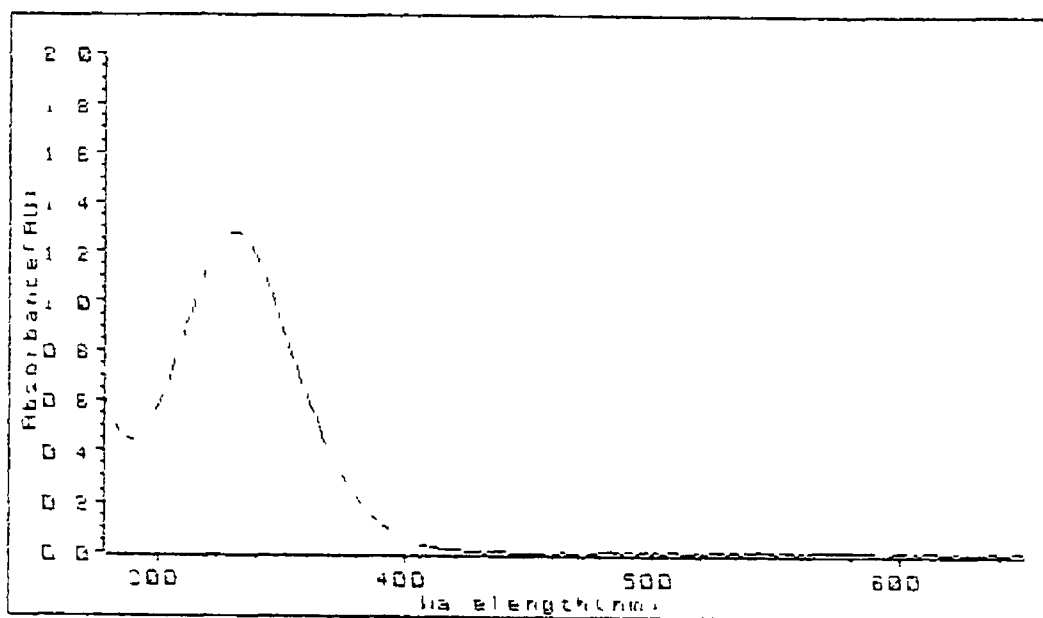
S = cyclohexane

Kinetic studies on the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ in the presence of CO and with varying concentrations of CpMn(CO)_3 , together with the measurement of its trir spectrum, enabled the characterisation of this species.

Figure 2.2.1.5: (a) uv/vis Difference spectrum observed following the flash photolysis of $\text{CpMn}(\text{CO})_3$ in cyclohexane solution. (b) uv/vis Spectrum of $\text{CpMn}(\text{CO})_3$ in cyclohexane solution.



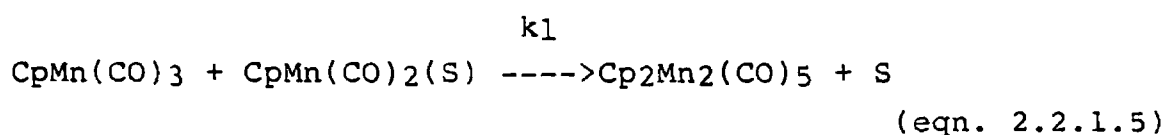
b



2.2.1.8 Kinetic Studies on the Formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

Figure 2.2.1.6 shows the the decay of the dicarbonyl species $\text{CpMn}(\text{CO})_2(\text{S})$ at 620nm, together with the grow-in of a second species, measured at 550nm. As can be seen from this Figure the rate of decay of the dicarbonyl species is the same as the rate of grow-in of the second species. Analysis of this rate data show all reactions obey first order kinetics. The most likely explanation for the observed kinetics is that the dicarbonyl is reacting with a species in solution whose concentration is so much greater than the dicarbonyl that the reaction appears first order.

The observed rate constants for the formation of this species, as the concentration of $\text{CpMn}(\text{CO})_3$ in solution was varied, are given in Table 2.2.1.6 and shown graphically in Figure 2.2.1.7. It can be seen that this rate constant increased linearly with the concentration of $\text{CpMn}(\text{CO})_3$. It was therefore concluded that the dicarbonyl molecule was reacting with the parent tricarbonyl to form the observed bridging species as in the following equation;



The rate constant for the formation of the bridging species k , is given by

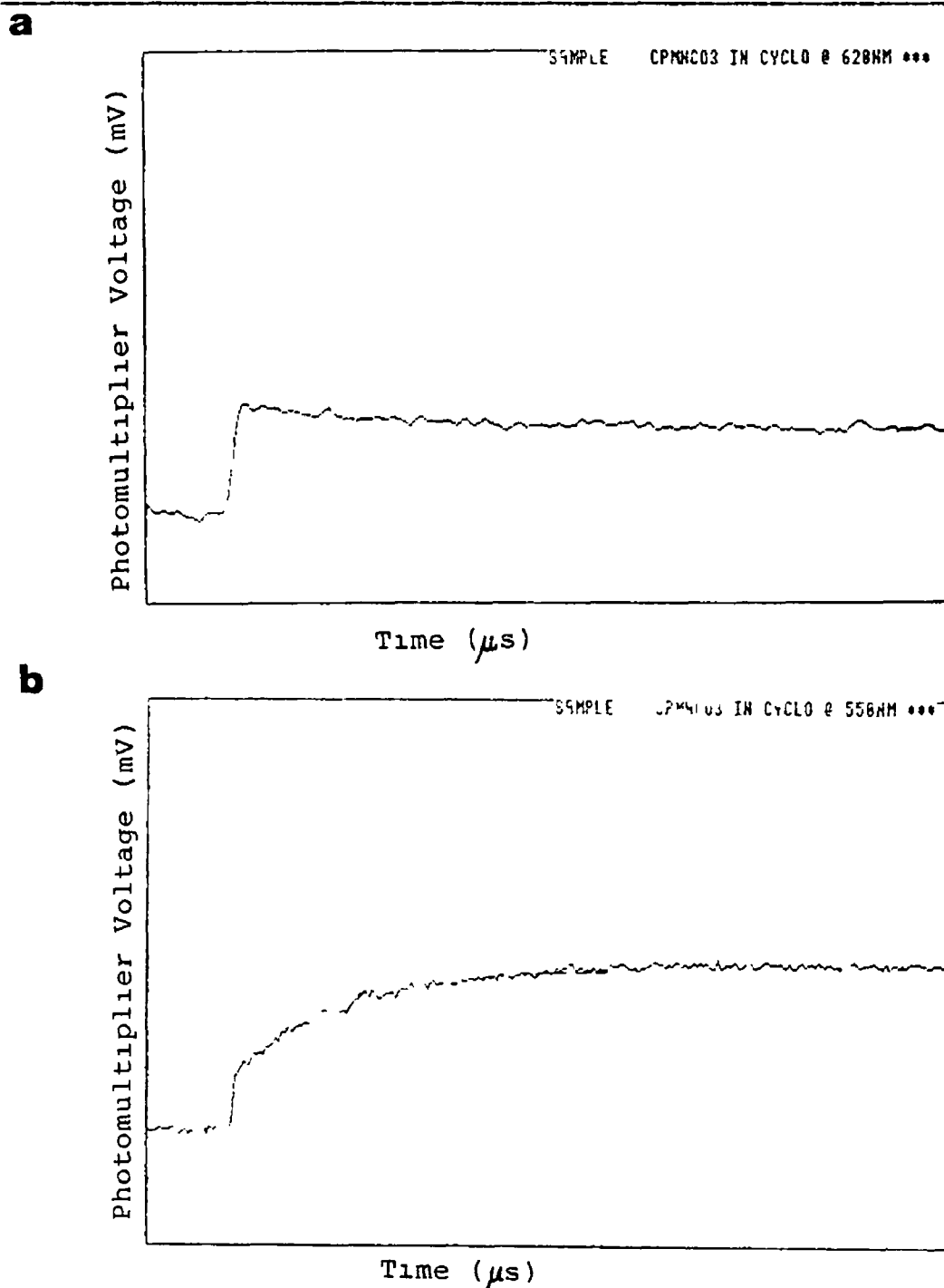
$$k = k_1[\text{CpMn}(\text{CO})_2(\text{S})][\text{CpMn}(\text{CO})_3] \quad (\text{eqn. 2.2.1.6})$$

$$\text{but as } [\text{CpMn}(\text{CO})_3] \gg [\text{CpMn}(\text{CO})_2(\text{S})]$$

$$\Rightarrow [\text{CpMn}(\text{CO})_3] \text{ is constant}$$

$$k_{\text{obs}} = k_1[\text{CpMn}(\text{CO})_2(\text{S})] \quad (\text{eqn. 2.2.1.7})$$

Figure 2.2.1.6: Kinetic traces recorded at 620nm (a) and 550nm (b) following the flash photolysis of CpMn(CO)_3 in cyclohexane solution. Horizontal scale is time in μs (after laser flash). Vertical scale is voltage output from the photomultiplier which is a measure of the absorbance of the solution.



From Figure 2.2.1.7, k_1 is found to be $1.16 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. A similar dimerisation reaction was observed upon flash photolysis of $\text{Cr}(\text{CO})_6$ in perfluoro solvents, where the photogenerated $\text{Cr}(\text{CO})_5$ fragment reacts with the parent hexacarbonyl, presumably to form $\text{Cr}_2(\text{CO})_{11}$.⁵⁸ The rate constant for this reaction is found to be ca. $4 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ in perfluoromethylcyclohexane solution. This increased reaction rate is most likely a result of the non-co-ordinating nature of the perfluoromethylcyclohexane solvent.

Table 2.2.1.6: Values for the rate constant for the formation of the dinuclear species at varying concentrations of $\text{CpMn}(\text{CO})_3$.

Concentration of $\text{CpMn}(\text{CO})_3$ (mol dm^{-3}) $\times 10^3$	k_{obs}^a $\times 10^{-3}$ (s^{-1})
0.510	1.136
0.787	1.422
0.910	1.582
1.180	2.207
1.910	2.500
2.230	2.775
2.300	3.745

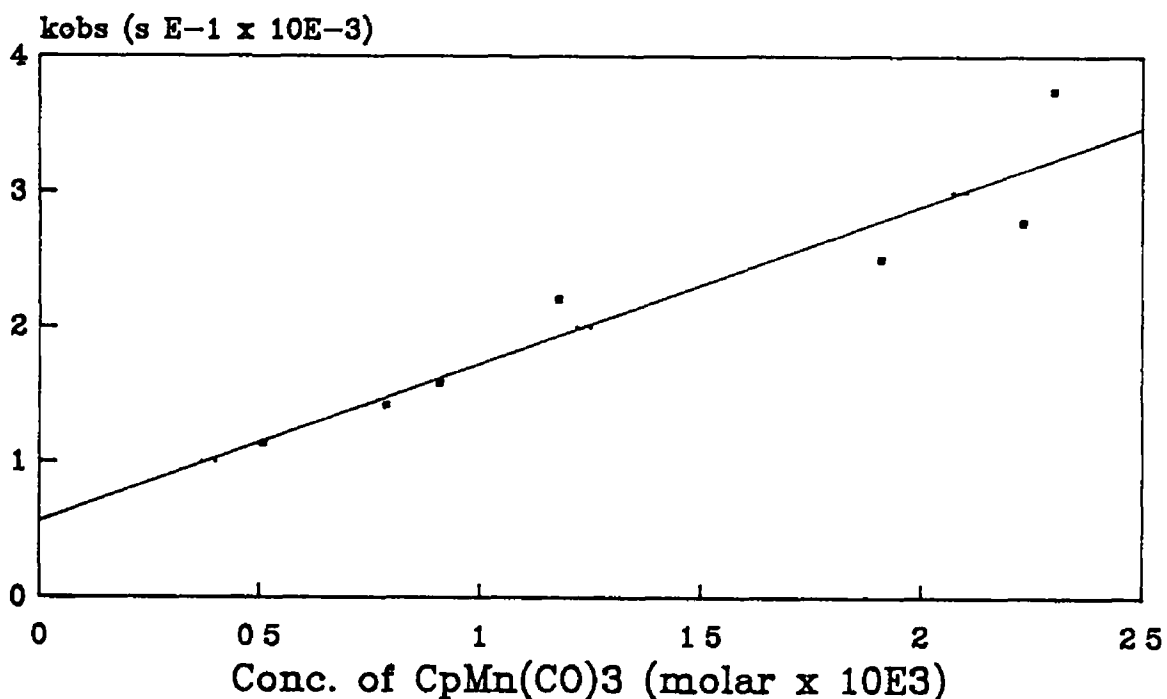
Slope = $1.165 \times 10^6 \pm 1.87 \times 10^5$

Intercept = 560 ± 340

Corr. coeff. = 0.94

k_1 for equation 2.2.1.4 is $1.16 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Figure 2.2.1.7: Plot showing the variation in k_{obs} (s^{-1}), for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$, with $\text{CpMn}(\text{CO})_3$ concentration (mol dm^{-3}).



Extrapolation of the plot in Figure 2.2.1.7, to zero concentration of CpMn(CO)_3 indicates that there is a further minor route for the decay of the $\text{CpMn(CO)}_2(\text{S})$ species. The reaction of the $\text{CpMn(CO)}_2(\text{S})$, with the photoejected CO may be partly responsible for this intercept. However, similar non-zero intercepts have been observed in the group 6 systems, where they were attributed to the reaction of the 16 valence-electron species with impurities in the solvent.⁵⁸

2.2.1.9 The Reaction of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ with CO

A series of experiments showed the effect of the presence of carbon monoxide on the yield of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ species. These results are summarised in Table 2.2.1.7. In carbon monoxide saturated cyclohexane the yield of the bridging species is reduced by 55 +/- 20%.

Table 2.2.1.7: Effect of CO saturation on the yield of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ in cyclohexane solution.

Sample conc'n mol dm ⁻³ (x 10 ³)	Absorbance (A.U. x 10 ²) recorded 850μs after the flash Wavelength in nm					
		360	390	500	550	620
2.75	CO absent	22.8	17.1	9.41	12.6	3.9
	CO present	11.13	7.96	4.24	5.14	3.14
	% difference	-50	-53	-55	-59	-10
2.2	CO absent	7.37	4.64	3.46	4.22	0.70
	CO present	4.00	2.84	1.06	1.31	0.32
	% difference	-46	-40	-69	-69	-50
2.3	CO absent	7.64	4.90	3.33	4.20	1.38
	CO present	4.07	2.46	0.91	1.37	0.47
	% difference	-47	-50	-70	-70	-66
1.9	CO absent	12.5	7.95	2.71	5.50	1.30
	CO present	5.97	4.21	1.1	1.83	0.67
	% difference	-50	-48	-59	-66	-48

a There is a 10% error in all of the above absorbance values

This is a further indication that the $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ complex is formed following the further reaction of the initially produced $\text{CpMn}(\text{CO})_2(\text{S})$ species with the parent tricarbonyl. When carbon monoxide is present this reaction is inhibited through competition for the dicarbonyl species. The presence of CO also considerably decreased the lifetime of the bridging species. In most cases the observed transient absorption appeared to return to the pre-flash value, indicating the reversibility of the system. The effect of CO on $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ will be discussed in more detail later.

2.2.1.10 The Trir Spectrum of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

The trir spectrum of the second transient observed shows 5 ν_{CO} 's bands which are shown in Figure 2.2.1.8 and summarised in Table 2.2.1.8. The most significant feature of this spectrum was the relatively weak band at 1777cm^{-1} which occurred in a region characteristic of bridging carbonyl bands. Studies with ^{13}CO enriched $\text{CpMn}(\text{CO})_3$ confirmed that the absorption rises from a single bridging group. This was achieved by calculating the CO stretching frequency of a pentacarbonyl complex with one bridging C=O group. The position and intensities of the strongest bands at 1955 and 1934cm^{-1} are probably affected by depletion of the parent tricarbonyl at 1938cm^{-1} .

Figure 2.2.1.9 shows the trir kinetic traces recorded at 1934cm^{-1} and 1895cm^{-1} which correspond to the bridging and dicarbonyl species respectively. This figure is a further indication that the bridging complex is formed from the dicarbonyl species.

Figure 2.2.1.8: trir Difference spectrum, recorded following the flash photolysis, of CpMn(CO)_3 in n-heptane solution (a) 1500 s after the flash. (b) Part of the spectrum recorded 1500 μs after the flash, obtained with a sample of CpMn(CO)_3 , 30% enriched with ^{13}C .

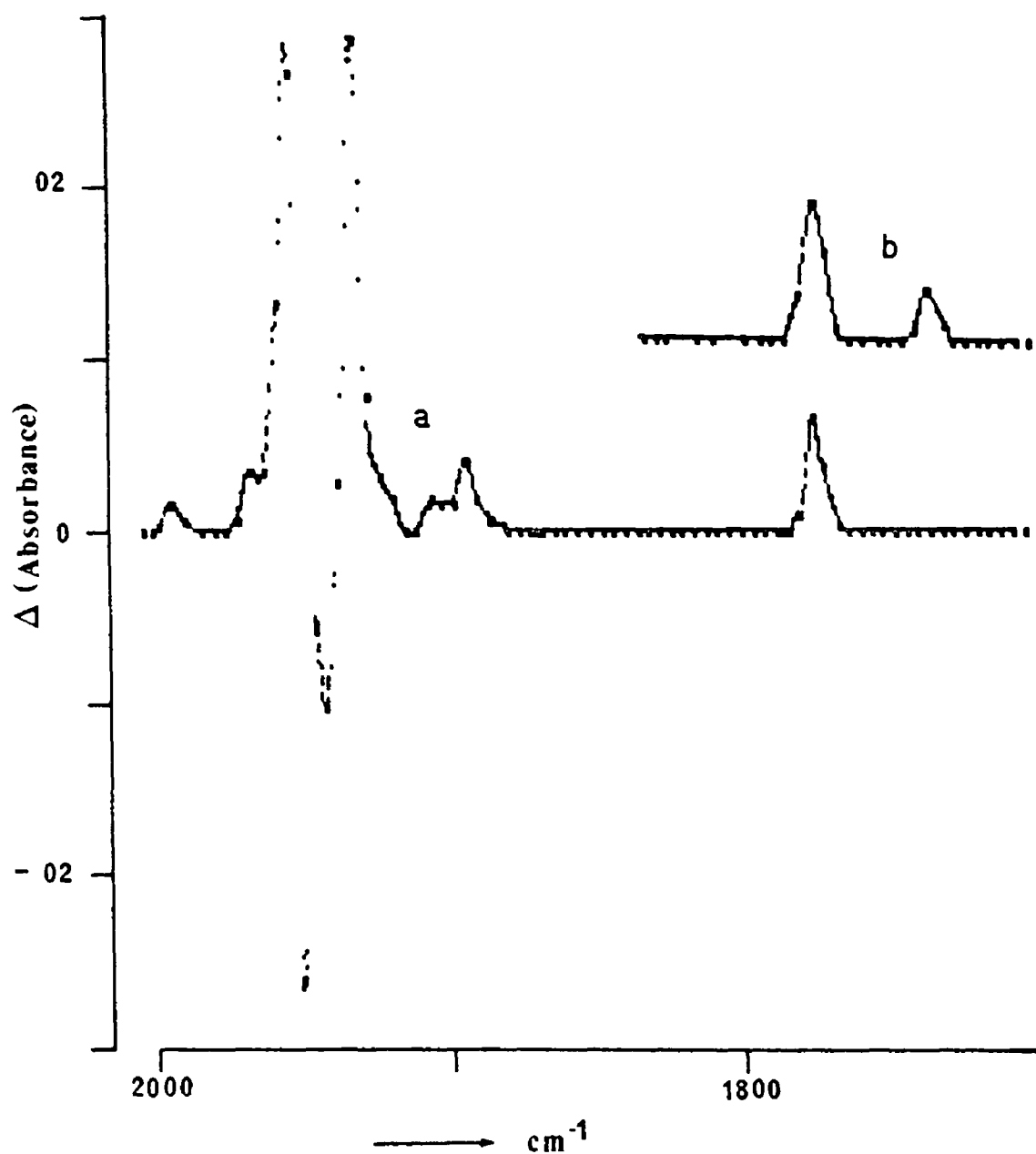


Table 2.2.1.8: Ir data for $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ and related species in hydrocarbon solution at room temperature.

Compound	ν (co bridge) cm-1		ν (co terminal) cm-1	
$\text{Cp}_2\text{Mn}_2(\text{CO})_5^{\text{a}}$	1777	1740 ^b	1993 1934 ^c	1955 ^c 1907
$[\text{CpFe}(\text{CO})_2]_2^{\text{d}}$		1792	2004	1960
$\text{Cp}_2\text{Co}_2(\text{CO})_3^{\text{e}}$		1812	1963	
$\text{Cp}_2\text{Fe}_2(\text{u-CO})_3^{\text{f}}$		1823		
$\text{Cp}_2\text{Mn}_2(\text{u-CO})_3^{\text{g}}$		1785		
$\text{C}_5\text{Me}_5\text{Re}_2(\text{CO})_5^{\text{h}}$		1714	1877 ^w 1930 ^s	1901 ^s 1971 ^w
$\text{Cp}_2\text{Re}_2(\text{CO})_5^{\text{i}}$		1740	1992 1923	1956 1904

a This work

b ^{13}CO satellite, calculated 1737cm-1

c The maxima of these bands may be affected by partial overlap with the band of $\text{CpMn}(\text{CO})_3$.

d Reference 65, cyclohexane solution.

e Reference 66, methylcyclohexane solution.

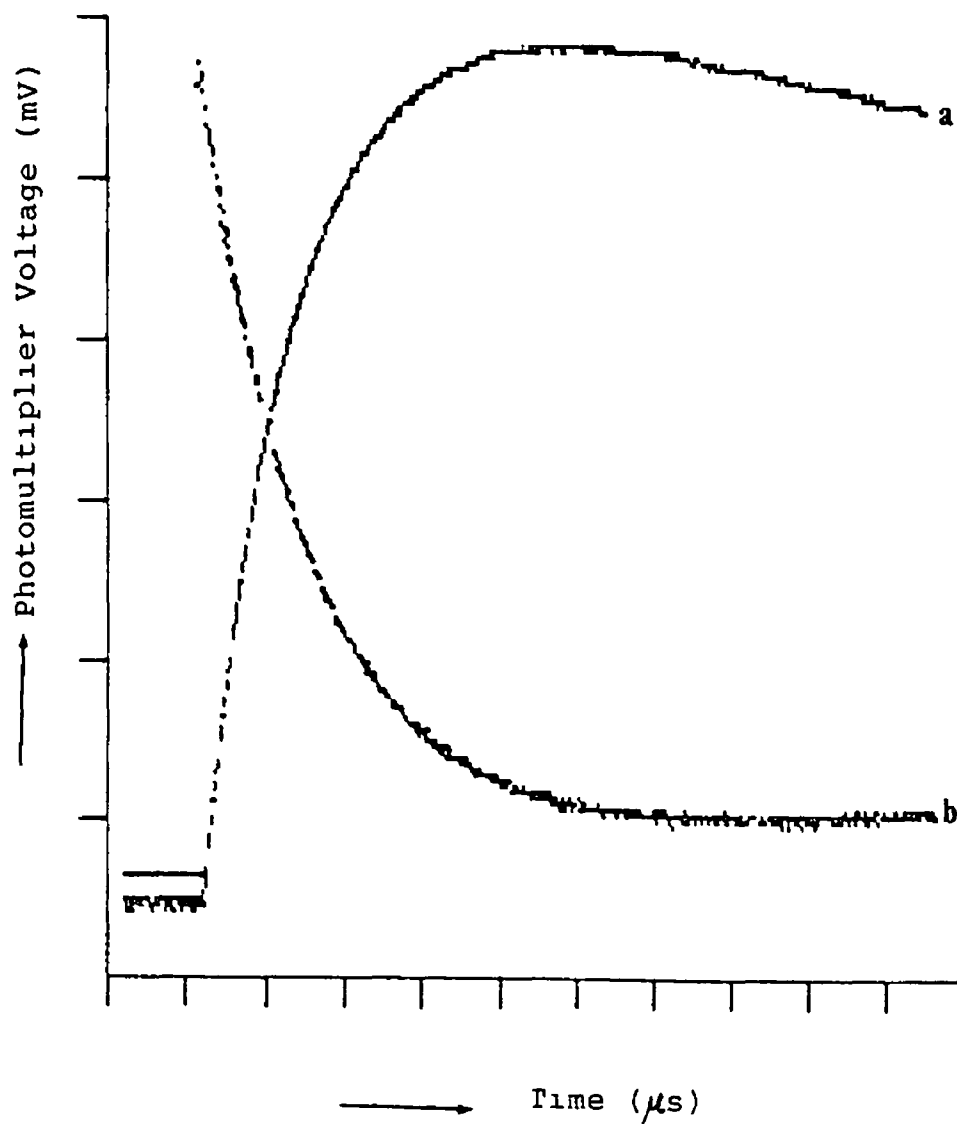
f Reference 67, trir spectrum in cyclohexane solution.

g Reference 68, n-hexane solution.

h Reference 69, cyclohexane solution.

i Reference 70, cyclohexane solution.

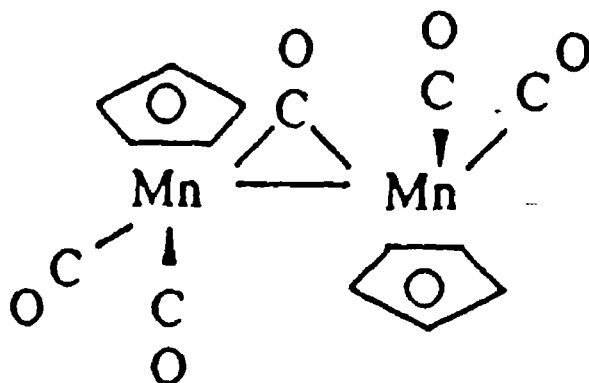
Figure 2.2.1.9: trir Kinetic traces recorded following the flash photolysis of $\text{CpMn}(\text{CO})_3$ in n-hexane(S). (a) Trace recorded at 1933cm^{-1} showing grow-in of dimeric species. (b) Trace recorded (on same timescale as (a)) at 1891cm^{-1} showing decay of $\text{CpMn}(\text{CO})_2(\text{S})$. Vertical Scale is photomultiplier voltage which is a direct measure of the sample absorbance.



2.2.1.11 A Discussion of the trir Spectrum of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

From all of the above experiments it was concluded that the second observable species was a dimetallic complex containing one C=O bridging ligand and four terminal C=O ligands. Figure 2.2.1.10 shows a possible structure for the dinuclear species. It was formed from the reaction of the photochemically produced $\text{CpMn}(\text{CO})_2(\text{S})$ complex with the parent tricarbonyl. Based on this assignation an explanation of the observed ir spectrum can be made.

Figure 2.2.1.10: Possible structure of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$.



It has been previously reported that Cp may be co-ordinated either as a monodentate or as a bridging π -olefin ligand to the complex fragment $\text{CpMn}(\text{CO})_2$ produced photolytically in solution.²¹ However in this case such a structure could not account for the presence of the bridging carbonyl ligand in the dinuclear compound, as indicated by trir spectroscopy.

The ir bands at 1777 and 1740 cm^{-1} (from the ^{13}CO enriched $\text{CpMn}(\text{CO})_3$ solution) can be conclusively assigned to a single C=O bridging ligand. Table 2.2.1.8 shows the ir data for $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ and related species in hydrocarbon solution at room temperature. A related species

$\text{Cp}_2\text{Re}_2(\text{CO})_5$ was isolated by Graham et al.⁶⁹ and its ir spectrum in hexane was recorded. Its carbonyl stretching frequencies were similar to the manganese dimer (ν_{CO} terminal = 1992, 1956, 1923 and 1904cm^{-1} , and ν_{CO} bridging = 1740cm^{-1}). These workers also isolated a pentamethylcyclopentadienyl rhenium compound $(\text{Me}_5\text{Cp})_2\text{Re}_2(\text{CO})_5$ and carried out preliminary studies on its structure.¹⁸ These preliminary structure also revealed a simple bridging carbonyl. The existence of such a compound, formed by photolysis of $\text{CpRe}(\text{CO})_3$ and $\text{Me}_5\text{CpRe}(\text{CO})_3$ in hexane does however lead credence to our assumed dinuclear structure.

The bands of the dimer recorded at 1993, 1955, 1934 and 1907cm^{-1} are characteristic of C=O terminal stretching vibrations. Because of the limited emission of the CO laser, which was used as a monitoring source in the trir experiments (see experimental section), the maximum wavenumber which can be studied is 2000cm^{-1} and therefore it is not possible to determine if there are any ir absorption bands at higher wavenumbers. In addition, overlap with parent tricarbonyl bands affects the intensity of the recorded absorption bands. However the rhenium complex discussed earlier also has 4 ν_{CO} bands in this region (Table 2.2.1.8), which could suggest that the bands at 1954 and 1934cm^{-1} are the symmetric and antisymmetric stretch of four identical terminal C=O ligands.

2.2.1.12 A Study of the Activation Parameters for the Formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

A probable structure for $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ based on its uv/vis and trir spectra is shown in Figure 2.2.1 10. This species has been shown to form via a reaction between photogenerated $\text{CpMn}(\text{CO})_2(\text{S})$ and parent $\text{CpMn}(\text{CO})_3$. A study of the activation parameters associated with the

formation of this bridging species was undertaken to determine the exact nature of the reaction. The reaction was studied by both uv/vis and trir flash photolysis. The results are summarised in Tables 2.2.1.9 and 2.2.1.10 and shown graphically in Figures 2.2.1.11 and 2.2.1.12. The formation of the bridging species has an E_a value of ca. 30 KJmol⁻¹ (as determined by uv/vis flash photolysis studies). This value is similar to that found for the low temperature oxidative addition of a variety of R₃SiH compounds to CpMn(CO)₂.²⁵ The entropy of activation $\Delta S^\ddagger$ is ca. -20 Jmol⁻¹K⁻¹ which indicates an associative rate determining step. This value is almost identical to Wrighton's $\Delta S^\ddagger$ values for the oxidative addition reaction of R₃SiH to CpMn(CO)₂.²⁵

Table 2.2.1.9: Experimental data for the calculation of energy, entropy and enthalpy of activation for the formation of Cp₂Mn₂(CO)₅ as determined by uv/vis flash photolysis.

Sample conc.'n moldm ⁻³ (x 10 ³)	1/K x10 ³	Ln(R _b)	Ln(R _t C)
	3.527	13.91	8.26
	3.472	14.07	8.4
	3.419	14.31	8.63
1.738	3.361	14.62	9.11
	3.306	14.82	9.25
	3.247	14.98	9.25
	3.205	15.13	9.38
	3.534	13.93	8.28

=> $E_a = 32.0 \pm 1.2$ KJmol⁻¹, $\Delta H^\ddagger = 30.7 \pm 3.1$ KJmol⁻¹, and $\Delta S^\ddagger = -20.4 \pm 20$ Jmol⁻¹K⁻¹.

Table 2.2.1.9:cont'd

Sample conc.'n mol dm ⁻³ (x 10 ³)	1/K x10 ³	Ln(R)	Ln(R _t)
1.89	3.527	14.17	8.52
	3.472	14.52	8.94
	3.410	14.80	9.12
	3.361	15.01	9.32
	3.311	15.18	9.47
	3.247	15.35	9.62
	3.205	15.48	9.74
	3.390	14.68	9.00

=> E_a = 33.2 +/- 2.5 KJmol⁻¹, ΔH[‡] = 29.9 +/- 2.9 KJmol⁻¹, and ΔS[‡] = -20.4 +/- 20 Jmol⁻¹K⁻¹.

1.12	3.390	14.68	9.00
	3.240	15.25	9.52
	3.268	15.11	9.39
	3.300	14.91	9.19
	3.331	14.81	9.11
	3.365	14.7	9.01
	3.460	14.27	9.60

=> E_a = 34.8 +/- 2.4 KJmol⁻¹, ΔH[‡] = 32.3 +/- 2.5 KJmol⁻¹ and ΔS[‡] = -13.7 +/- 20 Jmol⁻¹K⁻¹

a All of the below values are averages of at least two separate measurements.

b R=k_{obs}/(conc'n of CpMn(CO)₃) (dm³mol⁻¹s⁻¹)

c R_t=(k_{obs}/(conc'n of CpMn(CO)₃))/T (dm³mol⁻¹s⁻¹K⁻¹)

Table 2.2.1.10: Experimental data^a for the calculation of energy, enthalpy and entropy of activation for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$, as determined by trir flash photolysis.

Sample Conc'n mol dm ⁻³ (x10 ⁻⁴)	1/K x10 ³	Ln(R)	Ln(R _t)
0.986	3.39	15.00	9.31
	3.32	15.29	9.57
	3.27	15.66	9.94
	3.22	15.81	10.07
	3.18	16.18	10.42
	3.13	16.53	10.76
	3.08	16.83	11.16
	3.03	17.04	11.24
	3.18	16.13	10.38

=> $E_a = 49.4 \pm 1.8 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 48.0 \pm 2.4 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = 41 \pm 15 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

a All of the above values are averages of at least two separate measurements.

b R and R_t have the same meaning as before

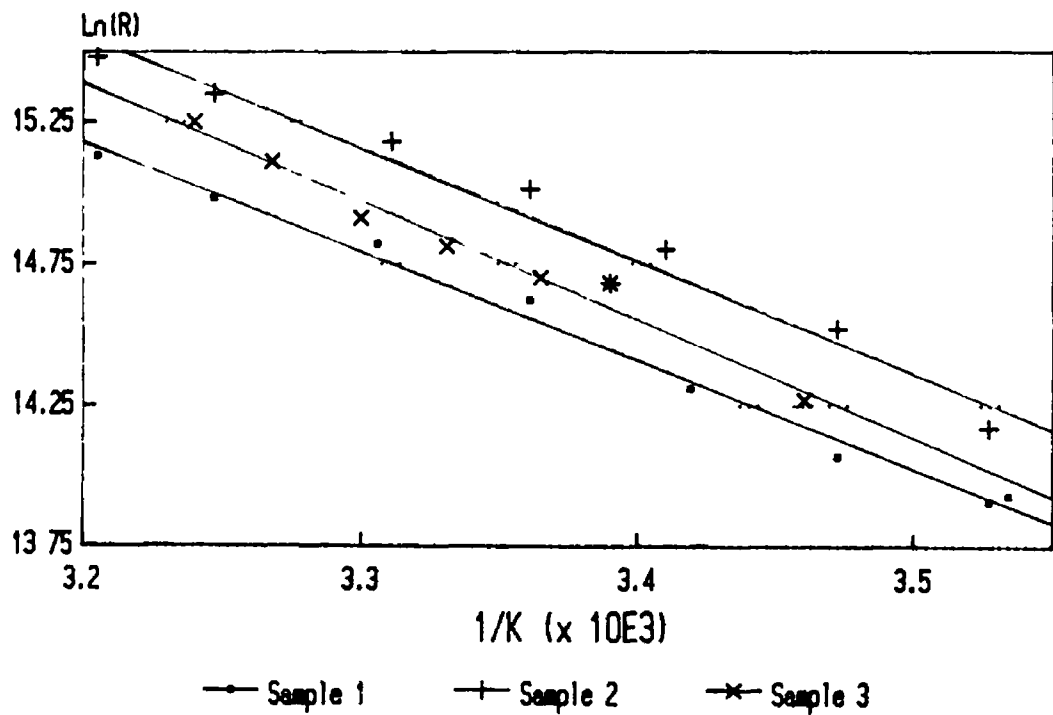
Table 2.2.1.10:cont'd

Sample Conc'n mol dm ⁻³ (x10 ⁻⁴)	1/K x10 ³	Ln(R)	Ln(R _t)
	3.38	14.76	9.07
	3.30	15.16	9.45
	3.25	15.61	9.88
	3.20	15.77	10.03
1.33	3.11	15.89	10.12
	3.08	15.89	10.12
	3.08	16.25	10.47
	3.03	16.53	10.73

=> $E_a = 36.4 \pm 4.5 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 33.9 \pm 4.4 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -6.6 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Figure 2.2.1.11: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ as determined by uv/vis flash photolysis system.

(a)



(b)

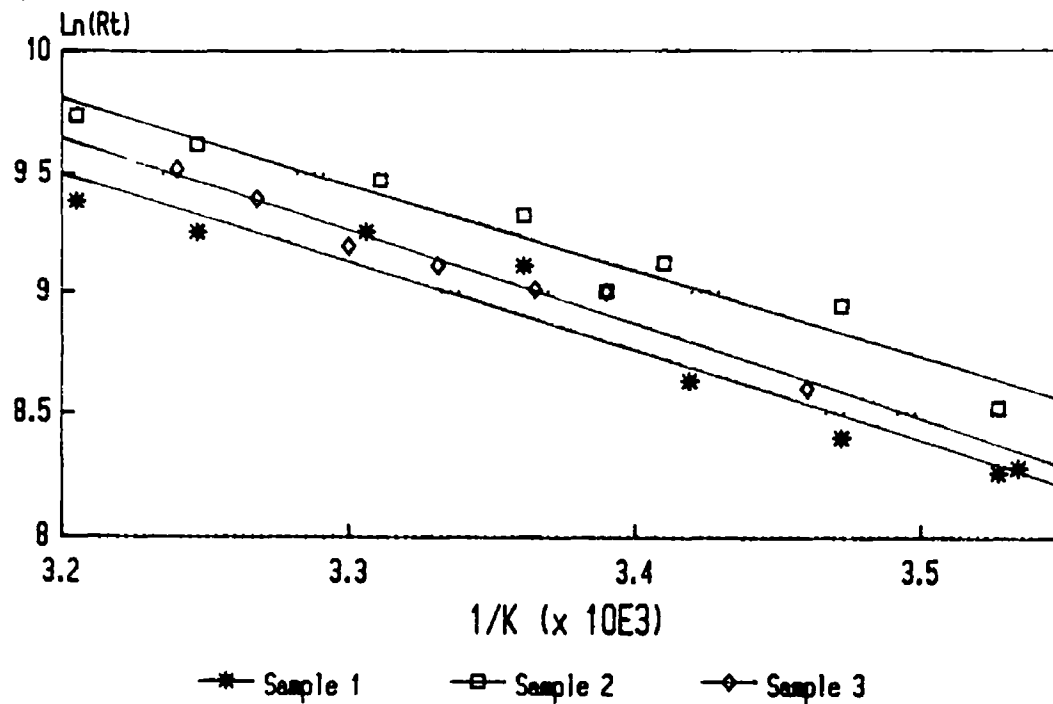
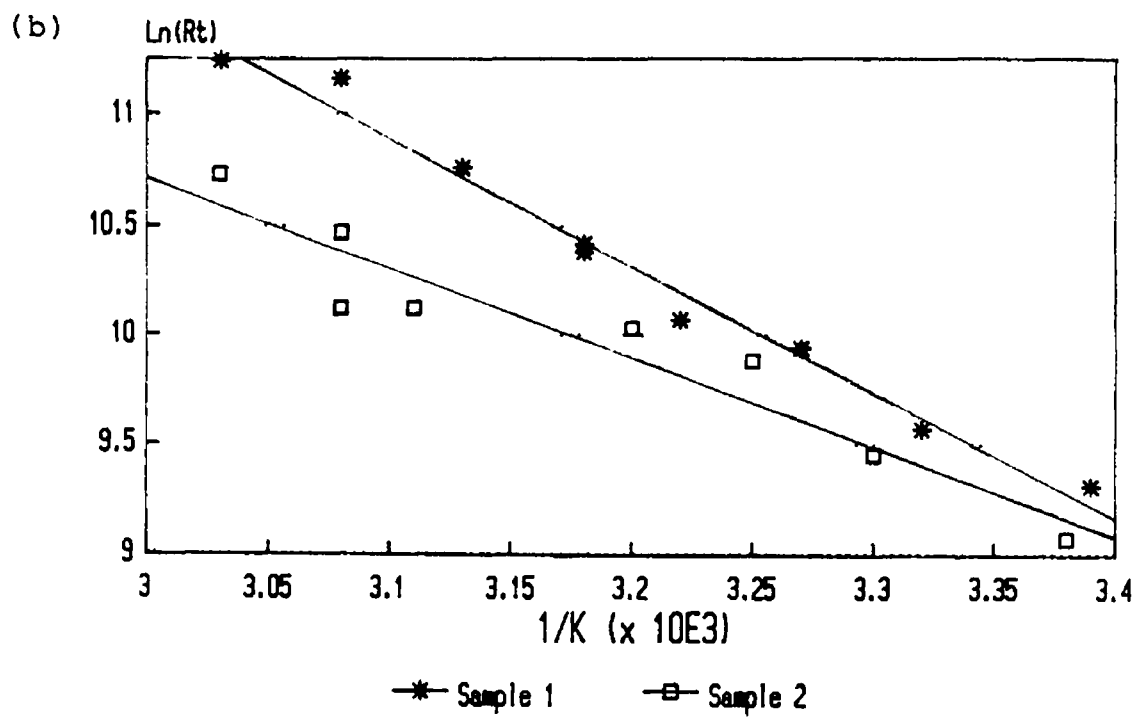
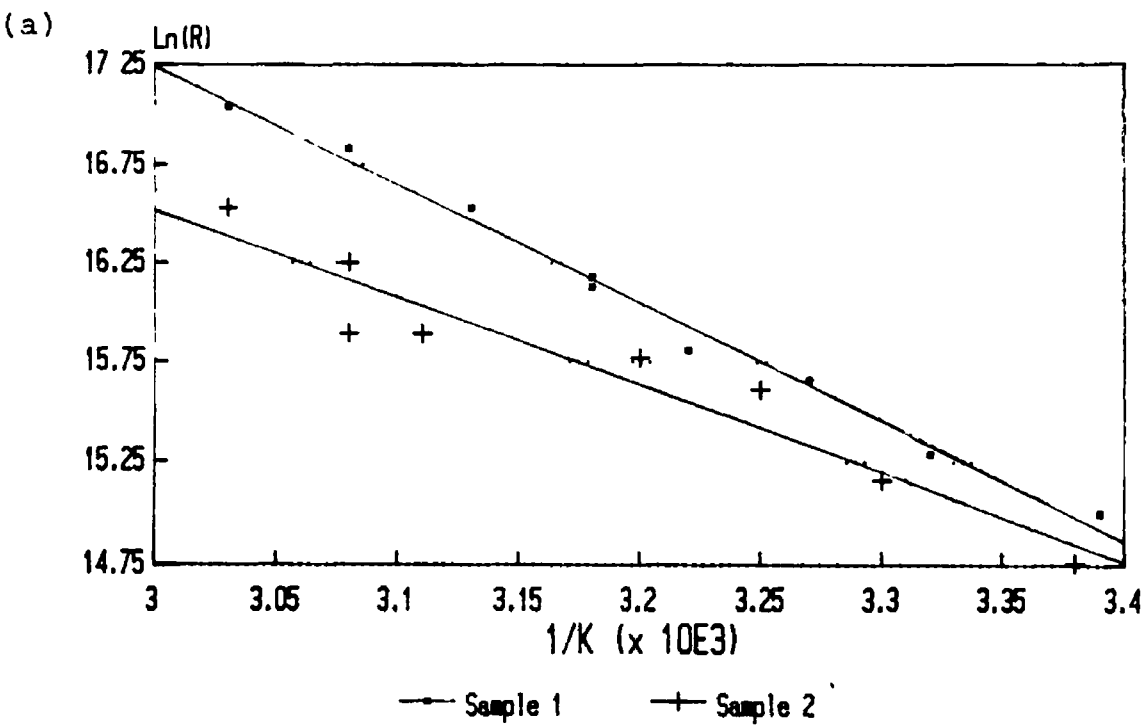


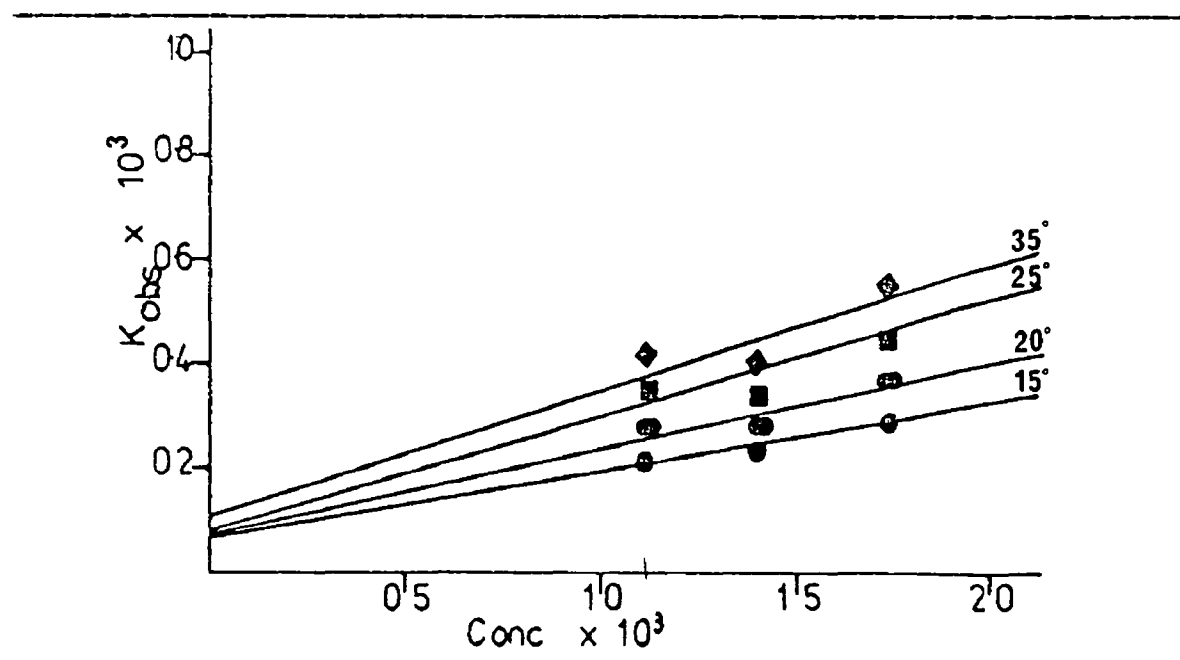
Figure 2.2.1.12: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$, as determined by trir flash photolysis system.



As can be seen from Tables 2.2.1.9 and 2.2.1.10 a significant difference exists between the activation energy for the dimer formation as determined by uv/vis and trir flash photolysis studies. The rate constant for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ is greater in n-heptane than in cyclohexane solution, suggesting that n-heptane may co-ordinate more weakly to the metal centres. Thus the higher activation energy cannot be attributed to the greater interaction of $\text{CpMn}(\text{CO})_2$ fragment with the solvent. However the most likely explanation for these results is the following;

the concentration used to determine the thermodynamic parameters was considerably lower in the trir study, and thus the side reactions in this system (i.e. that which gives rise to the non-zero intercept in Figure 2.2.1.7) were of greater significance. The effect of this side reaction was studied and the results are plotted in Figure 2.2.1.13.

Figure 2.2.1.13: Plot showing the effect of temperature on k_{obs} (s^{-1}), for the formation of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$, at varying concentrations of $\text{CpMn}(\text{CO})_3$ (mol dm^{-3}).



This plot indicates that the side reaction does not contribute to the observed rate constant at elevated temperatures (in uv/vis studies).

2.2.1.13 A Study of the Rate of Reaction of $\text{CpMn(CO)}_2(\text{S})$ With Various Ligands

A study of the reactivity of $\text{CpMn(CO)}_2(\text{S})$ towards nucleophilic ligands was undertaken. The bimolecular rate constant for the reaction of CpMn(CO)_2 with a variety of ligands (4-vinylpyridine, triphenylphosphine, trimethylphosphite, 4-picoline, hexene, CO and N_2) were measured and the results detailed in Table 2.2.1.11.

Table 2.2.1.11: Rates of reaction of $\text{CpMn(CO)}_2(\text{S})$ with ligands(X).

Ligand	Rate constant for the formation of $\text{CpMn(CO)}_2(\text{X})$ $\text{dm}^3\text{mol}^{-1}\text{s}^{-1} (\times 10^{-6})$
CpMn(CO)_3	1.16
PPh_3	5.04
N_2	3.72
CO	0.32
4-vinylpyridine	3.40
1-hexene	0.30
4-picoline	30.84
P(OMe)_3	7.10

In general the CpMn(CO)_2 fragment reacts slower with the above ligands than does the Cr(CO)_5 fragment.^{16,54} The rate constants are generally an order of magnitude smaller. As has already been stated this apparent stability of the solvated dicarbonyl fragment (in comparison to the chromium pentacarbonyl species) is probably because of the presence of the cyclopentadienyl ligand. The rate of reaction of $\text{CpMn(CO)}_2(\text{S})$ with 4-picoline is an order of magnitude greater than for all the other ligands studied here. These differences in reaction rates might be attributed to steric hindrance (as the rate constant for the reaction of 4-vinylpyridine is less than that for 4-picoline)

It can be seen from the above table that the rate of reaction of 4-vinylpyridine is between that of 1-hexene and 4-picoline. One could not conclude from these rate data whether the 4-vinylpyridine molecule co-ordinated via the vinyl or pyridyl moiety. For this reason the transient spectra of $\text{CpMn(CO)}_2(4\text{-vinylpyridine})$ and $\text{CpMn(CO)}_2(1\text{-hexene})$ were recorded (at a time interval equivalent to when the product was fully formed). These spectra are given in Figure 2.2.1.14 and the spectrum of $\text{CpMn(CO)}_2(\text{pyridine})$ is given in Figure 2.2.1.15.²¹

The most interesting feature of these spectra is the similarity between Figure 2.2.1.14(b) and Figure 2.2.1.15. This similarity would suggest that the 4-vinylpyridine co-ordinates via the nitrogen to the available co-ordination site. Substitution of CO by N donor ligands leads to a lowering of the energy of absorptions in the uv/vis region. The low energy bands in such complexes have been characterised by Giordani and Wrighton¹⁹ who have proposed that pyridine derivatives of metal carbonyls should generally exhibit low energy charge transfer (CT) absorptions owing to the low oxidation state of the metal. The $\text{CpMn(CO)}_2(\text{X})$ complexes were viewed as pseudo C_{4v} species. The lowest energy absorption in such complexes is intense and very dependent on the substituents on the cyclopentadienyl ring. These absorptions have large solvent

dependences typical of organometallic metal to ligand charge transfer (MLCT) absorptions. The solvent dependency of the spectra of $\text{CpMn}(\text{CO})_2(\text{X})$ complexes was not investigated in these studies but it is thought likely that the observed peaks in the visible region in Figures 2.2.1.14 and 2.2.1.15 are because of $\text{M} \rightarrow \pi^*$ (pyridine) CT plus LF transitions within the molecule.

Figure 2.2.1.14: uv/vis Difference spectra of $\text{CpMn}(\text{CO})_2(1\text{-hexene})$ (a) and $\text{CpMn}(\text{CO})_2(4\text{-vinylpyridine})$ (b).

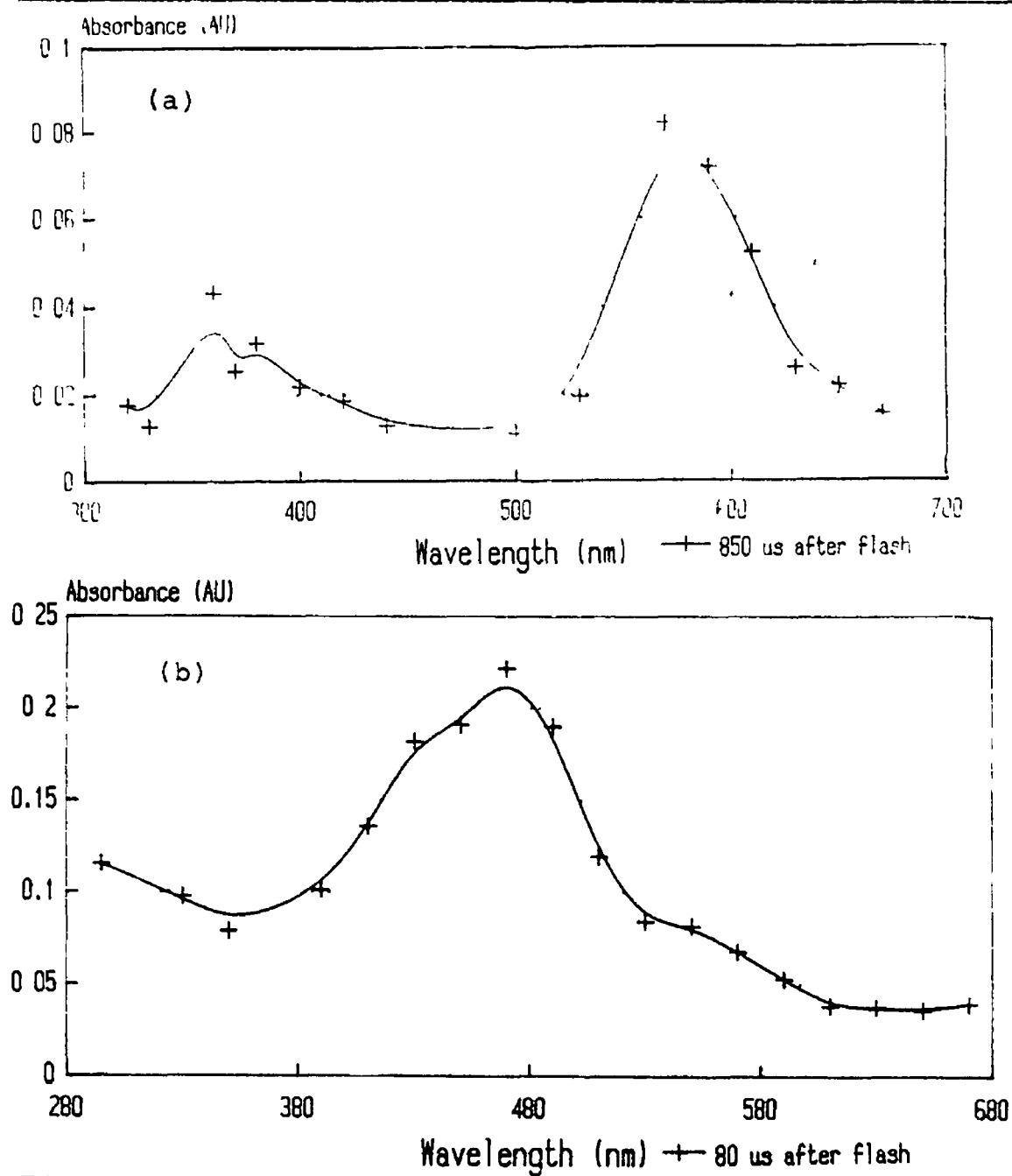
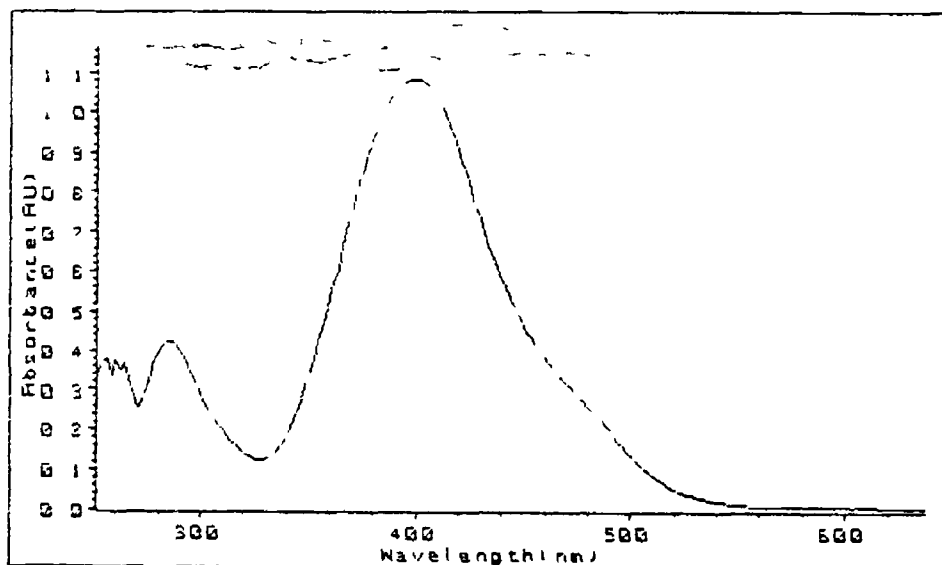


Figure 2.2.1.15: uv/vis Spectrum of
 CpMn(CO)₂(pyridine).



2.2.1.14 A Study of the Activation Parameters for the
 Reaction of CpMn(CO)₂(S) With Various Ligands

The thermodynamic parameters determined in these sets of experiments are given in Tables 2.2.1.12, 2.2.1.13, 2.2.1.14 and 2.2.1.15 and shown graphically in Figures 2.2.1.16, 2.2.1.17, 2.2.1.18 and 2.2.1.19. These data suggest that there are no significant differences in the activation energies for the formation of CpMn(CO)₂(4-picoline), CpMn(CO)₂(4-vinylpyridine), CpMn(CO)₂(1-hexene), CpMn(CO)₂(PPh₃), and CpMn(CO)₂CpMn(CO)₃ from CpMn(CO)₂(S) and the appropriate ligand. This value was typically 30 $\pm$ 4 kJmol⁻¹s⁻¹. The values obtained are again very similar to the value reported for low temperature oxidative addition of a range of R₃SiH compounds to CpMn(CO)₂²⁵

Table 2.2.1.12: Experimental data for the calculation of the energy, enthalpy and entropy of activation for the formation of $\text{CpMn(CO)}_2(4\text{-vinylpyridine})$ as determined by uv/vis flash photolysis. Concentration of 4-vinylpyridine was $7.42 \times 10^{-3} \text{ moldm}^{-3}$. Concentration of CpMn(CO)_3 was $1.03 \times 10^{-3} \text{ moldm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.54	14.51	8.86
3.47	14.72	9.05
3.43	14.97	9.30
3.37	15.11	9.42
3.31	15.29	9.58
3.30	15.34	9.63
3.26	15.54	9.81
3.21	15.67	9.93
3.47	14.75	9.09

<u>Arrhenius Plot.</u>	<u>Eyring Plot.</u>
Slope = 3542 ± 97	Slope = 3258 ± 103
Int. = 27.045 ± 0.034	Int. = 20.394 ± 3.24
Corr. coeff. = 0.997	Corr. coeff. = 0.996
$\Rightarrow E_a = 29.4 \pm 0.8 \text{ KJmol}^{-1}, \Delta H^\ddagger = 27.1 \pm 0.9 \text{ KJmol}^{-1}, \text{ and } \Delta S^\ddagger = 27.9 \pm 14 \text{ Jmol}^{-1}\text{K}^{-1}$	

Table 2.2.1.13: Experimental data for the calculation of energy, enthalpy and entropy of activation for the formation of $\text{CpMn(CO)}_2(1\text{-hexene})$ as determined by uv/vis system. Concentration of 1-hexene was $12.03 \times 10^{-3} \text{ mol dm}^{-3}$. Concentration of CpMn(CO)_3 was $7.54 \times 10^{-4} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.52	12.33	6.68
3.54	12.27	6.62
3.48	12.52	6.86
3.41	12.60	6.92
3.36	12.79	7.10
3.31	13.11	7.40
3.26	13.24	7.51
3.21	13.55	7.81
3.51	12.29	6.64

Arrhenius Plot.

Slope = 3738 ± 234

Int. = $25.45 \pm .08$

Corr. coeff. = 0.987

Eyring Plot.

Slope = 3449 ± 228

Int. = $18.78 \pm .08$

Corr. coeff. = 0.985

=> $E_a = 31.1 \pm 2 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 28.7 \pm 2 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -41.3 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.1.14: Experimental data for the determination of energy, enthalpy and entropy of activation for the reaction of $\text{CpMn(CO)}_2(\text{S})$ with PPh_3 (as determined by trir flash photolysis). Concentration of PPh_3 was $1.33 \times 10^{-3} \text{ mol dm}^{-3}$. Concentration of CpMn(CO)_3 was $1.02 \times 10^{-3} \text{ mol dm}^{-3}$

$1/K$ $\times 10^3$	Ln(R)	$\text{Ln(R}_t\text{)}$
3.37	16.58	10.89
3.30	16.87	11.15
3.26	17.06	11.33
3.22	17.27	11.54
3.18	17.49	11.74
3.12	17.64	11.87
3.07	17.91	12.13
3.02	18.07	12.27

Arrhenius Plot.

Slope = 4317 ± 139

Int. = $31.14 \pm .44$

Corr. coeff. = 0.997

Eyring Plot.

Slope = 4019 ± 140

Int. = $24.4 \pm .45$

Corr. coeff. = 0.996

$\Rightarrow E_a = 35.9 \pm 1.1 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 33.4 \pm 1.1 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = \pm 5.4 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.1.15: Experimental data for the determination of the energy, entropy and enthalpy of activation for the formation of $\text{CpMn(CO)}_2(\text{Picoline})$.

(a) Concentration of $\text{CpMn(CO)}_3 = 1.65 \times 10^{-3} \text{ moldm}^{-3}$.
 Concentration of 4-picoline = $2 \times 10^{-3} \text{ moldm}^{-3}$

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.52	16.82	11.17
3.46	17.00	11.34
3.40	17.24	11.56
3.34	17.47	11.77
3.29	17.64	11.92
3.24	17.89	12.16
3.19	18.14	12 40

Arrhenius Plot.

Slope = 3975 ± 138

Int. = $30.77 \pm .04$

Corr. coeff. = 0.997

Eyring Plot.

Slope = 3682 ± 142

Int. = $24.09 \pm .04$

Corr. coeff. = 0.996

$\Rightarrow E_a = 33.0 \pm 1.1 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 30.6 \pm 1.2 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = 2.82 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.1.15:cont'd

(b) Concentration of $\text{CpMn(CO)}_3 = 1.58 \times 10^{-3} \text{ mol dm}^{-3}$.
 Concentration of 4-picoline = $8.04 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.39	17.84	12.15
3.53	17.35	11.71
3.47	17.63	11.96
3.41	17.72	12.04
3.36	17.99	12.29
3.30	18.17	12.45
3.26	18.29	12.56

Arrhenius Plot.

Slope = 3442 ± 178

Int. = 29.56 ± 0.04

Corr. coeff. = 0.994

Eyring Plot.

Slope = 3117 ± 158

Int. = 22.73 ± 0.04

Corr. coeff. = 0.990

=> $E_a = 28.6 \pm 1.5 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 25.9 \pm 2 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -8.48 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Figure 2.2.1.16: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CpMn(CO)}_2(4\text{-vinylpyridine})$ as measured by uv/vis flash photolysis system.

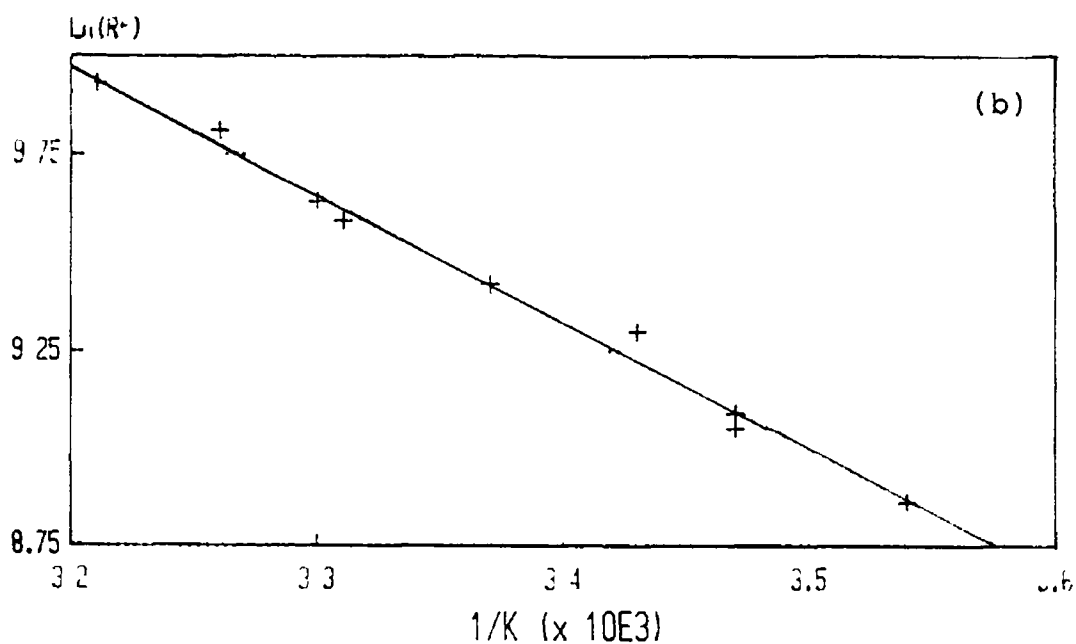
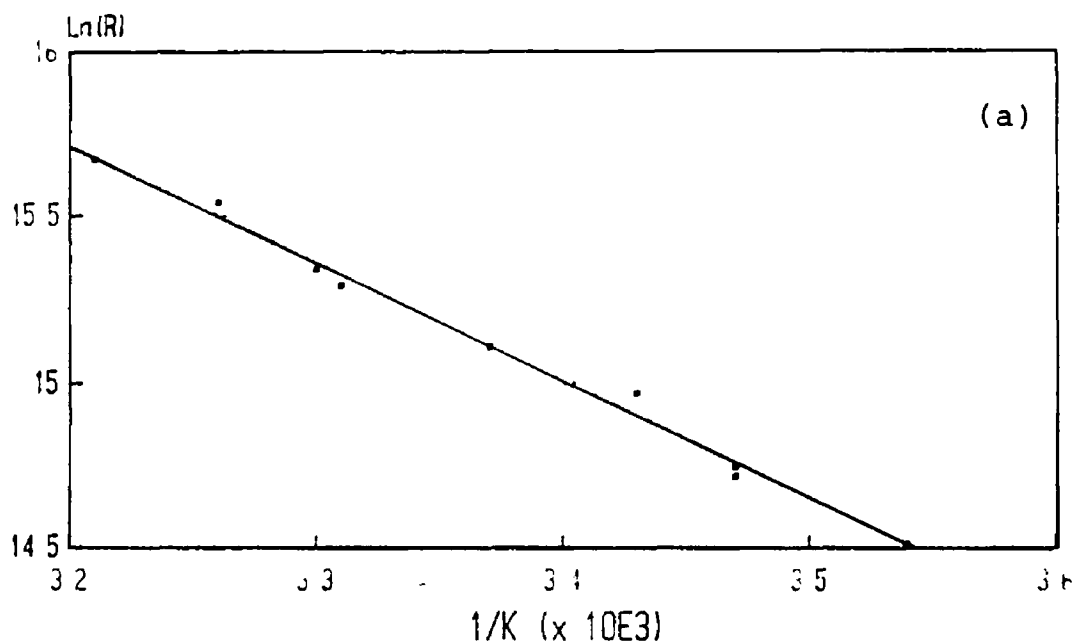


Figure 2.2.1.17: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CpMn(CO)}_2(1\text{-hexene})$ as measured by uv/vis flash photolysis system.

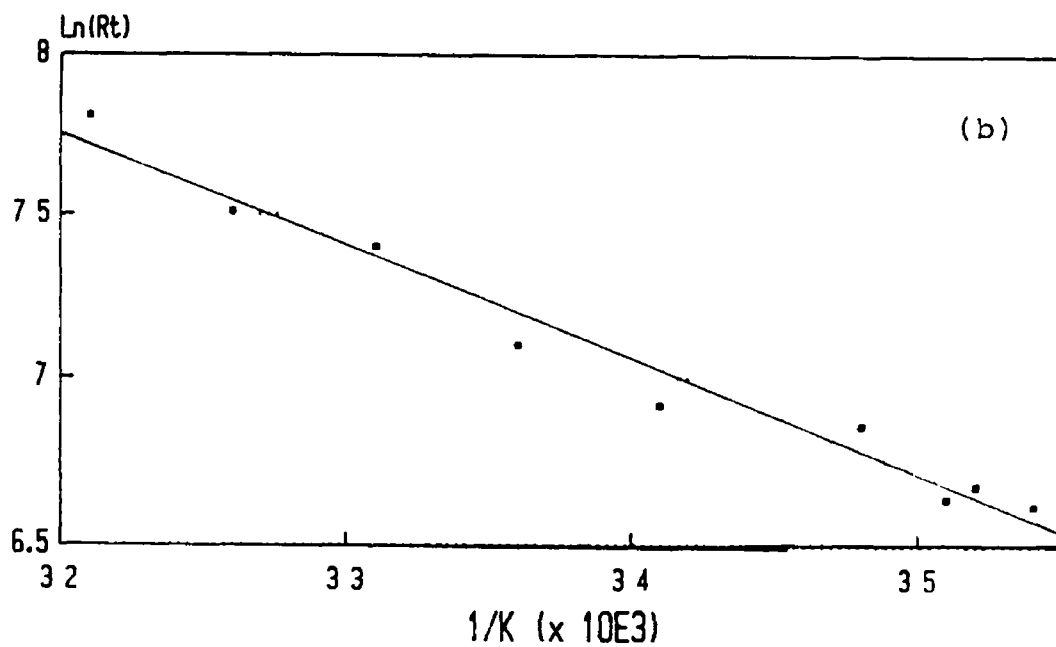
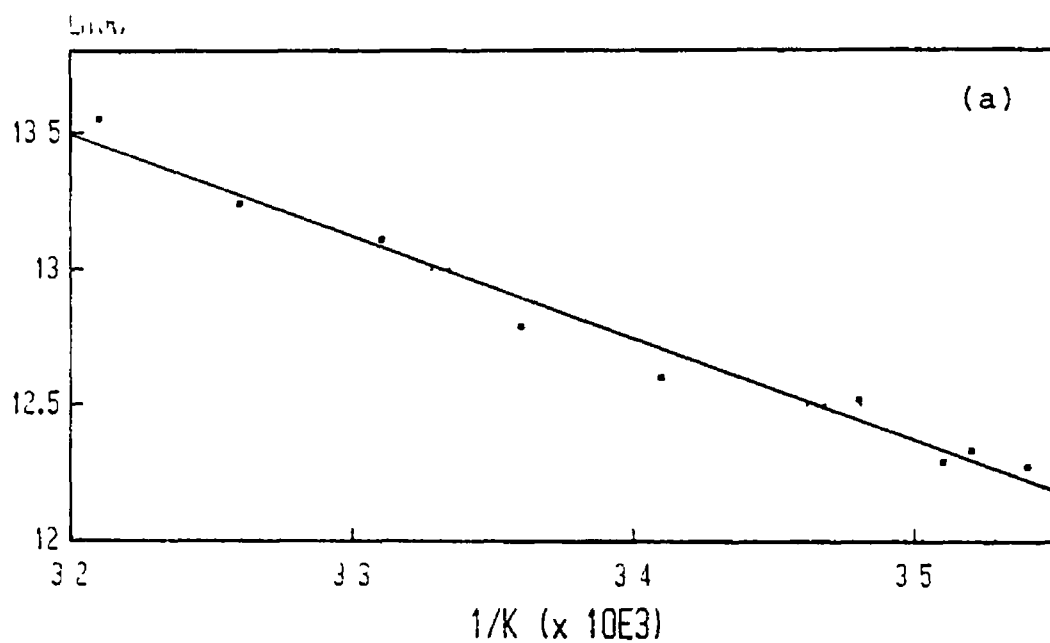


Figure 2.2.1.18: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CpMn(CO)}_2(\text{PPh}_3)$ as measured by trir flash photolysis system.

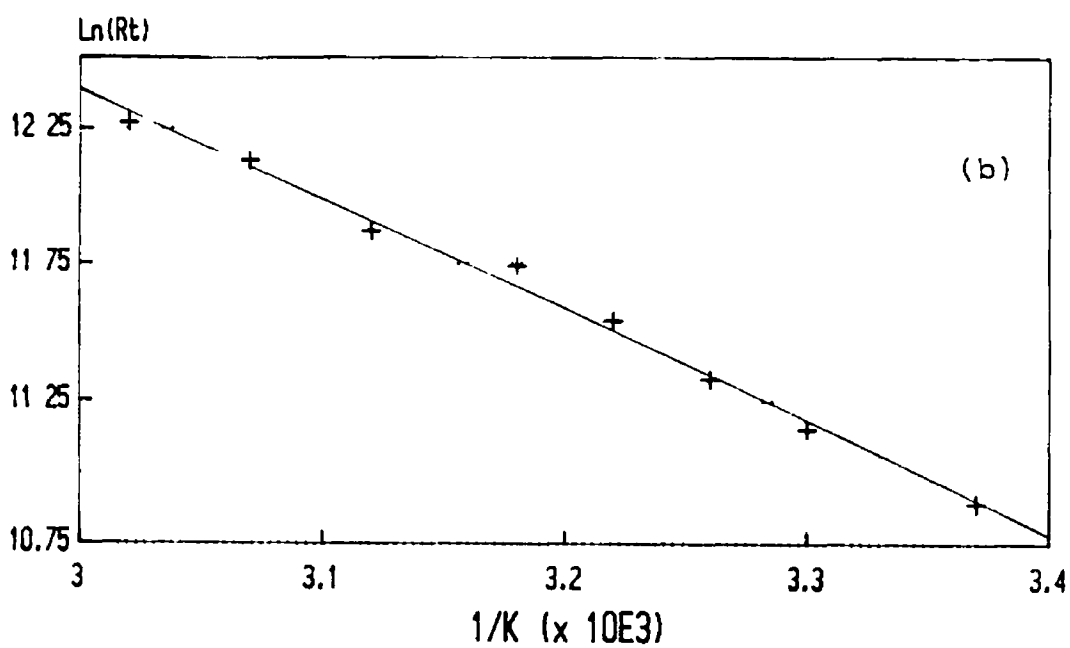
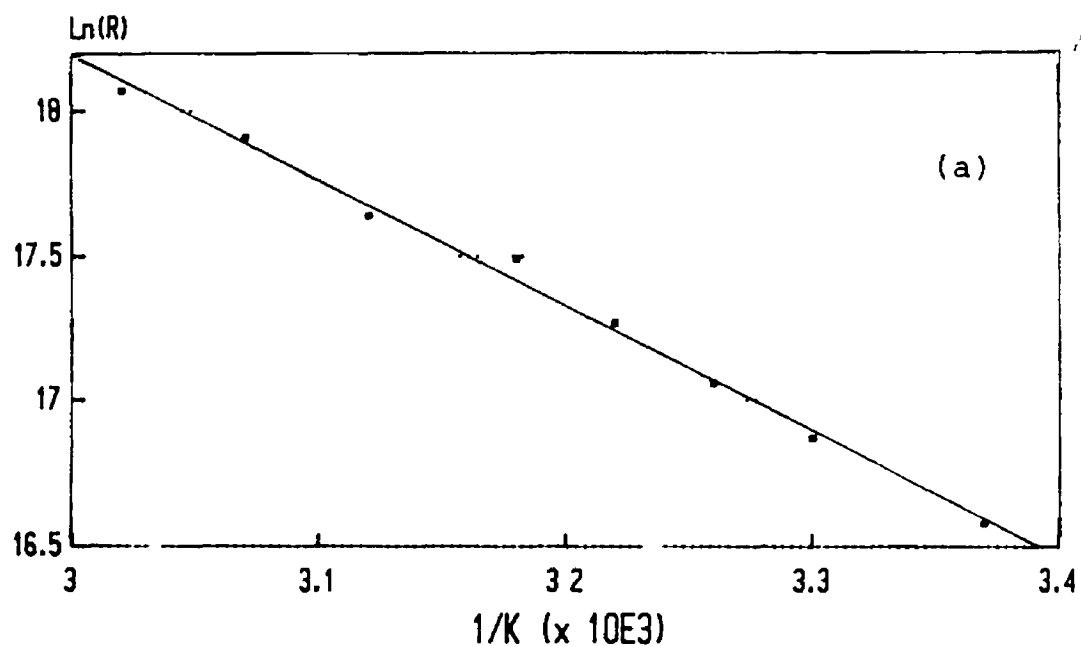


Figure 2.2.1.19: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CpMn(CO)}_2(4\text{-picoline})$ as measured by uv/vis flash photolysis system.

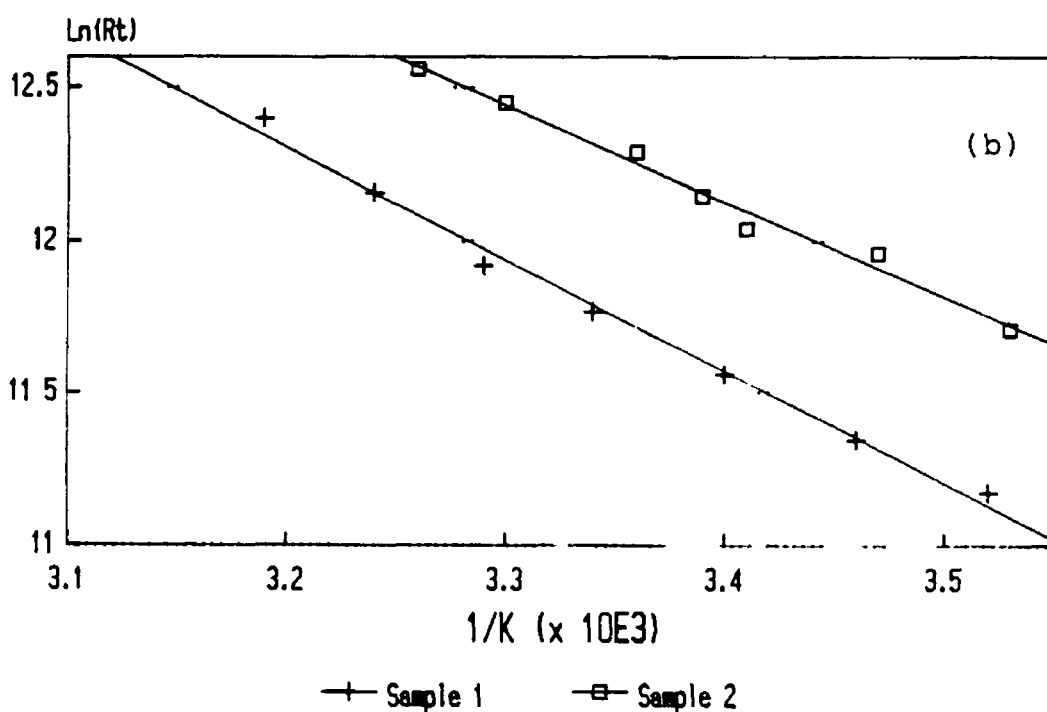
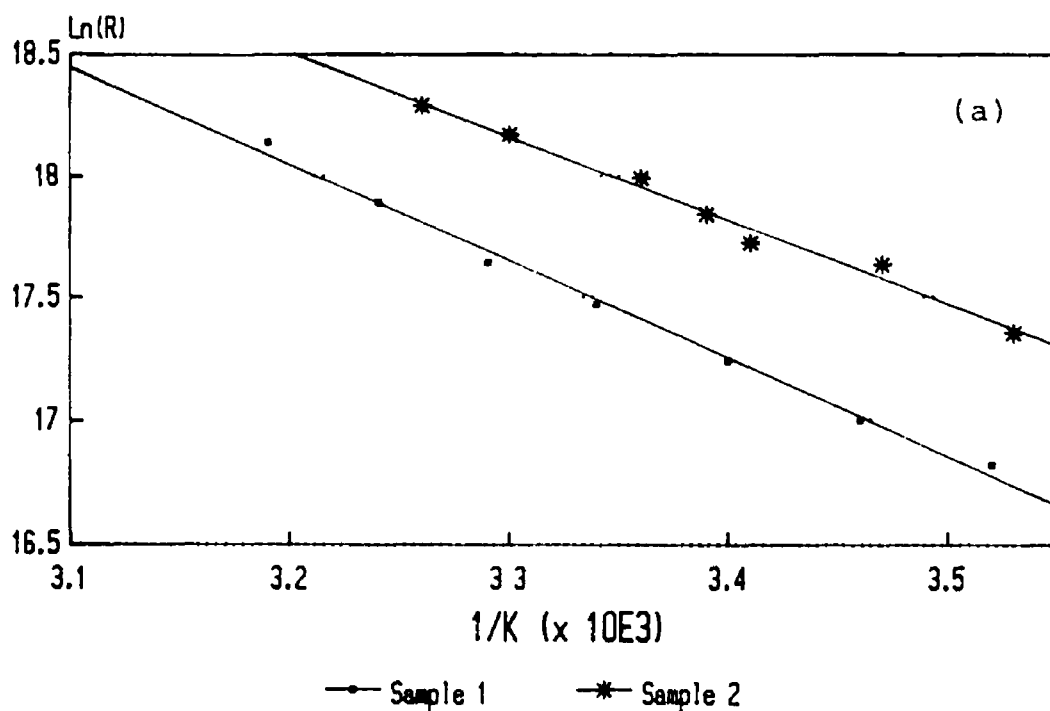


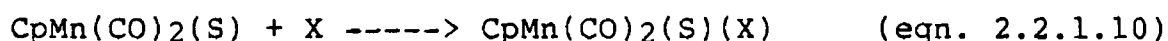
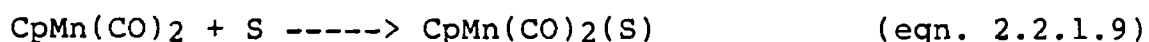
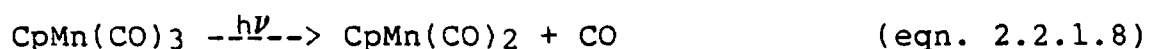
Table 2.2.1.16 summarises the above E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. The similarity in values of E_a and $\Delta S^\ddagger$ for all the ligands suggest there is a similar rate determining step in all of the above reaction. $\Delta S^\ddagger$ values indicate that formation of $\text{CpMn(CO)}_2(\text{X})$ ($\text{X} = \text{ligand}$) is via an associative mechanism. Errors in determining $\Delta S^\ddagger$ are significant (see experimental section) but the assumption that $\Delta S^\ddagger$ is largely negative in the above reactions seems to be a valid one. The rate determining step could be given by equation 2.2.1.10 in the following scheme.

Table 2.2.1.16: Thermodynamic data associated with the reaction of $\text{CpMn(CO)}_2(\text{S})$ with various ligands X, ($\text{X} = \text{CpMn(CO)}_3$, 4-picoline, 1-hexene, 4-vinylpyridine and PPh_3) in alkane solution.

Ligand X	E_{act} kJmol^{-1}	$\Delta H^\ddagger$ kJmol^{-1}	$\Delta S^\ddagger$ a $\text{Jmol}^{-1}\text{K}^{-1}$
CpMn(CO)_3	33.10	30.4	-20.01
4-picoline	30.83	28.3	- 2.83
4-vinylpyridine	29.50	27.1	-28.00
1-hexene	31.10	28.7	-41.20
triphenylphosphine ^b	35.10	33.4	5.4

a Errors in $\Delta S^\ddagger$ values are +/- 50%

b Determined by trir flash photolysis in n-hexane. All remaining data were determined by uv/vis flash photolysis.



These results will be discussed in more detail further on.

2.2.1.15 Initial Studies on the Decay of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

An investigation of the parameters governing the decay of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ was undertaken. If this bridging species decays via a dissociation reaction to regenerate CpMn(CO)_3 , then the rate of decay should decrease as the concentration of parent tricarbonyl is increased. If the decay was the result of a further decarbonylation of the dimer its decay would not depend on the concentration of CpMn(CO)_3 but rather on the presence of CO. Therefore the dependence of the lifetime of the dimeric compound on CO and CpMn(CO)_3 concentration was investigated.

The rate of decay of the dimer at various concentrations of $\text{CpMn}(\text{CO})_3$ and at various wavelengths is detailed in Table 2.2.1.17.

Table 2.2.1.17: Rate of decay^a (in μs) of the dimer at various concentrations of $\text{CpMn}(\text{CO})_3$ and in the presence and absence of CO.

Sample conc mol dm^{-3} ($\times 10^3$)	CO	Analysis Wavelength in nm.		
		360	440	520
0.51	absent	30,000	38,000	84,000
5.30	absent	50,000	75,000	80,000
2.24	absent	400,000	80,000	80,000
2.30	absent	15,000	10,960	105,000
	present	6,000	6,500	7,100
1.06	absent	80,000	90,000	78,000
2.20	absent	93,500	98,150	92,000
	present	6,400	7,600	7,800
2.01	absent	97,500		93,400
	present	7,000		7,200

^a The errors in the above values are $\pm 25\%$.

It is evident from these data that there is little consistency in the dimer decay. It is a problem inherent in the flash photolysis technique that the system is unable to accurately record transients whose lifetimes are greater than ca. 20ms. This is because of diffusion of the transient species away from the monitoring beam over extended timescales. Thus the apparent effect of the concentration of CpMn(CO)_3 on the decay of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ is perturbed by diffusion of the bridging species away from the monitoring beam and useful kinetic analysis at longer timescales was not possible.

The effect on the lifetime of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$, upon saturating the CpMn(CO)_3 solution with CO, was also investigated and the results given in Table 2.2.1.17. It is likely that the dimer has indeed a lifetime of ca. 50ms and this is reduced considerably in the presence of carbon monoxide (see equation 2.2.1.12). However because the experimental problems mentioned already kinetic data were unreliable.



2.2.1.16 Attempted Synthesis of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

Because of the apparent lifetime of $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ at room temperature of 50 +/- 25ms it was thought that the dimeric species should be stable at low temperatures, thus enabling it's isolation under suitable conditions. Three routes to the isolation of this complex were attempted and these are fully described in the experimental section. The initial attempt to synthesise $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ was by photolysis of a solution of CpMn(CO)_3 in n-pentane at 180K. However this method failed and the failure could be explained as follows.

(1) $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ upon formation is itself photosensitive and was photodecomposed to give the brown product observed (assumed to be oxides of manganese).

(11) The dimer is only stable for ca. 2 minutes under these conditions. Its instability could be due to its reaction with impurities in the solvent or the purging argon. Organometallic manganese compounds are notoriously air-sensitive.

$(\text{MeCp})\text{Mn}(\text{CO})_3$ was also used as starting material. A red compound was seen to form and this time the photoproduct was stable for 30-45 minutes. An infrared spectrum taken at room temperature during this experiment, show the disappearance of the parent compound with the appearance of two bands at 1905 and 1960 cm^{-1} . The origin of these bands is unknown. The instability of this compound at room temperature prevented its successful isolation.

Irradiation of sample of $\text{CpMn}(\text{CO})_3$ in solid pentane at liquid nitrogen temperatures under vacuum, appeared to have no effect. Upon warming the solution slightly to above the melting point of the solvent, a red complex was seen to form. It is known that irradiation of $\text{CpMn}(\text{CO})_3$ in either N_2 doped Ar or CH_4 matrix leads to the formation of $\text{CpMn}(\text{CO})_2$ and $\text{CpMn}(\text{CO})_2\text{N}_2$.²⁴ It seems feasible that the $\text{CpMn}(\text{CO})_2$ species formed upon photolysis of $\text{CpMn}(\text{CO})_3$ in frozen pentane could react with the $\text{CpMn}(\text{CO})_3$ when the pentane was allowed to melt, to form the dimeric species. Following melting, the solution was frozen and the red colour persisted for some 2-3 hours.

On the basis of these experiments it would appear that isolation of the dimeric species is more likely for the pentasubstituted $(\text{Me}_5\text{Cp})\text{Mn}(\text{CO})_3$ or $(\text{Ph}_5\text{Cp})\text{Mn}(\text{CO})_3$ materials than for the unsubstituted $\text{CpMn}(\text{CO})_3$ compound.

Their stability is possibly because of their insolubility in solvents caused by the presence of bulky groups on the ligand (such as phenyl groups). At present there is further work being carried out on this synthesis. Efforts at present are centred on the low temperature photolysis of CpMn(CO)_3 in co-ordinating solvents.

2.2.2 Flash Photolysis of $\text{CbFe}(\text{CO})_3$ in Cyclohexane Solution

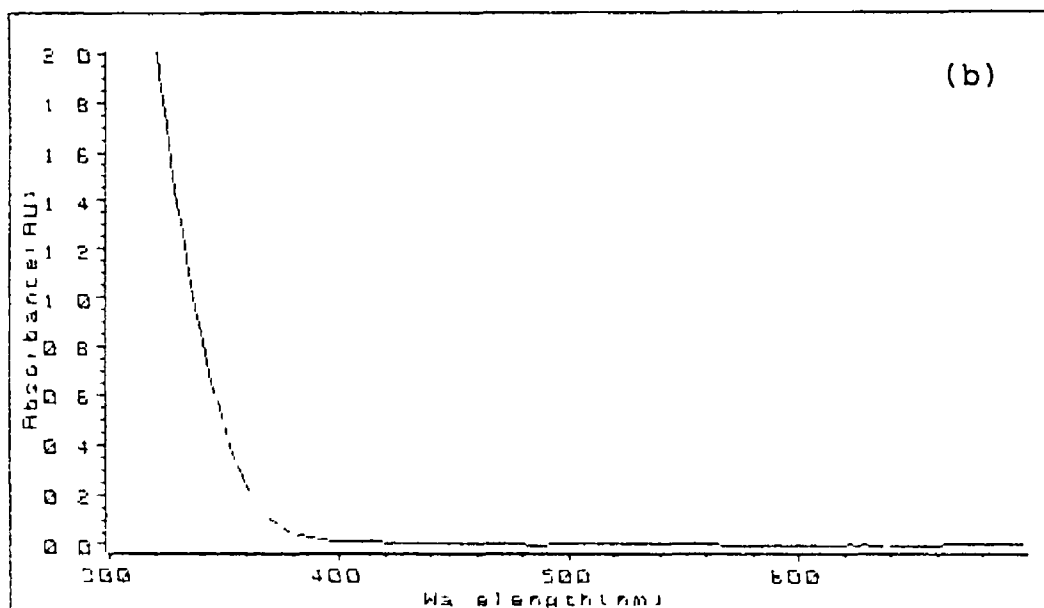
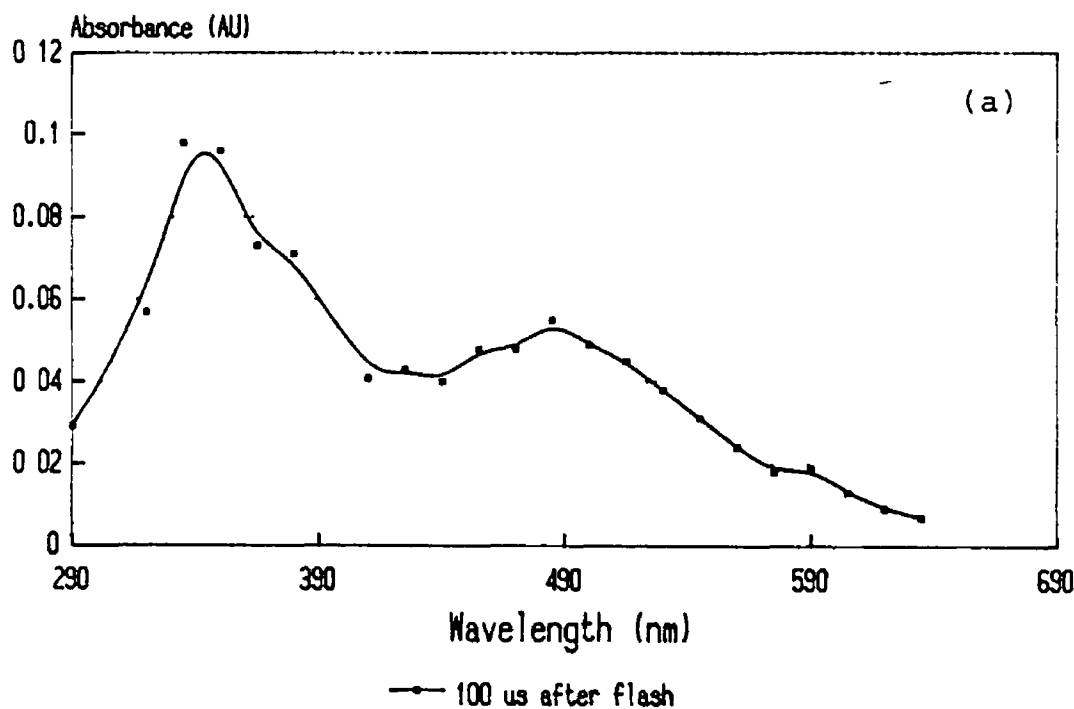
Abstract

A study of the initial photochemical reactions of $\text{CbFe}(\text{CO})_3$ in cyclohexane at ambient temperature has been conducted using laser flash photolysis with a uv/vis detection system. At least three transient species are formed upon flash photolysis, two of which have been characterised by their uv/vis spectra and their reactions with various nucleophiles. The initially formed species has been identified as $\text{CbFe}(\text{CO})_2(\text{S})$ (S = cyclohexane). This species then reacts with the parent tricarbonyl to form a dinuclear complex which further reacts to form a third as yet unidentified species. The behaviour of $\text{CbFe}(\text{CO})_3$ upon flash photolysis is very similar to other systems which have been studied including $\text{CpMn}(\text{CO})_3$ ⁷¹, $\text{ArCr}(\text{CO})_3$ ⁷². The activation parameters for the reaction of $\text{CbFe}(\text{CO})_2(\text{S})$ with various nucleophiles are also presented.

2.2.2.1 Primary Photoproduct: Formation of $\text{CbFe}(\text{CO})_2(\text{S})$

The uv/vis transient spectrum of the first species produced upon flash photolysis of $\text{CbFe}(\text{CO})_3$ in cyclohexane is shown in Figure 2.2.2.1. The spectrum of $\text{CbFe}(\text{CO})_3$ in cyclohexane is also given. The main features of this spectrum are a broad band centred around 480nm and a further band in the uv region whose true shape is obscured because of depletion of the parent tricarbonyl. This species (species I) was fully formed within the rise time of the detection system used (50ns). Previous workers had noted that uv photolysis of $\text{CbFe}(\text{CO})_3$ in inert matrices had led to production of $\text{CbFe}(\text{CO})_2(\text{matrix species})$.^{24,40}

Figure 2.2.2.1: (a) uv/vis Difference spectrum recorded following the flash photolysis of $\text{CbFe}(\text{CO})_3$ in cyclohexane solution. (b) uv/vis Spectrum of $\text{CbFe}(\text{CO})_3$ in cyclohexane solution.



It is assumed the CbFe(CO)_2 fragment produced upon photolysis would co-ordinate to a solvent molecule. This assumption is based on the previous work on the flash photolysis of CpMn(CO)_2 ⁷¹ and on work carried out on many other carbonyl systems. For these reasons the uv/vis absorption bands at 480nm and in the uv region were assigned to a $\text{CbFe(CO)}_2(\text{S})$ species (S = cyclohexane). Co-ordination of the solvent molecule perturbs the LF energy levels within the molecule and the absorption band centred at 480nm could be as a result of this co-ordination. The assignation of the initially observed species as $\text{CbFe(CO)}_2(\text{S})$ was confirmed by the reaction of this species with CO and other nucleophiles.

2.2.2.2 Flash Photolysis of $\text{CbFe(CO)}_2(\text{S})$ in CO Saturated Cyclohexane

The yield and lifetime of this first observable species in the presence and absence of carbon monoxide were investigated and the results presented in Table 2.2.2.1. It is evident from this Table that the yield of $\text{CbFe(CO)}_2(\text{S})$ varies little with the addition of CO (from -18% to +5%, depending on the analysis wavelength chosen). These results are consistent with the formation of the first observable species being as a result of a physical process (i.e. photon excitation). However the effect on the lifetime of this species is considerable as the presence of CO ensures increased backreaction of equation 2.2.2.1. These results are consistent with loss of CO being the primary photoreaction (equation 2.2.2.1).

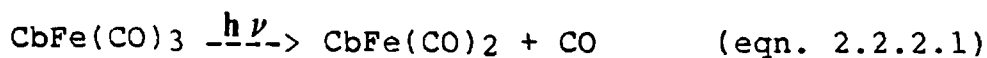


Table 2.2.2.1: The effect of the presence of CO on the yield of $\text{CbFe}(\text{CO})_2(\text{S})$ in cyclohexane solution (conc. of $\text{CbFe}(\text{CO})_3 = 8.6 \times 10^{-4} \text{ mol dm}^{-3}$).

Absorbance (A.U.) recorded $10\mu\text{s}$ after the laser flash			
(wavelength in nm)			
	380	365	515
CO absent	.066	.064	.038
CO present	.056	.052	.040
% difference	-15%	-18%	+5%

(11) The effect of the presence CO on the lifetime of $\text{CbFe}(\text{CO})_2(\text{S})$ in cyclohexane solution (conc. of $\text{CbFe}(\text{CO})_3 = 8.6 \times 10^{-4} \text{ mol dm}^{-3}$).

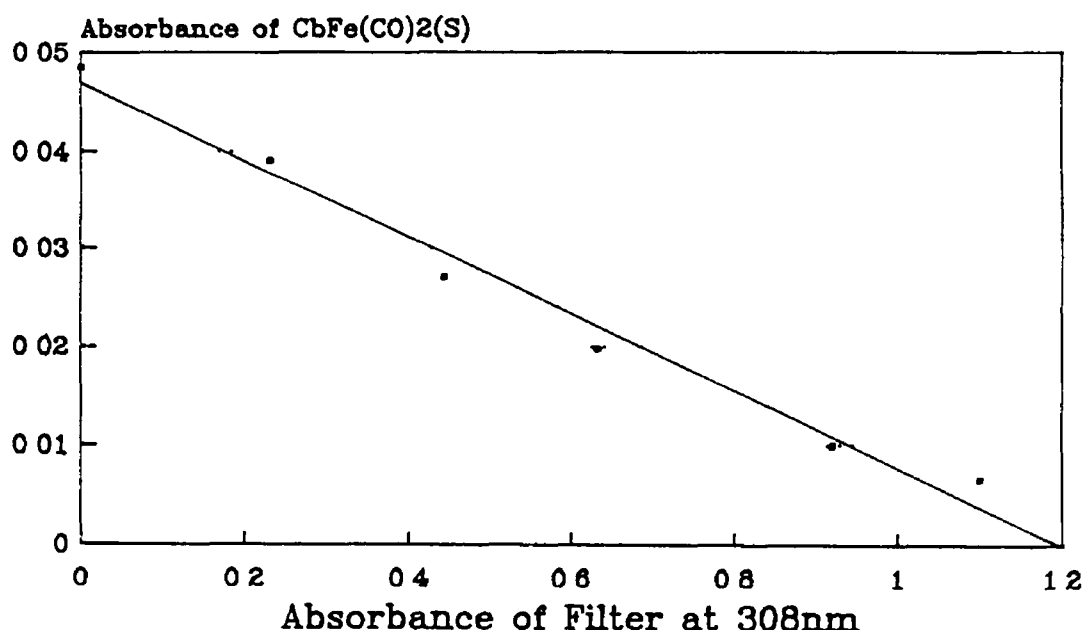
Wavelength (nm)	Lifetime ^a of $\text{CbFe}(\text{CO})_2(\text{S})$ (absence of CO) (μs)	Lifetime ^a of $\text{CbFe}(\text{CO})_2(\text{S})$ (presence of CO) (μs)
380	1577	440
365	1560	407
515	1580	430

a Lifetime is given as $1/k_{\text{obs}}$

Loss of Cb has been reported as a primary photoreaction in the solution photochemistry of $\text{CbFe}(\text{CO})_3$ but that the quantum yield of CO loss is at least ten times that of loss of Cb 35 If this were the case here the effect of CO on

the lifetime of the transient species monitored at different wavelengths would vary markedly corresponding to the presumed different reaction of CbFe(CO)_2 and Fe(CO)_3 with CO. Additionally the lifetime of the first observed species would differ significantly at different wavelengths. This was not the case in these studies (though low quantum yield for the reaction involving loss of CO may prevent its detection). The photochemistry probably originates from the population of LF states as in the analogous ArCr(CO)_3 and CpMn(CO)_3 species.²⁴ Replacement of the CO ligand by a solvent molecule would change the energy of the molecular orbitals in the $\text{CbFe(CO)}_2(\text{S})$ molecule, giving rise to the observed differences in the uv/vis spectrum between it and the parent tricarbonyl.

Figure 2.2.2.2: Plot showing the variation in absorbance of $\text{CbFe(CO)}_2(\text{S})$, recorded 100 μs after the laser flash, with laser flash intensity.



The formation of $\text{CbFe(CO)}_2(\text{S})$ is as a result of single photon excitation of the parent tricarbonyl. This was confirmed by measuring the absorbance of $\text{CbFe(CO)}_2(\text{S})$ as the power of the laser pulse was reduced. Figure 2.2.2.2 indicates the linearity of the relationship

2.2.2.3 The Reaction of $\text{CbFe(CO)}_2(\text{S})$ with Nucleophiles

The rate of reaction of various nucleophilic ligands with $\text{CbFe(CO)}_2(\text{S})$ was determined by measuring the lifetime of the $\text{CbFe(CO)}_2(\text{S})$ species in the presence and absence of the nucleophile. The results are given in Table 2.2.2.2. In all cases the reactions were found to follow pseudo first order kinetics (see Appendix 1).

Table 2.2.2.2: Bimolecular rate constants^a ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$) for the reaction of $\text{CbFe(CO)}_2(\text{S})$ ($\text{S} = \text{cyclohexane}$) with various nucleophiles at 295K.

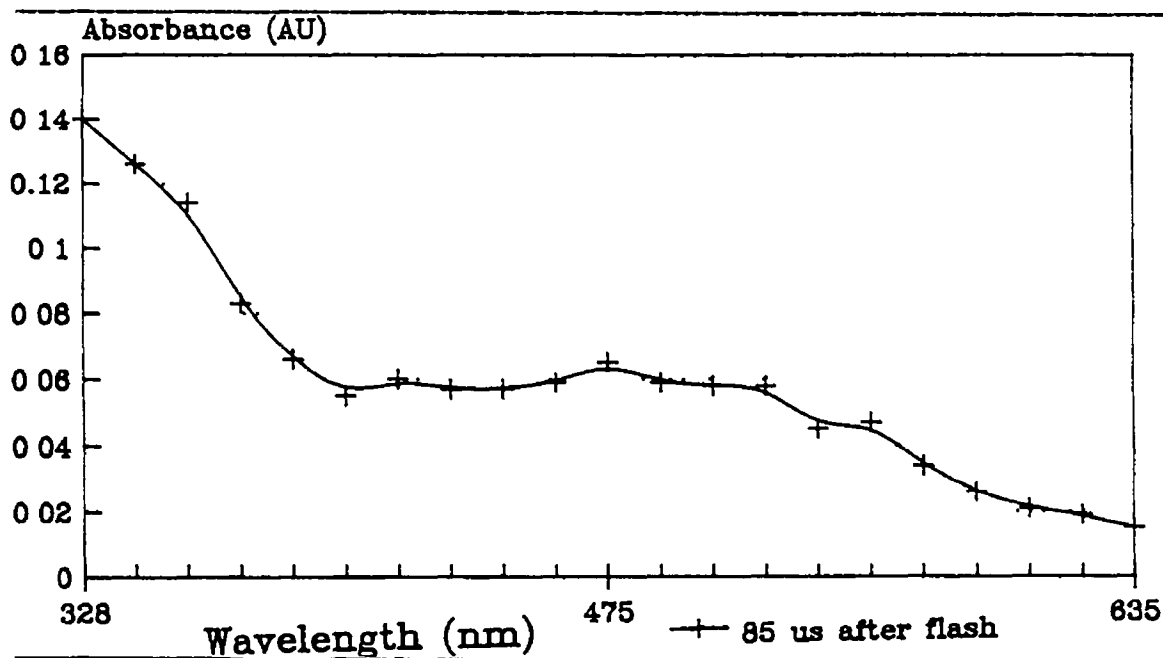
Ligand	Rate constant ($\times 10^{-6}$) for reaction of ligand with $\text{CbFe(CO)}_2(\text{S})$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)
1-hexene	7.0
4-picoline	4.1
CO	0.3

(a) These rate constants have been corrected to allow for the presumed formation of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ (vide infra).

These reaction rates are of a similar order of magnitude to those already reported for formation of $\text{CpMn}(\text{CO})_2(\text{ligand})$ complexes (see Section 2.2.1.4). The difference in measured reaction rates for the different nucleophiles indicates that while the 16 valence-electron species is highly reactive, steric effects come into play in the co-ordination of a ligand. The rate of reaction of $\text{CbFe}(\text{CO})_2(\text{S})$ with 1-hexene is greater, by a factor of two, than with 4-picoline.

Uv photolysis of $\text{CbFe}(\text{CO})_3$ in the presence of 1-hexene or 4-picoline led to immediate formation, via the dicarbonyl $\text{CbFe}(\text{CO})_2(\text{S})$ molecule, of a stable product. Substitution of a CO ligand by an alkene or nitrogen ligand leads to a lower energy absorption. This is because both 1-hexene and 4-picoline have low lying π^* orbitals which give rise to MLCT bands in the uv/vis spectra of substituted $\text{CbFe}(\text{CO})_2(\text{X})$ compounds. The yellow $\text{CbFe}(\text{CO})_3$ compound has a well defined uv max at ca. 270nm whilst the lowest energy absorption for $\text{CbFe}(\text{CO})_2(1\text{-hexene})$ is at ca. 475nm (Figure 2.2.2.3).

Figure 2.2.2.3: uv/vis Difference spectrum of $\text{CbFe}(\text{CO})_2(1\text{-hexene})$ in cyclohexane solution.

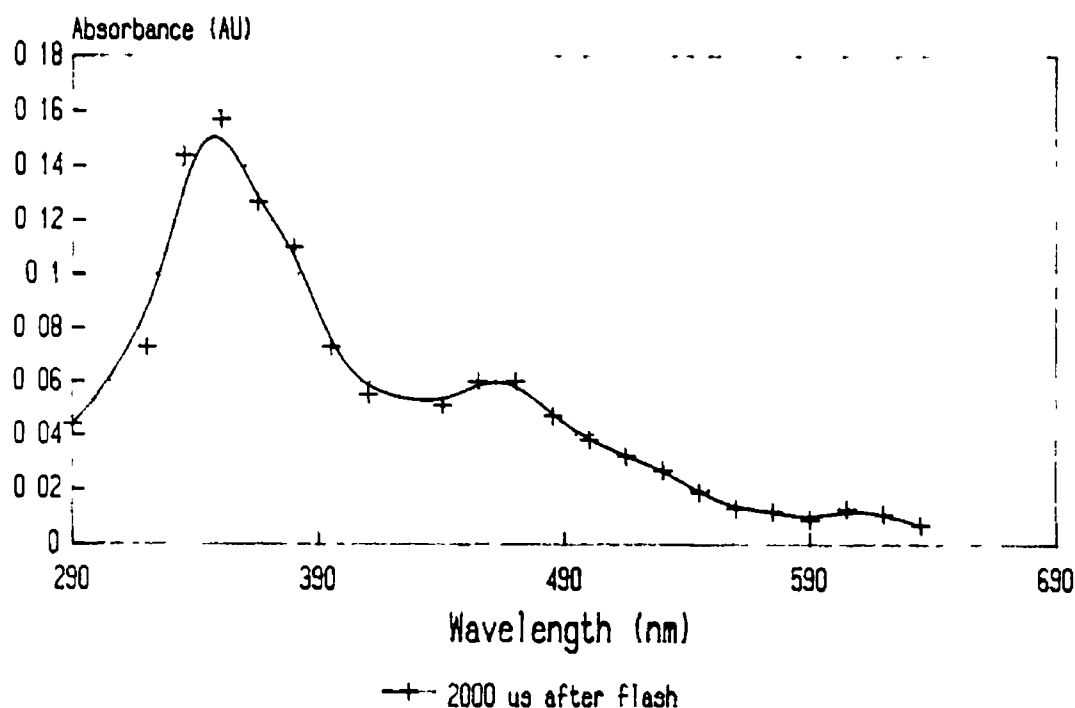


Quantum yields for these reactions appear to be high and this would discount the loss of Cb making a significant contribution to the photochemical reaction.

2.2.2.4 The Reaction of $\text{CbFe(CO)}_2(\text{S})$ with CbFe(CO)_3

The initially formed species $\text{CbFe(CO)}_2(\text{S})$ whose spectrum is shown in Figure 2.2.2.1 was seen to decay on a microsecond timescale with a concomitant grow-in of a second species. The spectrum of this species is given in Figure 2.2.2.4 and shows a maximum in the visible region at 470nm and an apparent maximum in the uv/vis region at 350nm. The true shape of this peak is distorted because of overlap of this spectral feature with those of the parent tricarbonyl.

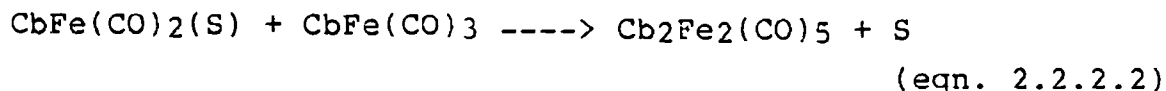
Figure 2.2.2.4: uv/vis Difference spectrum recorded following the flash photolysis of CbFe(CO)_3 in cyclohexane solution.



From our studies on the analogous CpMn(CO)_3 ⁷¹ complex and from work by previous groups on Cr(CO)_6 ,⁵⁸ it was thought that this species was formed via reaction of $\text{CbFe(CO)}_2(\text{S})$ with the parent molecule. Unfortunately in this study the ability to monitor the transient species by infrared spectroscopy was not available to us as was the case with the study of CpMn(CO)_3 . Thus structural information on this species is limited. The spectrum shown in Figure 2.2.2.4 was at least sufficiently different from the spectra of $\text{CbFe(CO)}_2(\text{S})$ and CbFe(CO)_3 to assign it to a different molecule. Experiments in which the concentration of CbFe(CO)_3 was varied confirmed that this species was formed via reaction of $\text{CbFe(CO)}_2(\text{S})$ with CbFe(CO)_3 .

2.2.2.5 Studies on the Dependence of k_{obs} , for the Formation of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$, on the Concentration of CbFe(CO)_3

A plot of k_{obs} for the formation of the second observed species versus the concentration of starting material CbFe(CO)_3 shows a linear relationship (see Figure 2.2.2.5 and also Table 2.2.2.3). The intercept of this graph is approximately zero (within experimental error) and indicates that $\text{CbFe(CO)}_2(\text{S})$ does not appear to react with any impurities which may be in the system (though perhaps there are no impurities in the system). The dependence of the formation of this second species on the concentration of CbFe(CO)_3 indicates that the initially formed $\text{CbFe(CO)}_2(\text{S})$ is reacting with the parent tricarbonyl complex as shown in equation 2.2.2.2.

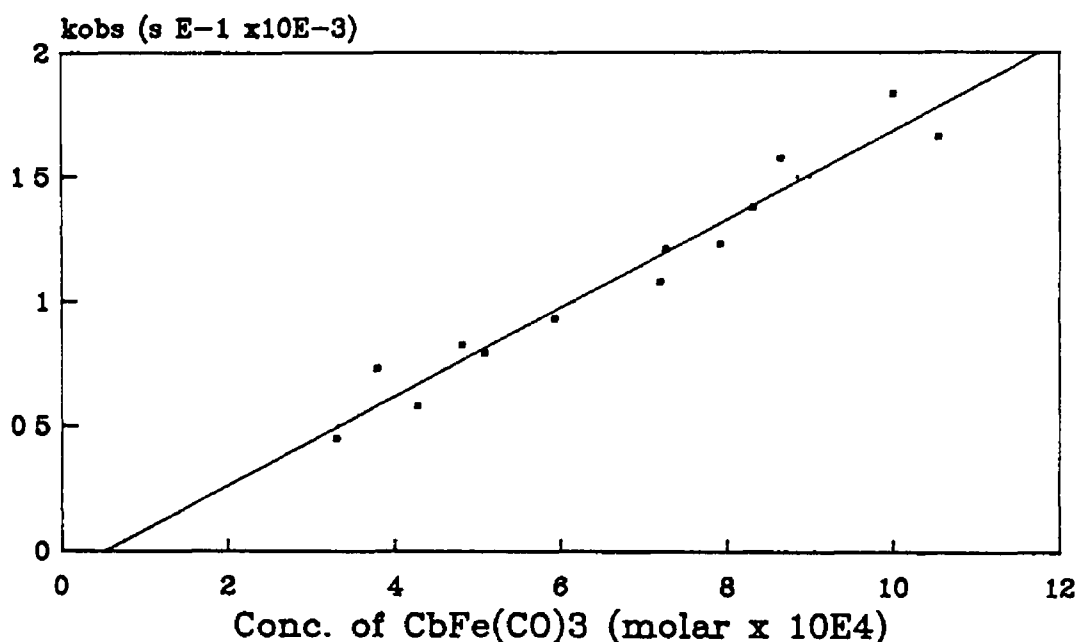


The concentration of $\text{CbFe(CO)}_2(\text{S})$ generated by each laser pulse is small compared to the concentration of parent tricarbonyl therefore the observed kinetics follow pseudo first order kinetics. Figure 2.2.2.5 provides an estimate of the second order constant for equation 2.2.2.2 of $1.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 295K.

Table 2.2.2.3: Values of k_{obs} for the formation of the dinuclear species with varying CbFe(CO)_3 concentration.

Concentration of CbFe(CO)_3 (mol dm^{-3}) $\times 10^4$	k_{obs} (s^{-1})
3.30	450
3.79	730
4.28	580
4.81	824
5.08	790,
5.93	932
7.19	1079
7.25	1211
7.91	1231
8.31	1379
8.64	1577
10.00	1835
10.55	1664

Figure 2.2.2.5: Plot showing the variation in k_{obs} (s^{-1}), for the formation of $Cb_2Fe_2(CO)_5$, with concentration of $CbFe(CO)_3$ ($mol\ dm^{-3}$).



2.2.2.6 The Reaction of $Cb_2Fe_2(CO)_5$ with CO in Cyclohexane Solution

The presence of carbon monoxide in solution should inhibit the formation of $Cb_2Fe_2(CO)_5$ by reaction with photogenerated $CbFe(CO)_2$. Table 2.2.2.4, which compares the yield of the dimer in the presence of CO saturated cyclohexane to that in degassed cyclohexane, shows this to be the case and this effect was observed at all wavelengths which were measured. The assignation of species II as $Cb_2Fe_2(CO)_5$ is consistent with these results.

Table 2.2.2.4: The effect of CO on the yield of species II (concentration of $\text{CbFe(CO)}_3 = 8.6 \times 10^{-4} \text{ mol dm}^{-3}$)

	Absorbance (A.U. $\times 10^2$), recorded $10\mu\text{s}$ after flash. (wavelength in nm)		
	380	365	515
CO absent	.130	.150	.024
CO present	.055	.064	.010
% difference	-58%	-58%	-58%

2.2.2.7 A Study of the Activation Parameters for the Formation of $\text{CbFe(CO)}_2(\text{X})$ ($\text{X} = \text{CbFe(CO)}_3$, 1-hexene, or 4-picoline)

While the reaction rates of $\text{CbFe(CO)}_2(\text{S})$ with varying nucleophiles have been shown to differ the actual nature of the reactions remain ambiguous. The activation parameters associated with the reactions given in Section 2.2.2.3 were measured in order to understand the actual reaction mechanism. The results are detailed in Tables 2.2.2.5 to 2.2.2.7 and shown graphically in Figures 2.2.2.6 to 2.2.2.8. These results are summarised in Table 2.2.2.6.

Table 2.2.2.5: Experimental data for the determination of activation energy, enthalpy, and entropy for the formation of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$.

(a) Concentration of $\text{CbFe}(\text{CO})_3 = 7.9 \times 10^{-4} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.53	13.81	8.16
3.48	14.18	8.52
3.39	14.26	8.57
3.36	14.72	9.02
3.32	14.74	9.03
3.28	14.81	9.09
3.06	15.52	9.73
3.14	15.31	9.54
3.19	15.22	9.47
3.24	14.66	8.94
3.27	14.66	8.94
3.31	14.73	9.02
3.36	14.63	8.94
3.40	14.19	8.50
3.47	14.09	8.43

Arrhenius Plot.

Slope = 3606 ± 229

Intercept = $26.6 \pm .1$

Corr. coeff. = .975

Eyring Plot.

Slope = 3303 ± 231

Intercept = $19.9 \pm .1$

Corr. coeff. = .970

=> $E_a = 30 \pm 1.9 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 27.5 \pm 2.0 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -32 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.2.5:cont'd

(b) Concentration of $\text{CbFe}(\text{CO})_3 = 1.12 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.42	14.55	8.87
3.53	14.08	8.44
3.48	14.22	8.56
3.42	14.34	8.67
3.37	14.78	9.09
3.32	14.86	9.15
3.28	14.93	9.21
3.24	14.93	9.21
3.21	14.98	9.24
3.18	15.11	9.36
3.17	15.37	9.61
3.18	15.07	9.32
3.24	14.92	9.18
3.28	14.65	8.93
3.37	14.54	8.85

Arrhenius Plot.

Slope = 2926 ± 255

Intercept = $24.5 \pm .1$

Corr. coeff. = .957

Eyring Plot.

Slope = 2586 ± 270

Intercept = $17.6 \pm .1$

Corr. coeff. = .934

$\Rightarrow E_a = 24.3 \pm 2.1 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 21.5 \pm 2.5 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -52 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.2.6: Experimental data for the determination of activation energy, enthalpy, and entropy for the formation of $\text{CbFe}(\text{CO})_2(1\text{-hexene})$.

(a) Concentration of $\text{CbFe}(\text{CO})_3 = 8.4 \times 10^{-4} \text{ mol dm}^{-3}$.
 Concentration of 1-hexene = $6.65 \times 10^{-3} \text{ mol dm}^{-1}$

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.39	13.30	7.61
3.32	13.53	7.83
3.30	13.61	7.90
3.25	13.75	8.02
3.23	13.96	8.22
3.18	14.03	8.28
3.12	14.09	8.32
3.27	13.79	8.07
3.31	13.63	7.92
3.40	13.40	7.72

Arrhenius Plot.

Slope = 2941 ± 265

Intercept = $23.4 \pm .1$

Corr. coeff. = .969

Eyring Plot.

Slope = 2624 ± 263

Intercept = $16.6 \pm .1$

Corr. coeff. = .962

$\Rightarrow E_a = 24.5 \pm 2.2 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 21.8 \pm 2.2 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -59 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.2.6:cont'd

(b) Concentration of $\text{CbFe(CO)}_3 = 6.8 \times 10^{-4} \text{ moldm}^{-4}$.
 Concentration of 1-hexene = $9.6 \times 10^{-3} \text{ moldm}^{-1}$

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.46	13.17	7.51
3.40	13.37	7.68
3.30	13.47	7.75
3.24	13.95	8.21
3.19	14.13	8.38
3.13	14.14	8.38
3.10	14.21	8.43
3.02	14.70	8.89
3.14	14.00	8.24
3.41	13.20	7.54

Arrhenius Plot.

Slope = 3230 ± 267

Intercept = $24.5 \pm .1$

Corr. coeff. = .975

Eyring Plot.

Slope = 2974 ± 264

Intercept = $17.7 \pm .1$

Corr. coeff. = .970

$\Rightarrow E_a = 26.9 \pm 2.2 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 24.7 \pm 2.2 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -50 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.2.7: Experimental data for the determination of activation energy, enthalpy, and entropy for the formation of $\text{CbFe}(\text{CO})_2(4\text{-picoline})$.

(a) Concentration of $\text{CbFe}(\text{CO})_3 = 7.2 \times 10^{-4} \text{ mol dm}^{-3}$.
 Concentration of 4-picoline = $6.16 \times 10^{-3} \text{ mol dm}^{-1}$

$1/K$ $\times 10^3$	$\ln(R)$	$\ln(R_t)$
3.41	15.08	9.40
3.35	15.39	9.69
3.30	15.57	9.86
3.25	15.55	9.82
3.19	15.76	10.01
3.15	15.88	10.12
3.10	16.24	10.46
3.28	15.47	9.75

Arrhenius Plot.

Slope = 3250 ± 346

Intercept = 26.2 ± 0.1

Corr. coeff. = .968

Eyring Plot.

Slope = 2930 ± 350

Intercept = 19.4 ± 0.1

Corr. coeff. = .961

$\Rightarrow E_a = 27.0 \pm 2.9 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 24.4 \pm 2.9 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -36 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 2.2.2.7:cont'd

(b) Concentration of $\text{CbFe}(\text{CO})_3 = 6.5 \times 10^{-4} \text{ moldm}^{-3}$.
Concentration of 4-picoline = $5.14 \times 10^{-3} \text{ moldm}^{-3}$

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.44	14.78	9.11
3.36	15.07	9.37
3.30	15.23	9.52
3.26	15.45	9.73
3.22	15.54	9.80
3.16	15.76	10.00
3.08	16.16	10.37
3.16	15.76	10.00

Arrhenius Plot.

Slope = 3709 ± 142

Intercept = 27.5 ± 0.05

Corr. coeff. = .996

Eyring Plot.

Slope = 3389 ± 141

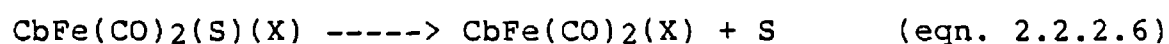
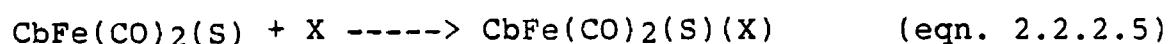
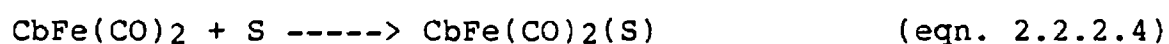
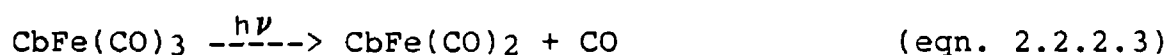
Intercept = 20.7 ± 0.05

Corr. coeff. = .995

$\Rightarrow E_a = 30.8 \pm 1.2 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 28.2 \pm 1.2 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -25 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

It is evident that there are no significant differences in the E_{act} , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for these reactions. The negative value of $\Delta S^\ddagger$ indicates that the rate determining

step in the formation of $\text{CbFe}(\text{CO})_2(\text{X})$ must have associative character. The large errors in $\Delta S^\ddagger$ have been explained in Section 2.3.1.X. but the magnitude of these errors is not great enough to discount the above conclusion. The thermodynamic parameters are consistent with the following reaction scheme where equation 2.2.2.5 corresponds to the rate determining step.



X = ligand, S = solvent

TABLE 2.2.2.8: Activation parameters for the reactions of $\text{CbFe}(\text{CO})_2(\text{S})$ with various ligands.

Ligand	E_{act} KJmol^{-1}	$\Delta H^\ddagger$ KJmol^{-1}	$\Delta S^\ddagger$ a $\text{Jmol}^{-1}\text{K}^{-1}$
$\text{CbFe}(\text{CO})_3$	27 +/- 3	25 +/- 4	-42
1-hexene	26 +/- 2	23 +/- 2	-55
4-picoline	29 +/- 3	26 +/- 3	-30

a Errors in $\Delta S^\ddagger$ values are +/- 20 $\text{Jmol}^{-1}\text{K}^{-1}$

Figure 2.2.2.6: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$.

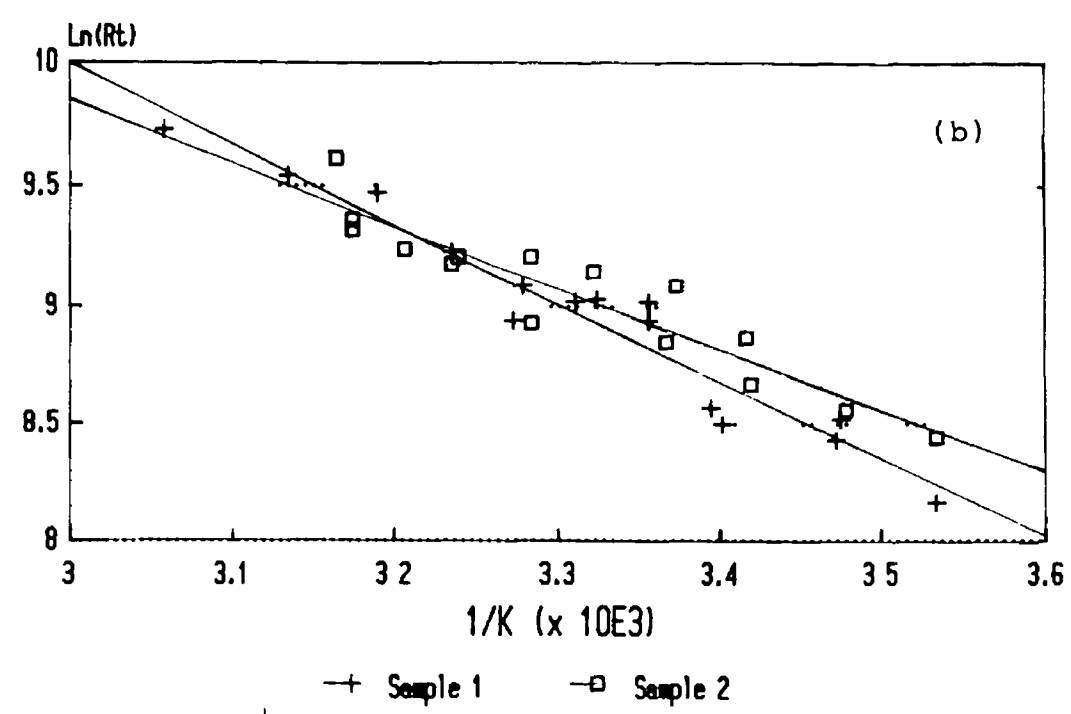
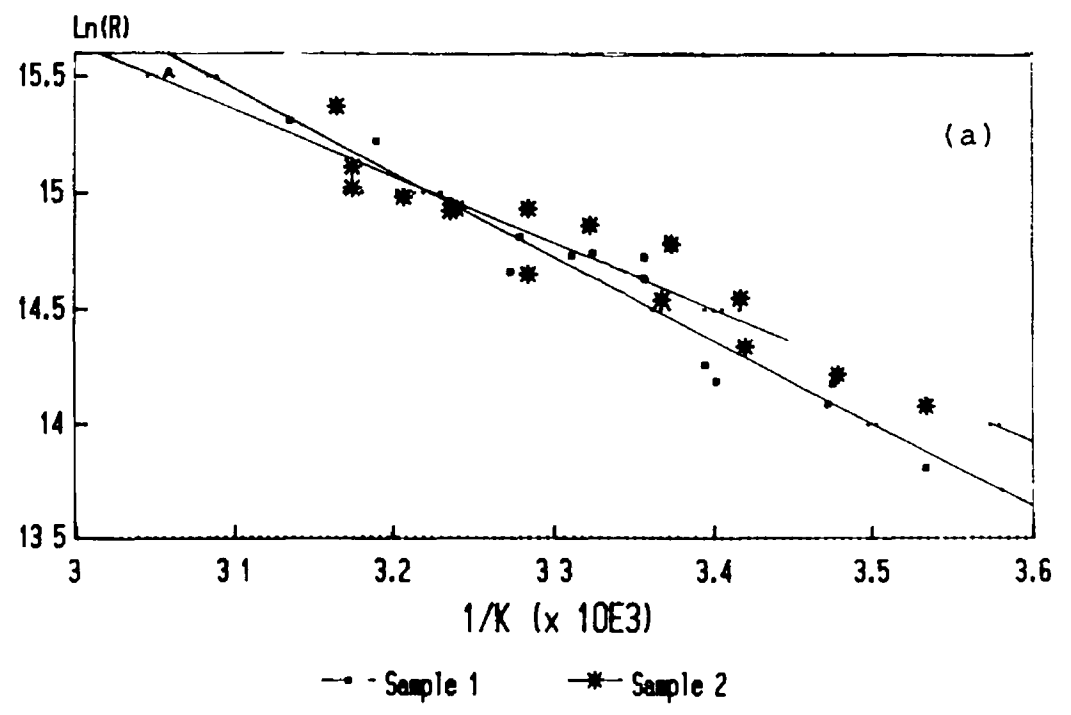


Figure 2.2.2.7: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CbFe}(\text{CO})_2(1\text{-hexene})$.

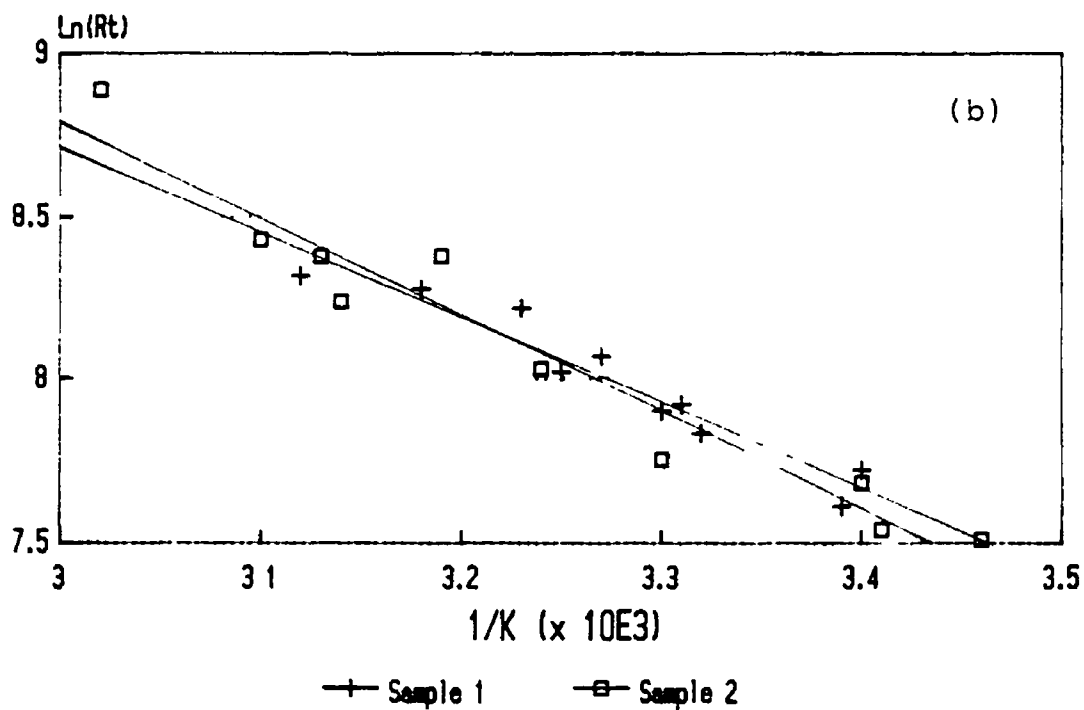
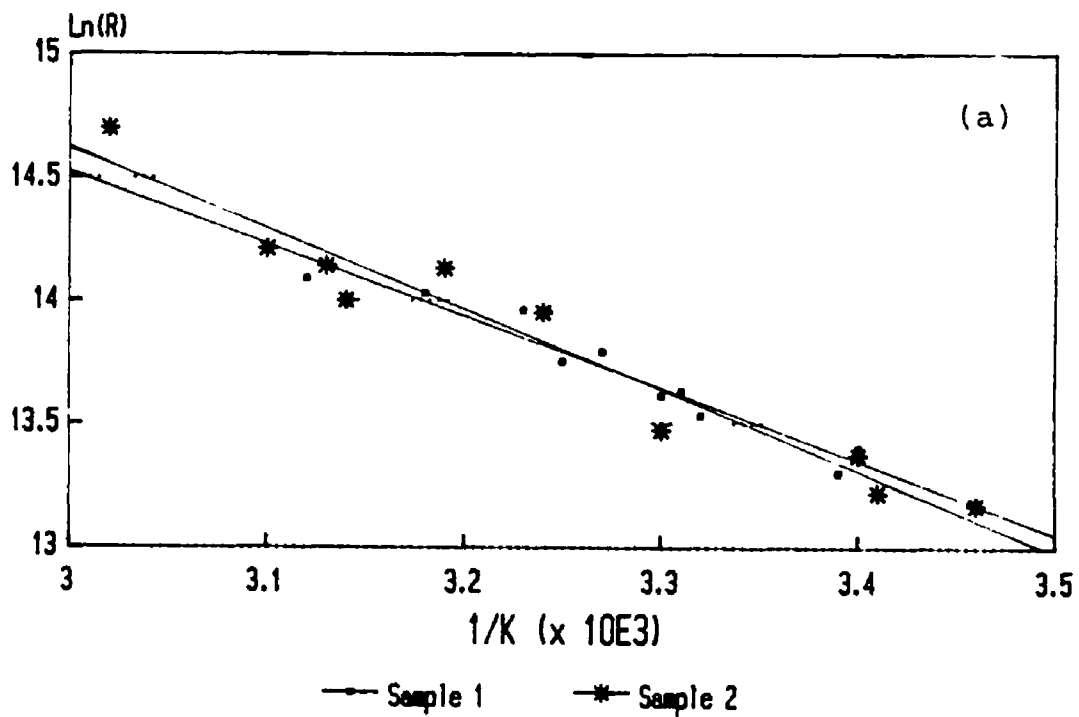
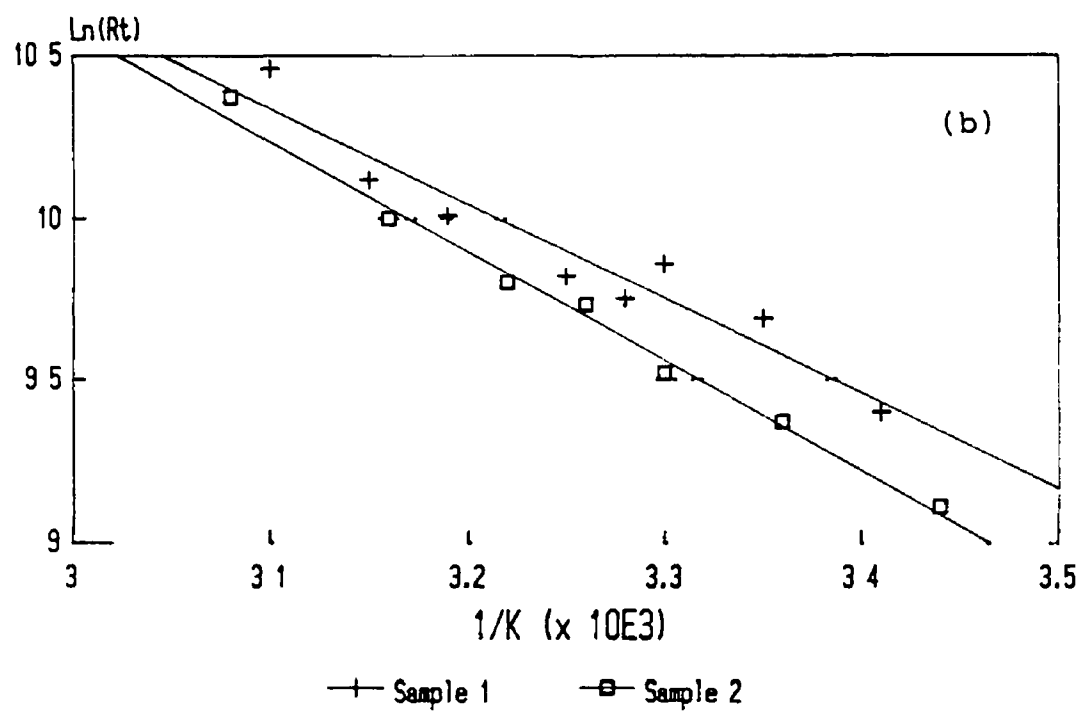
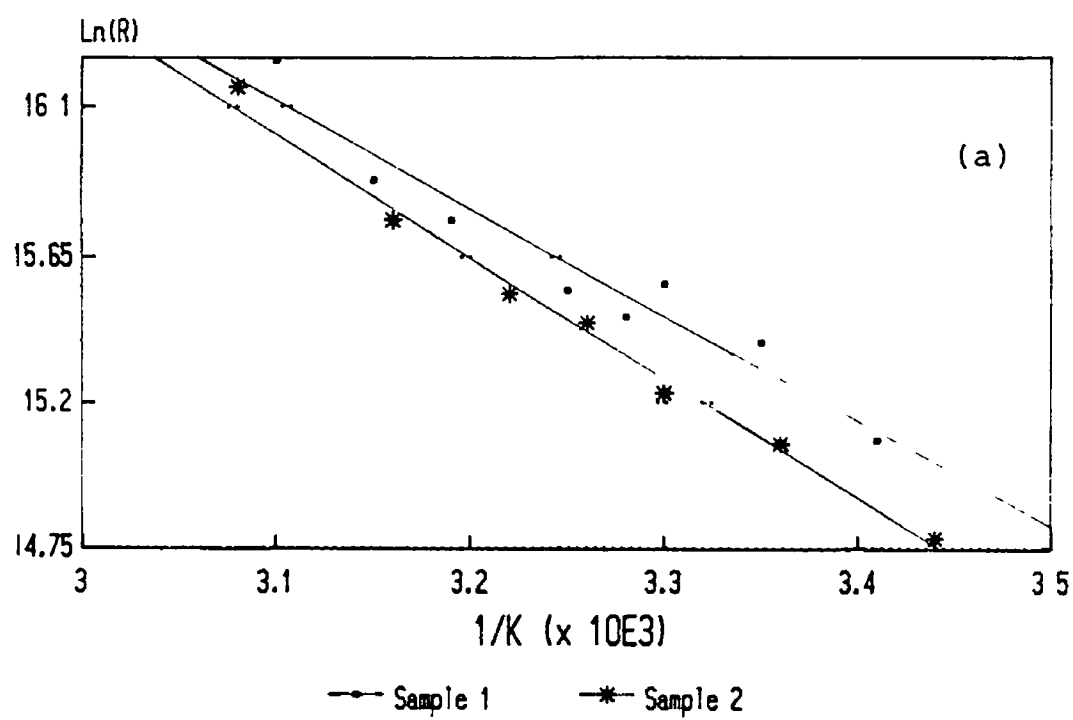


Figure 2.2.2.8: Arrhenius (a) and Eyring (b) plots for the formation of $\text{CbFe}(\text{CO})_2(4\text{-picoline})$.



2.2.2.8 The Reactions of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ in Cyclohexane Solution

The spectra of the second and third species observed are shown in Figure 2.2.2.9. These spectra are very similar to each other and the only true indication of the presence of the third species is in the difference in their extinction coefficients at 400nm. Monitoring the absorbance at 360nm, the initially formed species is seen to form the dimeric compound which in turn reacts to form a further complex species III. However observing the absorbance of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ over the same timescale but at a different wavelength (400nm), shows the dinuclear species to decay (see Figure 2.2.2.10).

Figure 2.2.2.9: uv/vis Difference spectra recorded following the flash photolysis of $\text{CbFe}(\text{CO})_3$ in cyclohexane solution.

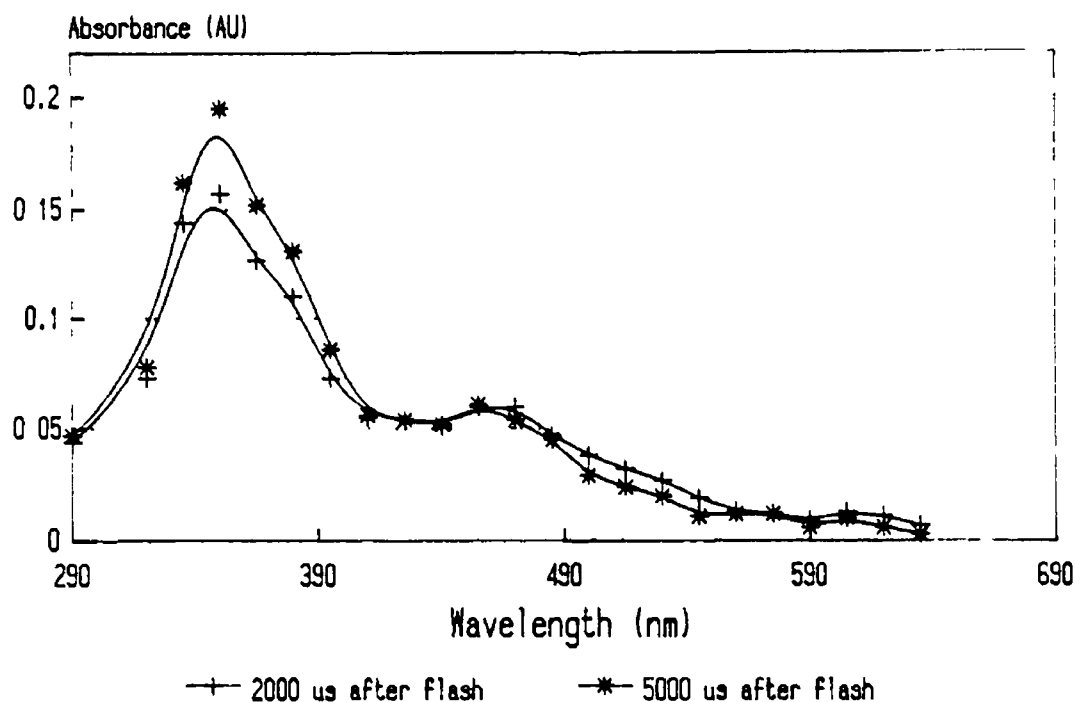
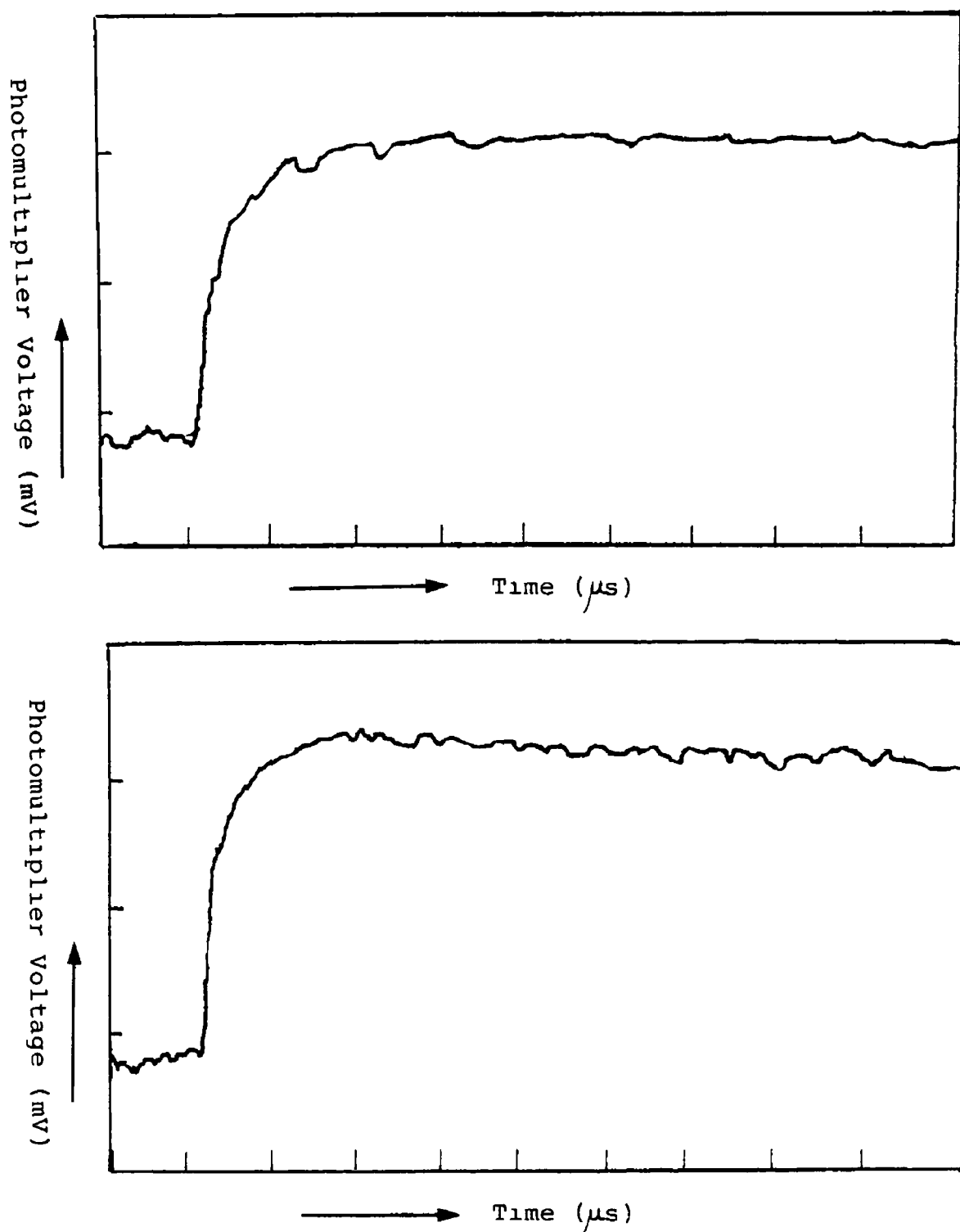


Figure 2.2.2.10: Kinetic traces recorded at 360nm (a) and at 400nm (b) following the flash photolysis of CbFe(CO)_3 in cyclohexane solution.



Structural information from these spectra is obviously minimal and thus the elucidation of the nature of species III could only be based on experimental observations on the reactivity of this complex. Transient infrared spectroscopic studies would perhaps have been useful. It is possible that this species is formed as a result of decarbonylation of the dinuclear species. Koerner von Gustorf and co-workers reported that irradiation of $\text{CbFe}(\text{CO})_3$ in thf solution at -40°C lead to a product formulated as $\text{Cb}_2\text{Fe}_2(\text{CO})_3$.³⁶ Similar decarbonylation reactions have previously been reported following the photolysis of $\text{CpV}(\text{CO})_4$.⁷²

If species III was formed via a decarbonylation reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_5$ then the presence of CO should decrease its yield. Unfortunately CO has a similar effect on the yield of $\text{Cp}_2\text{Fe}_2(\text{CO})_5$ (Section 2.2.2.7), which would cause a corresponding decrease in the yield of Species III. Table 2.2.2.9 shows the results of the CO experiments.

Table 2.2.2.9: The effect of CO on the lifetime^a of species II in cyclohexane solution (concentration of $\text{CbFe}(\text{CO})_3 = 8.6 \times 10^{-4} \text{ mol dm}^{-3}$).

Wavelength in nm	Lifetime in absence of CO (μs)	Lifetime in presence of CO (μs)
380	95,000	34,000
365	85,000	32,000

a lifetime is given as $1/k_{\text{obs}}$

Also if the observed grow-in of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ and species III could be deconvoluted it would be possible to determine if species III was formed from $\text{Cb}_2\text{Fe}_2(\text{CO})_5$. Varying the concentration of $\text{CbFe}(\text{CO})_3$ should show if Species III was formed via reaction of $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ with $\text{CbFe}(\text{CO})_3$. All of these experiments were complicated by the similarity between the spectra of the two species. The identity of Species III remains unknown at present. However species III was stable in solution for at least 2s therefore it is possible that low temperature photolysis experiments may allow its isolation.

2.2.3. Flash Photolysis of $\text{ArCr}(\text{CO})_3$ in Cyclohexane Solution

Our studies on the photoinitiated reactions of $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$ in alkane solvents indicated some differences in the observed chemistry between these isoelectronic species. These differences can be summarised as follows:

(1) there was no evidence for the formation of a third transient species in our studies on the manganese system,

(11) the dinuclear $\text{Cb}_2\text{Fe}_2(\text{CO})_5$ complex was considerably less stable than the $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ molecule.

It was decided to further investigate the formation of such dinuclear species by studying the photoinitiated reactions of $\text{ArCr}(\text{CO})_3$, which is isoelectronic with the manganese and iron compounds. These studies followed closely those already described for the $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$ systems.

2.2.3.1 Primary Photoproduct. Formation of $\text{ArCr}(\text{CO})_2(\text{S})$

The spectrum of the first species observed upon flash photolysis of $\text{ArCr}(\text{CO})_3$ in cyclohexane, was recorded using both the flash photolysis apparatus in Trinity College Dublin (excitation wavelength 308nm) and that in D.C.U. (excitation wavelength 355nm). The transient spectrum recorded immediately after the flash in both cases are identical (Figure 2.2.3 1). The spectrum of parent tricarbonyl is also given. The most significant feature in the transient spectrum is the negative band at ca. 330nm

which can be assumed to be because of depletion of parent tricarbonyl. The absorbance at higher wavelengths is very weak and broad. This species was fully formed within the time resolution of the instrument.

Figure 2.2.3.1: uv/vis Difference spectrum recorded following the flash photolysis (at 308nm (a) and at 355nm (b)) of $\text{ArCr}(\text{CO})_3$ in cyclohexane solution.

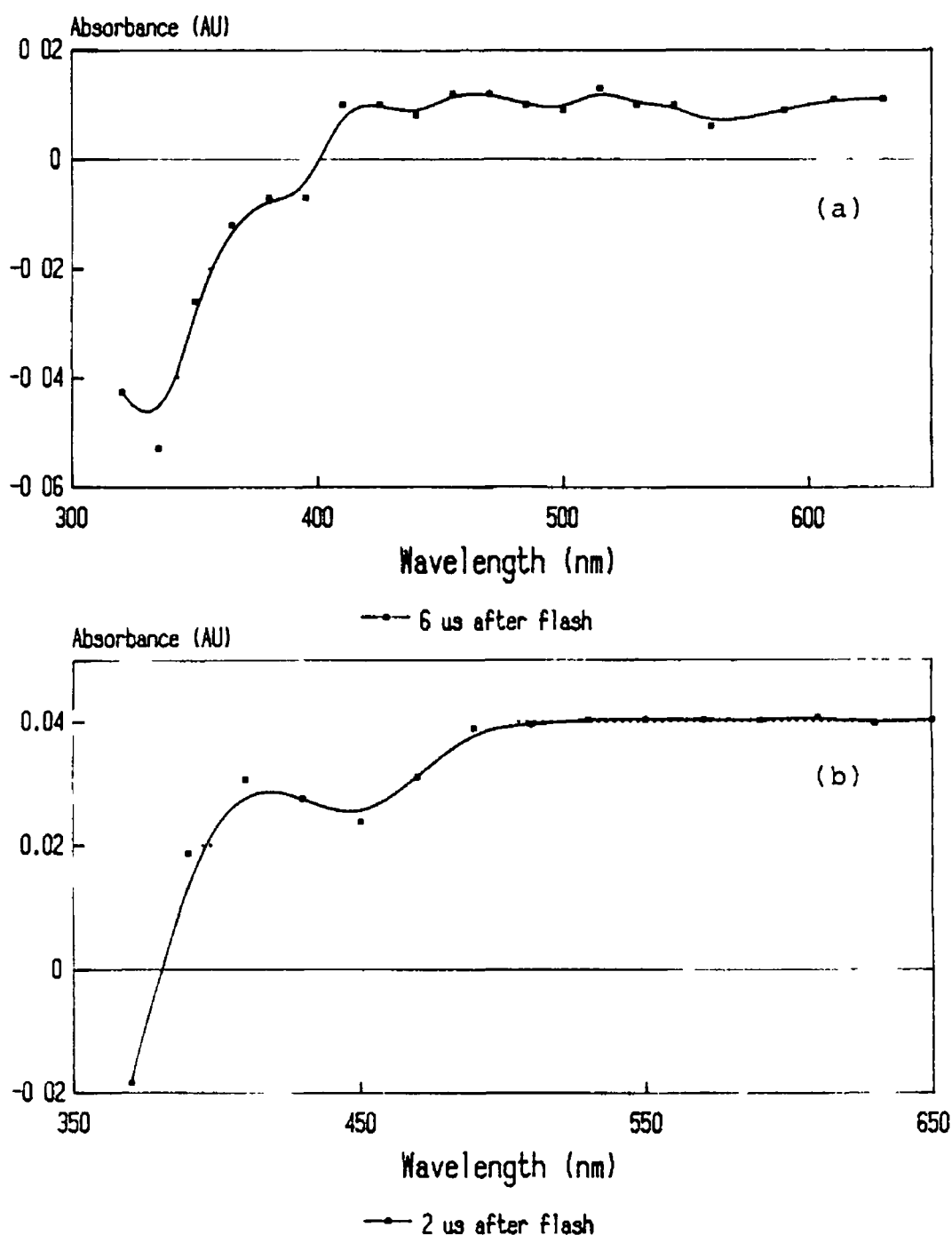
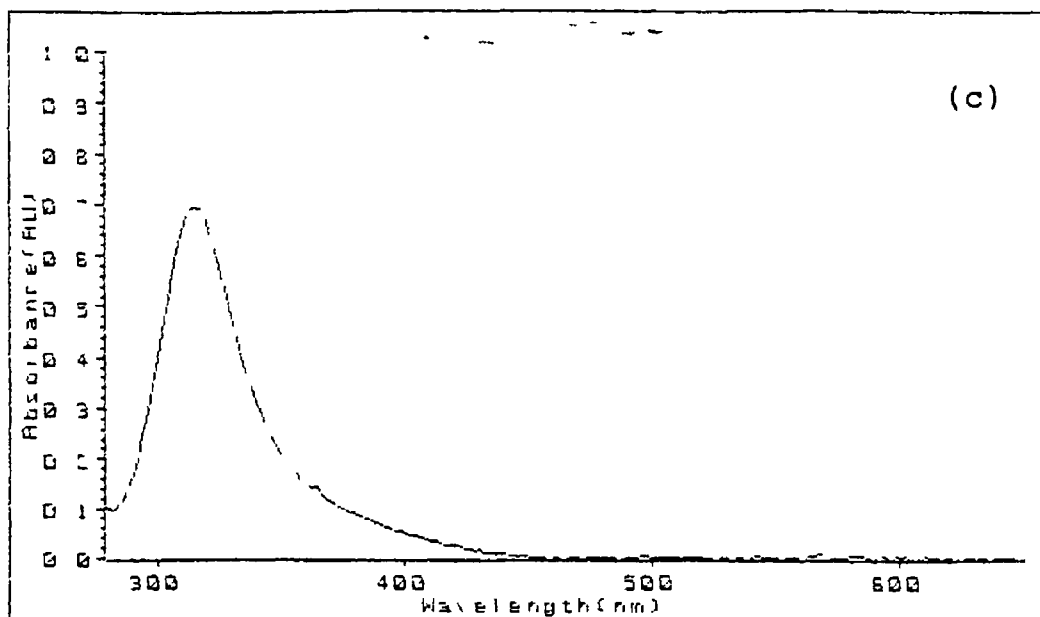


Figure 2.2.3.1: (c) uv/vis Spectrum of $\text{ArCr}(\text{CO})_3$ in cyclohexane solution.

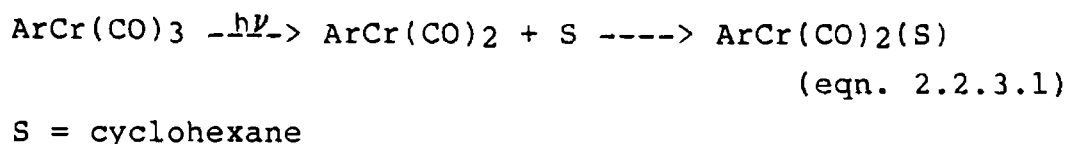


As with $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$, studies on the photolysis of $\text{ArCr}(\text{CO})_3$ in inert and reactive matrices have been carried out by several research groups.^{20,24,34} These studies have indicated that loss of CO to form $\text{ArCr}(\text{CO})_2(\text{X})$ (X = matrix species) is the primary photoreaction. These results coupled with our previous work on the flash photolysis of the isoelectronic $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$ complexes suggested that the first observed species was $\text{ArCr}(\text{CO})_2(\text{S})$ (S = cyclohexane).⁷¹ Loss of the arene ligand has been reported as a primary photoprocess.⁴⁰ The effect of saturating the $\text{ArCr}(\text{CO})_3$

cyclohexane solution with carbon monoxide was investigated and showed that loss of CO was the primary reaction upon photolysis.

2.2.3.2 Flash Photolysis of $\text{ArCr(CO)}_2(\text{S})$ in CO Saturated Cyclohexane

Table 2.2.3.1 shows the effect of the presence of CO in solution, on the yield and lifetime of the initially observed species. It is evident from this table that CO does not seem to affect the yield of the first species observed but it does affect its lifetime. This of course was the case for the initially observed species in the manganese and iron systems. Therefore loss of CO is thought to be the primary photoreaction in this system and is assumed to be followed by co-ordination of a solvent molecule to the co-ordinatively unsaturated ArCr(CO)_2 fragment (equation 2.2.3.1).



The results in Table 2.2.3.1 also indicate that loss of Ar is not a significant photoprocess (upon excitation of ArCr(CO)_3 at 355nm) as the effect on the lifetime of the first species is constant at all wavelengths. Transient IR spectroscopy was not available to us and therefore spectroscopic verification that the initially observed species is the dicarbonyl molecule was not possible.

Table 2.2.3.1: (1) The effect of CO on yield of $\text{ArCr}(\text{CO})_2(\text{S})$ (concentration of $\text{ArCr}(\text{CO})_3 = 6.4 \times 10^{-4} \text{ mol-l dm}^{-3}$).

	Absorbance (A.U.) at $2\mu\text{s}$ after the flash		
	Wavelength in nm		
	480nm	380nm	580nm
CO absent	.060	.003	.067
CO present	.055	.002	.061
% difference	-8	-33	-7.5

(11) The effect of CO on the lifetime^a of species I (concentration of $\text{ArCr}(\text{CO})_3 = 6.4 \times 10^{-4} \text{ mol-l dm}^{-3}$).

Wavelength in nm	Lifetime of $\text{ArCr}(\text{CO})_2(\text{S})$ in absence of CO (μs)	Lifetime of $\text{ArCr}(\text{CO})_2(\text{S})$ in presence of CO (μs)
380	11.48	6.27
580	13.90	5.62

^a Lifetime is given as $1/k_{\text{obs}}$

2.2.3.3 The Reaction of $\text{ArCr}(\text{CO})_2(\text{S})$ with nucleophiles

16 valence-electron species have been shown to be very reactive towards ligands and this was the case also with $\text{ArCr}(\text{CO})_2(\text{S})$. The reactivity of $\text{CpMn}(\text{CO})_2(\text{S})$ and $\text{CbFe}(\text{CO})_2(\text{S})$ towards different nucleophiles varied considerably and showed no underlying trend between nucleophiles. The corresponding co-ordinatively unsaturated $\text{ArCr}(\text{CO})_2$ fragment was expected to be equally reactive towards nucleophiles and undergo the same type of reactions. Table 2.2.3.2 shows the bimolecular rate constants for the reaction of $\text{ArCr}(\text{CO})_2(\text{S})$ with 1-hexene, 4-picoline and CO. As expected all reactions were found to follow pseudo-first-order kinetics. The significant differences in reaction rates indicate that formation of $\text{ArCr}(\text{CO})_2(\text{X})$ ($\text{X} = 4\text{-picoline or 1-hexene}$) was affected by the nature of the ligand; this is possibly a steric effect. The trend in reaction rates is similar to the manganese system (see Table 2.2.1.5).

Table 2.2.3.2: Bimolecular rate constants^a ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$) for the reaction of $\text{ArCr}(\text{CO})_2(\text{S})$ ($\text{S} = \text{cyclohexane}$) with various nucleophiles at 295K.

Ligand	Rate constants ^b ($\times 10^7$) for the reaction of ligand with $\text{ArCr}(\text{CO})_2(\text{S})$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)
1-hexene	1.3
4-picoline	8.2
CO	6.6

(a) These rate constants have been corrected to allow for the formation of $\text{Ar}_2\text{Cr}_2(\text{CO})_5$ (vide infra).

(b) Average of three separate measurements.

2.2.3.4 A Study of the Activation Parameters for the Formation of $\text{ArCr(CO)}_2(\text{X})$ ($\text{X} = 1\text{-hexene, 4-picoline}$).

Activation parameters for the formation of $\text{ArCr(CO)}_2(\text{X})$ were measured and the results detailed in Tables 2.2.3.3 and 2.2.3.4 and shown graphically in Figures 2.2.3.2 and 2.2.3.3.

Table 2.2.3.3: Experimental data for the determination of the energy, entropy and enthalpy of Activation for the formation of $\text{ArCr(CO)}_2(4\text{-picoline})$.

(a) Concentration of $\text{ArCr(CO)}_3 = 1.1 \times 10^{-4} \text{ mol dm}^{-3}$.
Concentration of 4-picoline = $1.88 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ ($\times 10^3$)	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.41	18.09	12.41
3.51	17.77	12.12
3.48	17.87	12.21
3.45	17.95	12.28
3.39	18.13	12.44
3.36	18.19	12.49
3.33	18.23	12.53
3.28	18.50	12.78
3.25	18.52	12.79

Arrhenius Plot.

Slope = 2852 ± 169

Int. = $27.8 \pm .04$

Corr. coeff. = 0.988

Eyring Plot.

Slope = 2555 ± 163

Int. = $21.1 \pm .04$

Corr. coeff = 0.986

$\Rightarrow E_a = 21.8 \pm 1.4 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 19.6 \pm 1.4 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -28.5 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

(b) Concentration of $\text{ArCr}(\text{CO})_3 = 1.57 \times 10^{-4} \text{ mol dm}^{-3}$.
 Concentration of 4-picoline = $2.05 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.40	18.13	12.45
3.53	17.65	12.00
3.46	17.88	12.21
3.41	17.96	12.28
3.37	18.02	12.33
3.32	18.17	12.46
3.28	18.38	12.66
3.41	17.96	12.27

Arrhenius Plot.

Slope = 2625 ± 319

Slope = $26.9 \pm .07$

Corr. coeff. = 0.9583

Eyring Plot.

Slope = 2352 ± 326

Slope = $20.33 \pm .07$

Corr. coeff. = 0.9470

$\Rightarrow E_a = 21.8 \pm 2.7 \text{ KJ mol}^{-1}$, $\Delta H^\ddagger = 19.6 \pm 2.7 \text{ KJ mol}^{-1}$, and $\Delta S^\ddagger = -28.5 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$.

(c) Concentration of $\text{ArCr}(\text{CO})_3 = 1.61 \times 10^{-4} \text{ mol dm}^{-3}$.
 Concentration of 4-picoline = $1.70 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.44	18.16	12.49
3.50	17.85	12.20
3.46	17.99	12.32
3.43	18.14	12.47
3.41	18.22	12.54
3.37	18.25	12.55

Table 2.2.3.3:cont'd'

3.33	18.39	12.69
3.30	18.42	12.71
3.28	18.47	12.75
3.24	18.62	12.91
3.39	18.17	12.48

Arrhenius Plot.

Slope = 2659 +/- 194

Int. = 27.22 +/- .05

Corr. coeff. = 0.977

Eyring Plot.

Slope = 2404 +/- 201

Int. = 20.67 +/- .05

Corr. coeff. = 0.970

=> $E_a = 22.1 \pm 1.6 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 20.0 \pm 1.6 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -25.6 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$.

Table 2.2.3.4: Experimental data for the determination of the energy, entropy and enthalpy of Activation for the formation of $\text{ArCr(CO)}_2(1\text{-hexene})$.

(a) Concentration of $\text{ArCr(CO)}_3 = 1.15 \times 10^{-4} \text{ moldm}^{-3}$.

Concentration of 1-hexene = $5.04 \times 10^{-3} \text{ moldm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.44	16.13	10.45
3.39	16.28	10.59
3.34	16.46	10.76
3.30	16.55	10.83
3.26	16.64	10.91
3.22	16.74	11.00
3.18	16.84	11.09
3.22	16.65	10.91
3.26	16.60	10.87

Table 2.2.3.4:cont'd

Arrhenius Plot.

Slope = 2519 +/- 175

Int. = 24.83 +/- .04

Corr. coeff. = 0.983

Eyring Plot.

Slope = 2240 +/- 178

Int. = 18.19 +/- .04

Corr. coeff. = 0.979

=> $E_a = 20.9 \pm 1.5 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 18.62 \pm 1.5 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -46.24 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

(b) Concentration of $\text{ArCr}(\text{CO})_3 = 1.46 \times 10^{-4} \text{ moldm}^{-3}$.

Concentration of 1-hexene = $3.20 \times 10^{-3} \text{ moldm}^{-3}$.

1/K.
x 10³

Ln(R)

Ln(R_t)

3.45

15.94

10.27

3.41

16.01

10.33

3.36

16.20

10.50

3.31

16.33

10.62

3.27

16.56

10.84

3.52

16.45

10.72

3.41

16.02

11.34

3.53

15.69

10.05

Arrhenius Plot.

Slope = 2963 +/- 229

Int. = 26.15 +/- .06

Corr. coeff. = 0.982

Eyring Plot.

Slope = 2963 +/- 229

Int. = 19.42 +/- .06

Corr. coeff. = 0.978

=> $E_a = 24.6 \pm 1.8 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 22.1 \pm 1.8 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -36.00 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

(c) Concentration of $\text{ArCr}(\text{CO})_3 = 1.41 \times 10^{-4} \text{ mol dm}^{-3}$.
 Concentration of 1-hexene = $8.00 \times 10^{-3} \text{ mol dm}^{-3}$.

$1/K$ $\times 10^3$	$\text{Ln}(R)$	$\text{Ln}(R_t)$
3.40	16.31	10.63
3.37	16.43	10.74
3.33	16.58	10.88
3.26	16.73	11.00
3.22	16.91	11.17
3.18	16.95	11.20
3.51	15.95	10.30
3.46	16.13	10.46

Arrhenius Plot.

Slope = 3050 ± 113

Int. = $26.84 \pm .04$

Corr. coeff. = 0.996

Eyring Plot.

Slope = 2789 ± 118

Int. = $20.12 \pm .04$

Corr. coeff. = 0.995

$\Rightarrow E_a = 25.7 \pm 1.0 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 23.2 \pm 1.0 \text{ KJmol}^{-1}$, and $\Delta S^\ddagger = -30.2 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Figure 2.2.3.3: Arrhenius (a) and Eyring (b) plots for the formation of $\text{ArCr}(\text{CO})_2(1\text{-hexene})$.

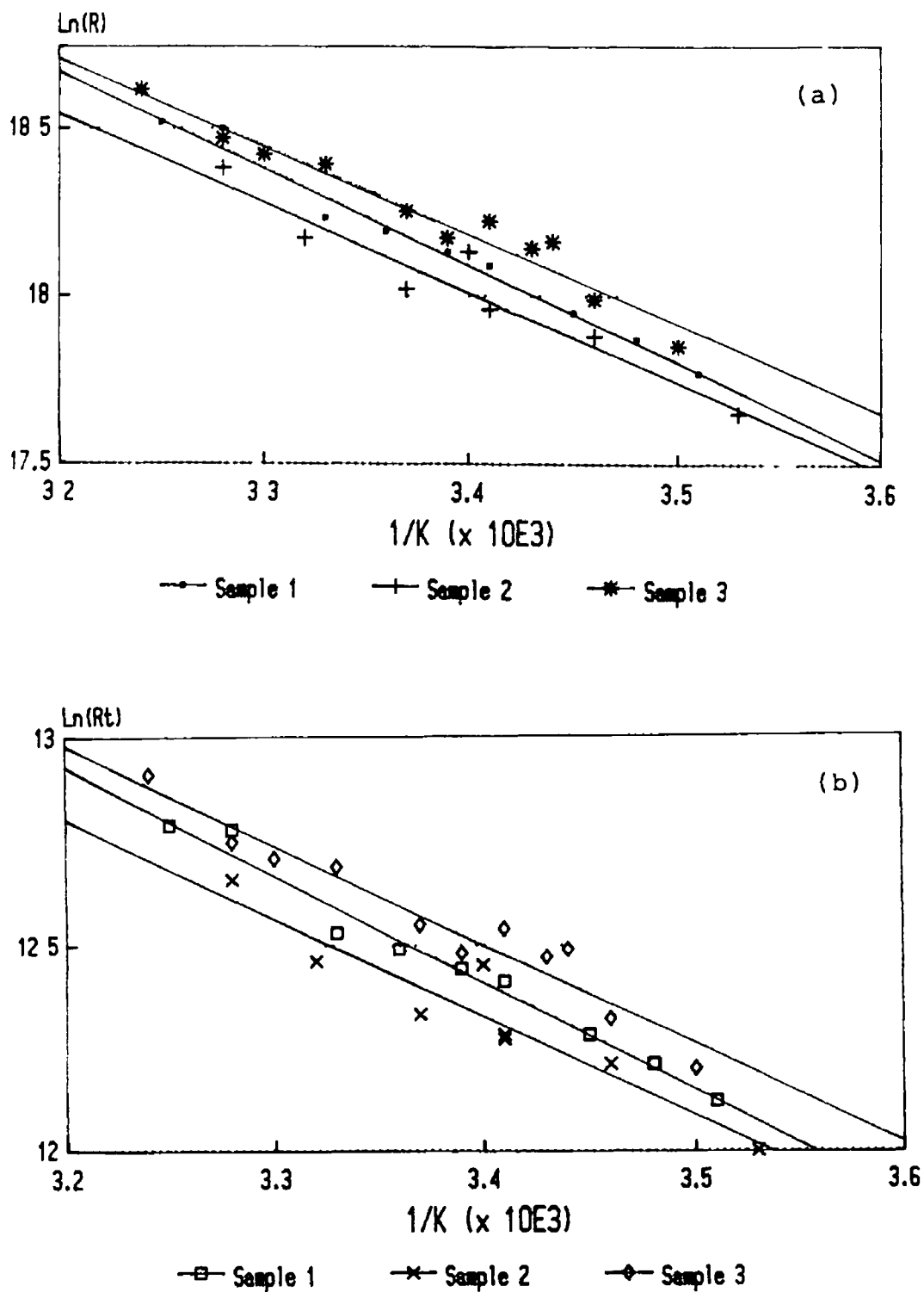
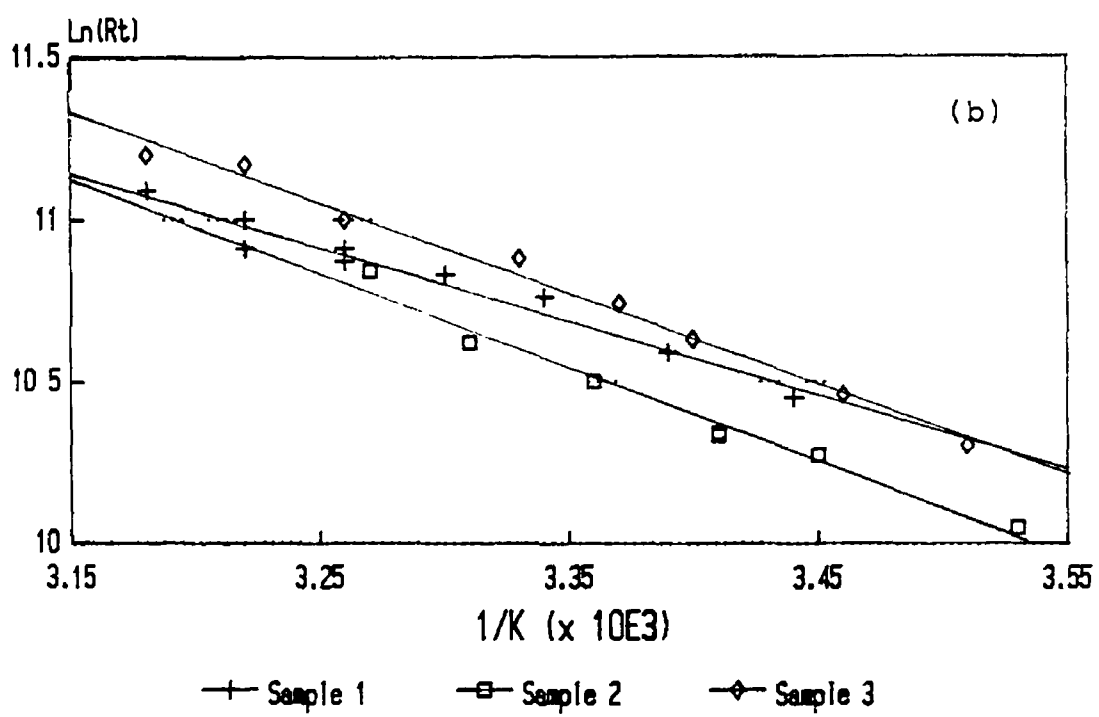
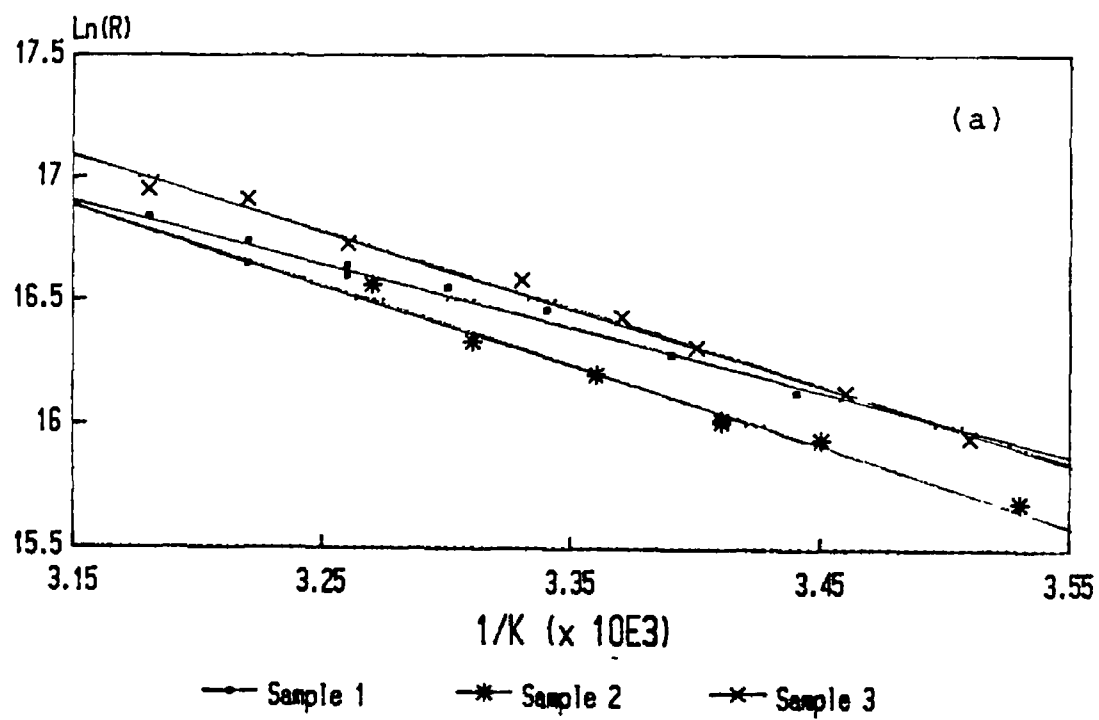
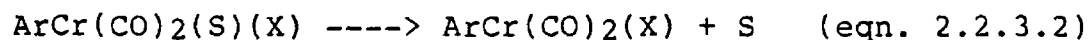
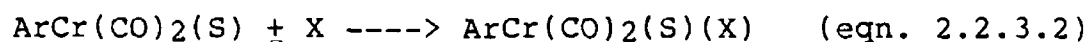


Figure 2.2.3.2: Arrhenius (a) and Eyring (b) plots for the formation of $\text{ArCr(CO)}_2(4\text{-picoline})$.



The thermodynamic parameters determined from these sets of data are similar in magnitude to those previously determined for $\text{CpMn(CO)}_2(\text{S})$ and $\text{CbFe(CO)}_2(\text{S})$ (see Sections 2.2.1.13 and 2.2.2.4). The negative values of $\Delta S^\ddagger$ indicate the associative nature of the transition state. These parameters are consistent with the following reaction scheme where equation 2.2.3.2 is the rate determining step;

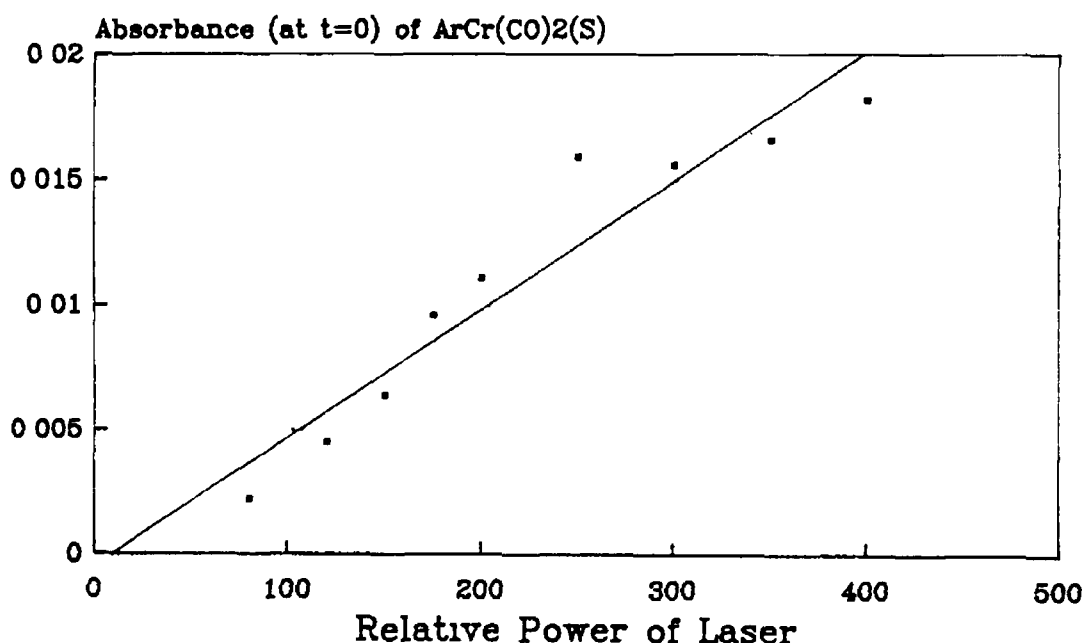


Hill and Wrighton studied the reaction of photogenerated ArCr(CO)_2 with trisubstituted silanes at low temperatures but were unable to measure activation parameters due to experimental problems involved.²⁵

2.2.3.5 A Study of the Excited State Photochemistry of ArCr(CO)_3

$\text{ArCr(CO)}_2(\text{S})$ is formed as a result of one photon excitation of the parent tricarbonyl. This was confirmed, in an analogous way to that for CpMn(CO)_3 and CbFe(CO)_3 systems, by measuring the absorbance of $\text{ArCr(CO)}_2(\text{S})$ as the laser power was varied. The results are shown graphically in Figure 2.2.3.4. This study was carried out using the Nd-YAG laser (wavelength = 355nm) as the weak nature of the transients produced upon flash photolysis at 308nm made it difficult to accurately measure changes in absorbance.

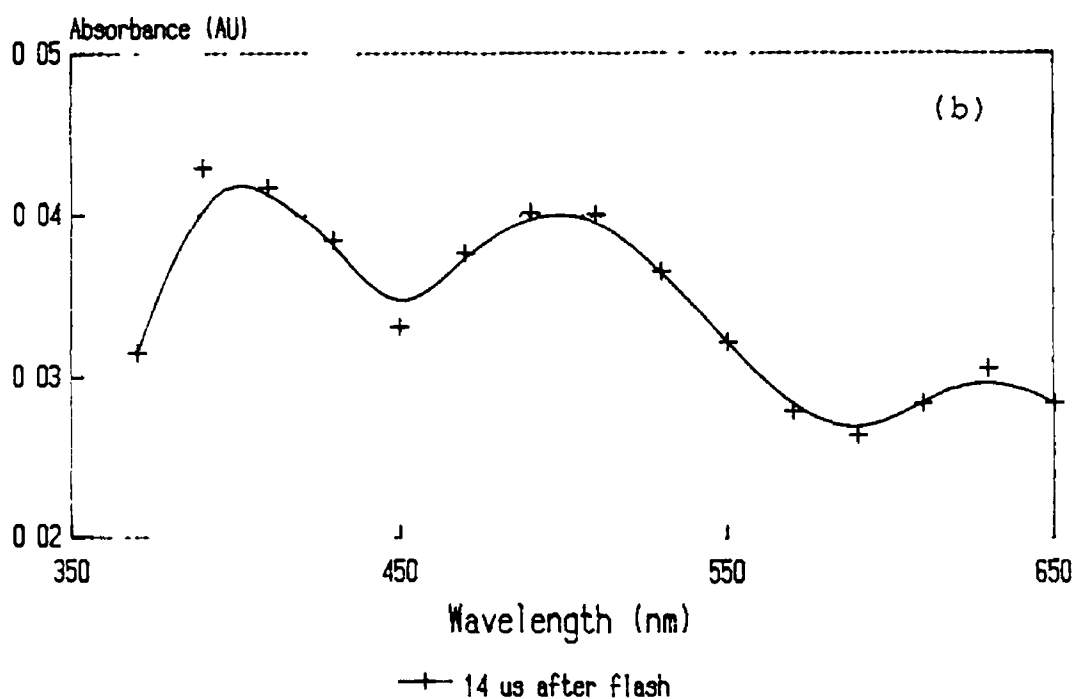
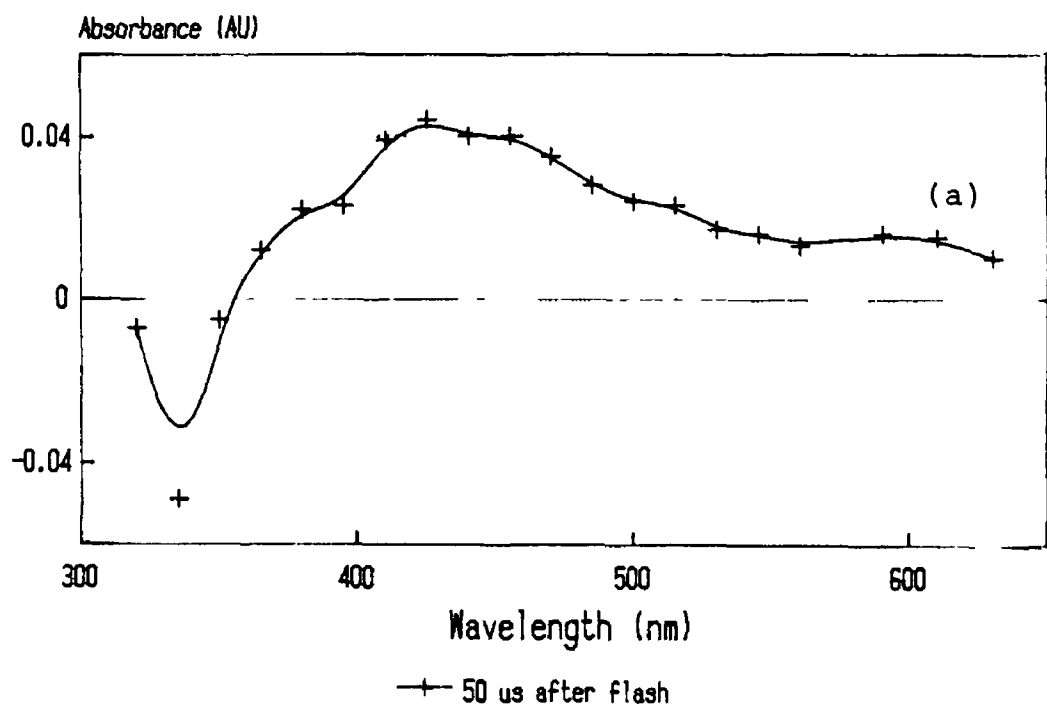
Figure 2.2.3.4: Plot showing the variation in absorbance of $\text{ArCr(CO)}_2(\text{S})$, recorded $2\mu\text{s}$ after the laser flash, with laser flash intensity.



2.2.3.6 The Reactions of $\text{ArCr(CO)}_2(\text{S})$

The reaction of photogenerated $\text{ArCr(CO)}_2(\text{S})$ in the absence of any added nucleophiles were studied upon excitation at 355nm and at 308nm. Upon excitation at 308nm a second species (Species 11) was seen to form on a μs timescale and this complex had an absorption maximum in the visible region at 425 nm. Figure 2.2.3.5(a) shows the spectrum recorded at 50 μs . Any bands in the lower uv/vis region would be obscured because of depletion of the parent tricarbonyl. The second observed species upon excitation at 355nm showed quite different features (Figure 2.2 3.5(b)).

Figure 2.2.3.5: uv/vis Difference spectrum, recorded following the flash photolysis (at 308nm (a) and at 355nm (b)) of ArCr(CO)_3 in cyclohexane solution.



This species exhibited absorption maxima at 510nm and 630nm in the visible region together with a further band in the uv region at ca. 390nm (see also spectrum of parent $\text{ArCr}(\text{CO})_3$). This species was formed on a much faster time scale than that observed upon excitation at 308nm. The differences in spectrum and lifetime of this second species can be explained in the following way;

the extinction coefficient of $\text{ArCr}(\text{CO})_3$ at 308nm is very large ($9243 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) thus necessitating the use of low concentrations of tricarbonyl in studies at this wavelength. Kelly et al.⁵⁴ have reported on the effects on impurities in cyclohexane solvent on the recorded spectra of the transients produced. This effects are more pronounced in systems in which the photoactive species was in low concentrations. The extinction coefficient of $\text{ArCr}(\text{CO})_3$ at 355nm is significantly lower ($2464 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and thus allowing a greater concentration of $\text{ArCr}(\text{CO})_2(\text{S})$ in solution. Kelly et al. have also shown that the presence of carbon monoxide in solution also greatly decreases the effects of impurities.

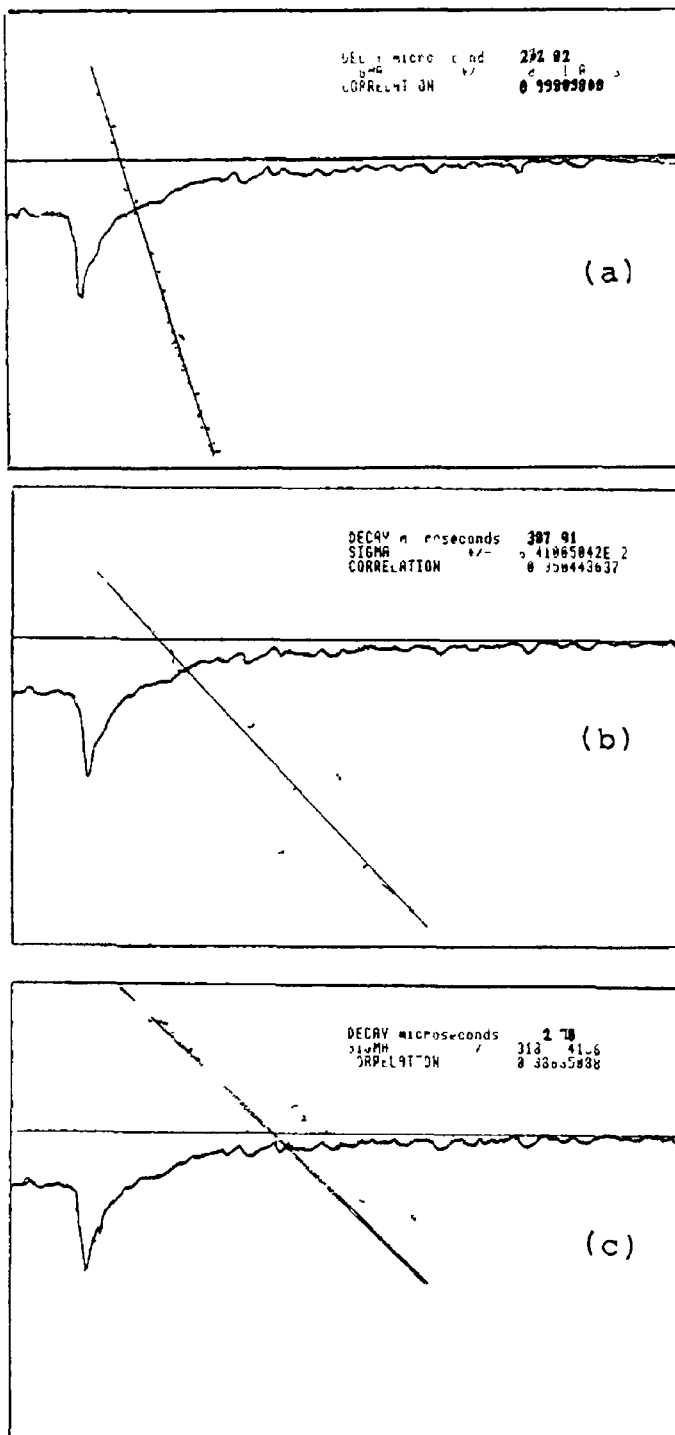
2.2.3.7 The Dependence of the Formation of Species II on the Concentration of $\text{ArCr}(\text{CO})_3$

Previous results on $\text{CpMn}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$ systems (see Section 2.2.1 and Section 2.2.2) indicated that these species formed a dinuclear complex on loss of a carbonyl ligand. This species II was thought to be a dimer and as such its rate of formation should increase as the concentration of parent tricarbonyl is increased. The rate of formation of the second species upon excitation at 355nm was greatly increased compared to excitation at 308nm, and kinetic data were found to be more reliable at the latter wavelength. Analysis of traces recorded at different concentrations of $\text{ArCr}(\text{CO})_3$ (upon excitation at 308nm),

but at the same wavelength, showed quite a variation. Figure 2.2.3.6 shows the analysis of the same trace in three different ways;

Figure 2.2.3.6: Kinetic traces recorded at 370nm, following the flash photolysis (308nm) of $\text{ArCr}(\text{CO})_3$ in cyclohexane solution.

All three traces are identical and each plot differs only in the method of analysis. Trace (a) was analysed over the initial part of the grow-in by first order kinetics. This was achieved by only analysing points over a short timescale. Trace (b) was analysed over an extended timescale, again by first order kinetics. Trace (c) corresponds to analysis of the data points by second order analysis. The "straight" line plots correspond to the fit of the analysis data points, to each kinetic plot.



(i) The initial part of the grow-in followed first order kinetics to a very good degree. The baseline is taken where the best fit for the resulting analysis occurs.

(ii) The baseline of the grow-in appears to flatten out very slowly and analysis over the extended period shows the kinetics vary from first order.

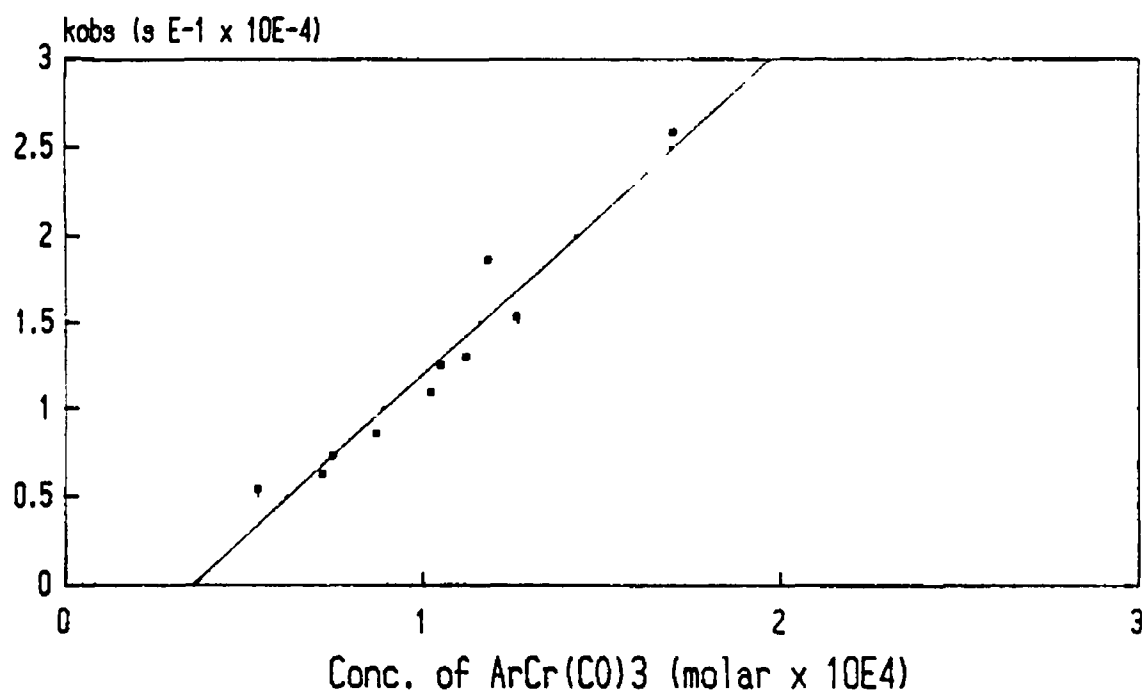
(iii) The observed grow-in did not observe second order kinetics.

The recorded traces were analysed over the initial grow-in period and the results given in Table 2.2.3.5.

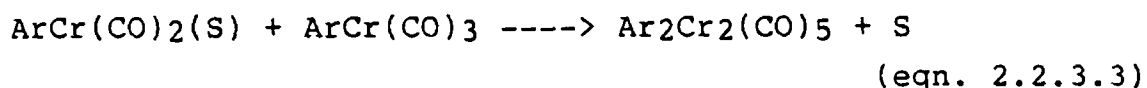
Table 2.2.3.5: Values for the rate constant for the formation of the dinuclear species at various concentrations of $\text{ArCr}(\text{CO})_3$.

Concentration of $\text{ArCr}(\text{CO})_3$ $\text{mol dm}^{-3} (\times 10^4)$	$k_{\text{obs}}(\text{s}^{-1})$
0.54	5405
0.72	6250
0.75	7300
0.87	8547
1.02	10934
1.05	12500
1.12	12987
1.18	18640
1.26	15384
1.70	25873

Figure 2.2.3.7: Plot showing the variation in k_{obs} (s^{-1}), for the formation of $Ar_2Cr_2(CO)_5$, with concentration of $ArCr(CO)_3$ ($mol\ dm^{-3}$).



Obviously because of the subjective method of analysis these results are not to be taken as absolute. However the trend in these results is quite definite. Figure 2.2.3.7 clearly demonstrates that as the concentration of parent tricarbonyl is increased the rate of formation of Species II increases and this indicates the dimeric nature of Species II (eqn 2.2.3.3). Preliminary studies on the initially observed species upon flash photolysis at 355nm indicated that its lifetime also depended upon the concentration of $ArCr(CO)_3$.



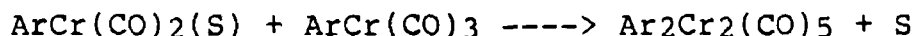
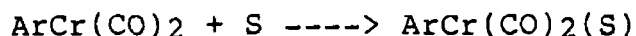
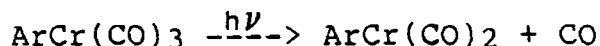
2.2.3.8 The Effect of CO on the Dinuclear Species

The assumption that the second observed species was formed via a decarbonylation reaction (equation 2.2.3.1) was confirmed upon examining the effects of carbon monoxide on the yield of this species. Table 2.2.3.6 summarises these results.

Table 2.2.3.6: The effect of carbon monoxide on the yield of the dinuclear species (concentration of $\text{ArCr(CO)}_3 = 6.4 \times 10^{-4} \text{ mol dm}^{-3}$)

	Absorbance(A.U.) 2 μ s after flash 480	Absorbance(A.U.) 2 μ s after flash 380 (Wavelength in nm)	Absorbance(A.U.) 2 μ s after flash 580
CO absent	0.131	0.115	0.115
CO present	0.049	0.051	0.061
% difference	-63%	-56%	-47%

These results are consistent with the following reaction scheme;



2.2.3.9 The Reaction to Produce the Dimeric Species

The spectrum recorded at $400\mu\text{s}$ together with that of the dimer (recorded at $50\mu\text{s}$), upon excitation at 308nm , is given in Figure 2.2.3.8. These spectra are practically identical and would appear to be due to the same species. Figure 2.2.3.9 shows a trace typical for the grow-in at 350nm . The behaviour recorded on these traces i.e. the apparent overlap of two grow-ins, indicated that a third transient species was perhaps present as was the case with CbFe(CO)_3 . This would also explain why the observed grow-in over extended timescales did not follow first order kinetics.

The presence of this third species was confirmed on studying the photoinitiated reactions of ArCr(CO)_3 in carbon monoxide saturated cyclohexane. Figure 2.2.3.10 shows the spectra recorded at 14 and $44\mu\text{s}$. Thus the presence of a third species is confirmed. Its spectrum is not remarkably different from that of the dimeric species, exhibiting absorption bands at 490nm , 650nm and ca. 370nm .

Figure 2.2.3.8: uv/vis Difference spectra recorded following the flash photolysis (308nm) of ArCr(CO)_3 in cyclohexane solution.

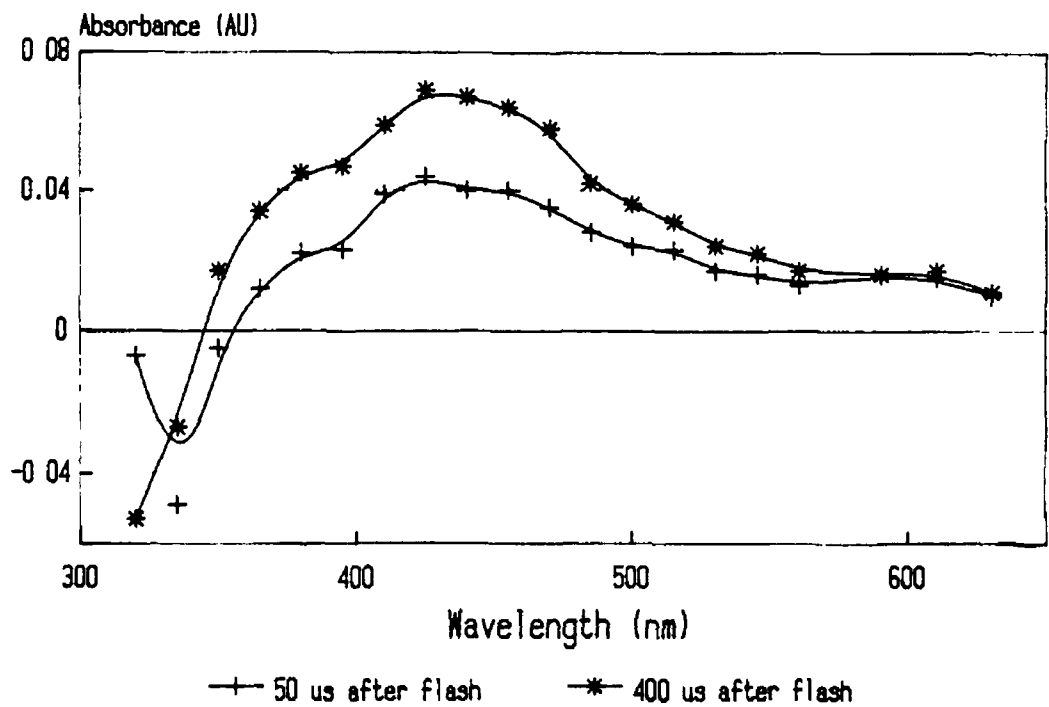


Figure 2.2.3.9: Kinetic trace recorded at 350nm, following the flash photolysis (308nm) of ArCr(CO)_3 in cyclohexane solution.

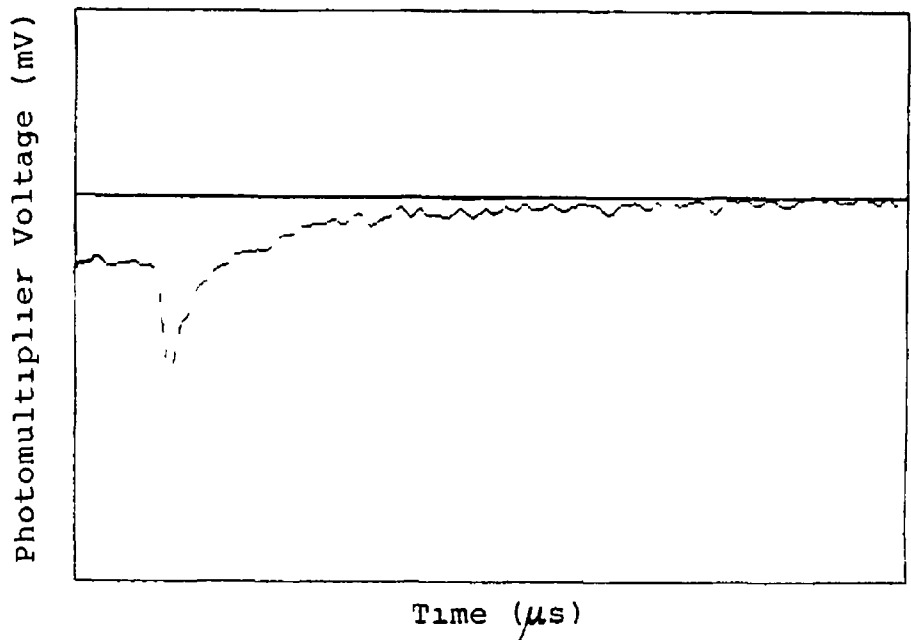
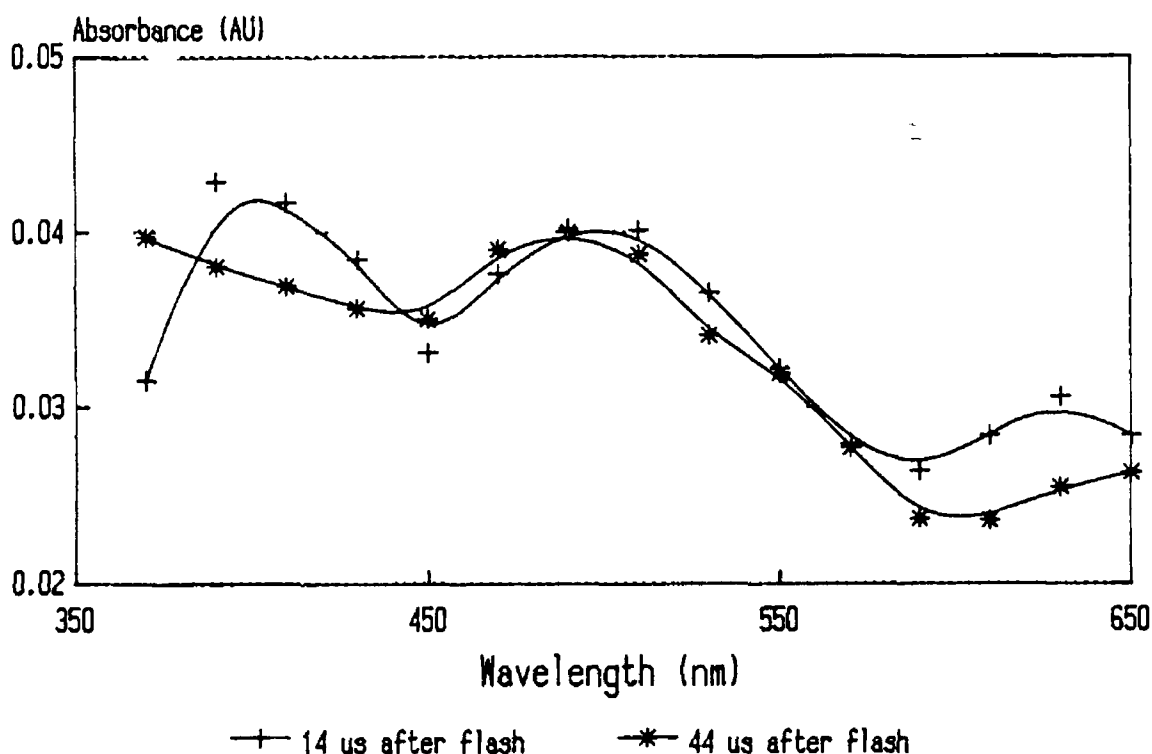


Figure 2.2.3.10: uv/vis Difference spectra recorded following the flash photolysis (355nm) of ArCr(CO)_3 in cyclohexane solution.



If this third species was formed via a decarbonylation process then the effect of CO on its yield and the lifetime of Species II should be marked. Unfortunately the overlap of the spectra of the dinuclear species with this third species is considerable and so we were unable to accurately determine the lifetime of either species. Species III is stable over at least two seconds. The uv/vis spectrum of a sample of ArCr(CO)_3 in cyclohexane after recording the transient spectrum of the dimer showed absorption centred around 510nm and thus species III must not be stable in solution over extended timescales.

2.2.3.10 A Study of the Activation Parameters for the formation of $\text{Ar}_2\text{Cr}_2(\text{CO})_5$

In order to measure the activation parameters for the formation of the dimer a decision about the exact position of the baseline had to be made. Such decisions are purely subjective and therefore lead to significant errors. Table 2.2.3.7 shows some typical results. The only definite conclusions to be made was that the reaction was endothermic indicated by the increase in k_{obs} as temperature increases.

Table 2.2.3.7: k_{obs} for the formation of the dinuclear species at various temperatures (concentration of $\text{ArCr}(\text{CO})_3 = 1.28 \times 10^{-4} \text{ mol dm}^{-3}$).

Temperature in K	k_{obs} (s^{-1})
285	3333
288	4310
294	5000
295	5435
298	5988
303	8695

2.2.4 SUMMARY

Previous studies on the photochemistry of the isoelectronic $\text{LM}(\text{CO})_3$ compounds showed their photochemical reactions to be similar ($\text{LM}(\text{CO})_3 = \text{CpMn}(\text{CO})_3, \text{CbFe}(\text{CO})_3$ and $\text{ArCr}(\text{CO})_3$). Photolysis in argon and methane matrices and low temperature alkanes showed loss of CO as the primary photoprocess. In our studies, on the solution photochemistry of the three compounds, loss of CO was also observed as the initial reaction to generate an unsaturated $\text{LM}(\text{CO})_2$ ($\text{LM} = \text{CpMn}, \text{CbFe},$ or ArCr) fragment which was assumed to be weakly co-ordinated to a solvent molecule. In the trir flash photolysis studies the bands of $\text{CpMn}(\text{CO})_2(\text{solvent})$ were assigned to such a dicarbonyl species based on ^{13}C studies and the similarities between these bands and those of the $\text{CpMn}(\text{CO})_2$ fragment in hydrocarbon glasses.

In studies on photolysis products of $\text{ArCr}(\text{CO})_3$ and $\text{CbFe}(\text{CO})_3$, loss of Ar and Cb has been reported as the primary photoreaction. These results were based on experiments whereby photolysis of these tricarbonyls in presence of ^{13}C labelled CO, Ar or Cb showed exchange of both arene and carbonyl ligand. However the relative yields of the two processes was 10:1 CO : organic ligand and the presence of CO was found to inhibit the loss of the organic ligand (indicating organic ligand photosubstitution must occur through intermediacy of a dicarbonyl species.) In our studies loss of arene was not seen as a primary photoprocess though a low quantum efficiency for this process may prevent its detection. Cp loss has never been claimed as a primary photoproduct upon photolysis of $\text{CpMn}(\text{CO})_3$ (though similar studies to those described above have not been carried out).

The reactivity of, the essentially co-ordinatively unsaturated $\text{LM}(\text{CO})_2(\text{solvent})$ complexes was studied by measuring the kinetics and thermodynamic parameters for

reaction of the dicarbonyl with various nucleophilic ligands (Table 2.2.4.1 and Table 2.2.4.3)

Table 2.2.4.1: Bimolecular rate constants
($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$) ($\times 10^{-6}$) for the
reaction of $\text{LM}(\text{CO})_2(\text{S})$ (S = cyclohexane;
LM = CpMn, CbFe, or ArCr) with various
nucleophilic ligands.

Ligand	Carbonyl		
	CpMn(CO) ₃	CbFe(CO) ₃	ArCr(CO) ₃
CO	0.32	0.30	66.00
1-hexene	0.30	7.00	12.70
4-picoline	30.84	4.10	81.80

In general the arene complex is by far the most reactive species, reacting in general, an order of magnitude faster with CO, 1-hexene and 4-picoline. This trend in reactivities follows that reported for the reaction of photogenerated $\text{LM}(\text{CO})_2$ with substituted silanes. The reactivity trend in Wrighton's study appeared to correlate with the electron density of the metal fragment as evidenced by the stretching frequencies, the more reactive fragments have the lower average stretching frequencies (see Table 2.2.4.2).

Table 2.2.4.2: Ir spectroscopic data^a for $\text{ML}(\text{CO})_2(\text{X})$
(X= matrix species or ligand) compounds.

Complex	T, K	$\nu(\text{CO}), \pm 2\text{cm}^{-1}$
$\text{CbFe}(\text{CO})_2^{\text{c}}$	12	1936, 2005
"	100	1923, 1991
$\text{CbFe}(\text{CO})_2(\text{HSiEt}_3)^{\text{b}}$	100	1950, 2010
$\text{CpMn}(\text{CO})_2^{\text{c}}$	12	1903, 1972
"	100	1880, 1950
$\text{CpMn}(\text{CO})_2(\text{HSiEt}_3)^{\text{b}}$	100	1914, 1977
$\text{ArCr}(\text{CO})_2^{\text{c}}$	12	1885, 1937
$\text{ArCr}(\text{CO})_2(\text{HSiEt}_3)^{\text{b}}$	100	1821, 1921

a In methylcyclohexane solvent unless otherwise noted

b In HSiEt_3

c In Ar, from reference 34.

In order to understand the reactivity differences between the three complexes a study of the activation parameters for these reactions was carried out and the results summarised in Table 2.5.2 together with Wrighton's results for the oxidative addition reaction of the dicarbonyls with HSiEt_3 .²⁵

TABLE 2.2.4.3: Thermodynamic parameters for the reaction of $\text{LM}(\text{CO})_2(\text{cyclohexane})$ with various ligands.

Ligand	$\text{CpMn}(\text{CO})_3$		$\text{ArCr}(\text{CO})_3$		$\text{CbFe}(\text{CO})_3$	
	E_a	$\Delta S^\ddagger$	E_a	$\Delta S^\ddagger$	E_a	$\Delta S^\ddagger$
1-hexene	31	-41	24	-34	26	-55
4-picoline	31	-3	23	-25	29	-30
HSiEt_3^c	33	-28	--	--	46	47

a E_a values are in KJmol^{-1} and have errors of $\pm 4 \text{ KJmol}^{-1}$ in each value

b $\Delta S^\ddagger$ values are in $\text{Jmol}^{-1}\text{K}^{-1}$ and errors are ca. = $\pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

c reference 25

For a given metal, the activation energy values vary little between $\text{LM}(\text{CO})_2(\text{X})$ complexes ($\text{X} = 4\text{-picoline, 1-hexene}$). Such small variations are consistent with a dissociative mechanism. Although the activation energies for the formation of $\text{ArCr}(\text{CO})_2(\text{X})$ complexes are smaller than the corresponding manganese and iron complexes, it does not account for the large differences in the reactivity of the $\text{LM}(\text{CO})_2(\text{S})$ complexes. These reactivity differences may be as a result of the smaller size of the chromium atom i.e the greater electron density on the metal atom, as has been already suggested by Wrighton et al.²⁵

Although the errors in $\Delta S^\ddagger$ are quite large, the large negative values of $\Delta S^\ddagger$, which are consistently more negative for 1-hexene than 4-picoline, indicated that the rate determining step had considerable associative character. The difference in $\Delta S^\ddagger$ values for the two ligands is perhaps a reflection of the greater steric hindrance in bonding of the 1-hexene molecule to photogenerated $\text{LM}(\text{CO})_2(\text{S})$ (however the large errors inherent in these $\Delta S^\ddagger$ values mean that no such definite conclusions can be made).

The lifetime of $\text{LM}(\text{CO})_2(\text{S})$ (in the absence of any added nucleophile) was shown for the three carbonyl complexes to be dependent on the concentration of $\text{LM}(\text{CO})_2(\text{S})$. $\text{CpMn}(\text{CO})_2(\text{S})$ was shown to form the dinuclear $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ complex, whose spectrum was recorded by trir. It was therefore assumed that $\text{CbFe}(\text{CO})_2(\text{S})$ and $\text{ArCr}(\text{CO})_2(\text{S})$ reacted in a similar manner, and this has been shown to be the case. The dependence of the lifetime of these complexes on the concentration of the parent tricarbonyl was consistent with this assumption. However these latter two complexes were not as stable as the dinuclear $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ species and underwent further reactions in solution. The $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ molecule itself was not stable in room temperature solution for $>2\text{s}$. These dimeric complexes may undergo decarbonylation or rearrangement processes.

Initial attempts to isolate these dinuclear complexes were unsuccessful, but it is thought possible that such complexes may be synthesised by low temperature photolysis methods.

2.3 EXPERIMENTAL SECTION

2.3.1. Materials

The following materials were used without further purification: CpMn(CO)_3 , CbFe(CO)_3 , ArCr(CO)_3 and CpV(CO)_4 (Strem Chemicals Inc.), PPh_3 (BDH), CO (Irish Industrial Gases Ltd., reagent grade; BOC, research grade), Ar (Messer-Griesheim), n -heptane (Aldrich, HPLC grade) and ^{13}CO (92%, BOC Prochem). Cyclohexane (BDH, Spectrosol quality) was dried with molecular sieve (4x) before use. n -Pentane and n -hexane (Merck, extra pure grade) were distilled from LiAlH_4 under argon, before use. 1-hexene (Merck) was purified by distillation from sodium wire. 4-vinylpyridine, 4-picoline and MeCpMn(CO)_3 (Strem Chemicals Inc.) were vacuum distilled prior to use.

2.3.2. Sample Preparation

(1) Laser flash photolysis studies with uv/vis detection

A known amount of the carbonyl compound (and in some cases, ligand) was weighed out and made up to a known volume with cyclohexane. A measured aliquot of this solution was degassed by three cycles of a freeze-pump-thaw (f.p.t.) procedure followed by a liquid pumping stage (to remove water and CO_2), in a specially designed degassing bulb with fluorescence cell attached. The concentration of the carbonyl compound in solution was then determined from its uv/vis absorption by utilising its known extinction coefficient at its wavelength of maximum absorption. Uv/vis spectra were recorded on a Pye-Unicam SP-200 or a Hewlett-Packard 8425A spectrophotometer. (In variable temperature studies, argon, to a pressure of one atmosphere, was added to the cell to prevent boiling of the solution at above ambient temperatures.)

Because the area of the laser beam on the sample cell is so small and the reactions in the system are generally reversible the experimental solution suffers little degradation over the time span of a single flash. Uv/vis spectra of the sample recorded before and after the experiments showed at most 10% degradation of starting material, even in cases where a stable product was formed.

(11) Laser flash photolysis with trir detection

A weighed sample of CpMn(CO)_3 was placed in the degassing vessel with an arbitrary amount of solvent. After degassing by continuously pumping on the solvent the volume of solution was measured in a graduated vessels thus allowing determination of its concentration. If a ligand was to be added to the solution it was placed in a side-arm of the vessel under vacuum and isolated from the main vessel by a greaseless tap. It could then be added to the solution at the appropriate time. After degassing, argon, to a pressure of one atmosphere, was added to the cell.

(111) Preparation of ^{13}CO doped CpMn(CO)_3 .

CpMn(CO)_3 was enriched with ^{13}CO by uv photolysis (pyrex filter) of a sample of CpMn(CO)_3 in n-heptane solvent under 200 torr pressure of ^{13}CO . The degree of ^{13}CO enrichment (ca. 30%) was estimated from ir spectroscopy (see Appendix 2). The ^{13}CO enriched sample of CpMn(CO)_3 was not isolated from the solvent prior to use.

2.3.3 Apparatus

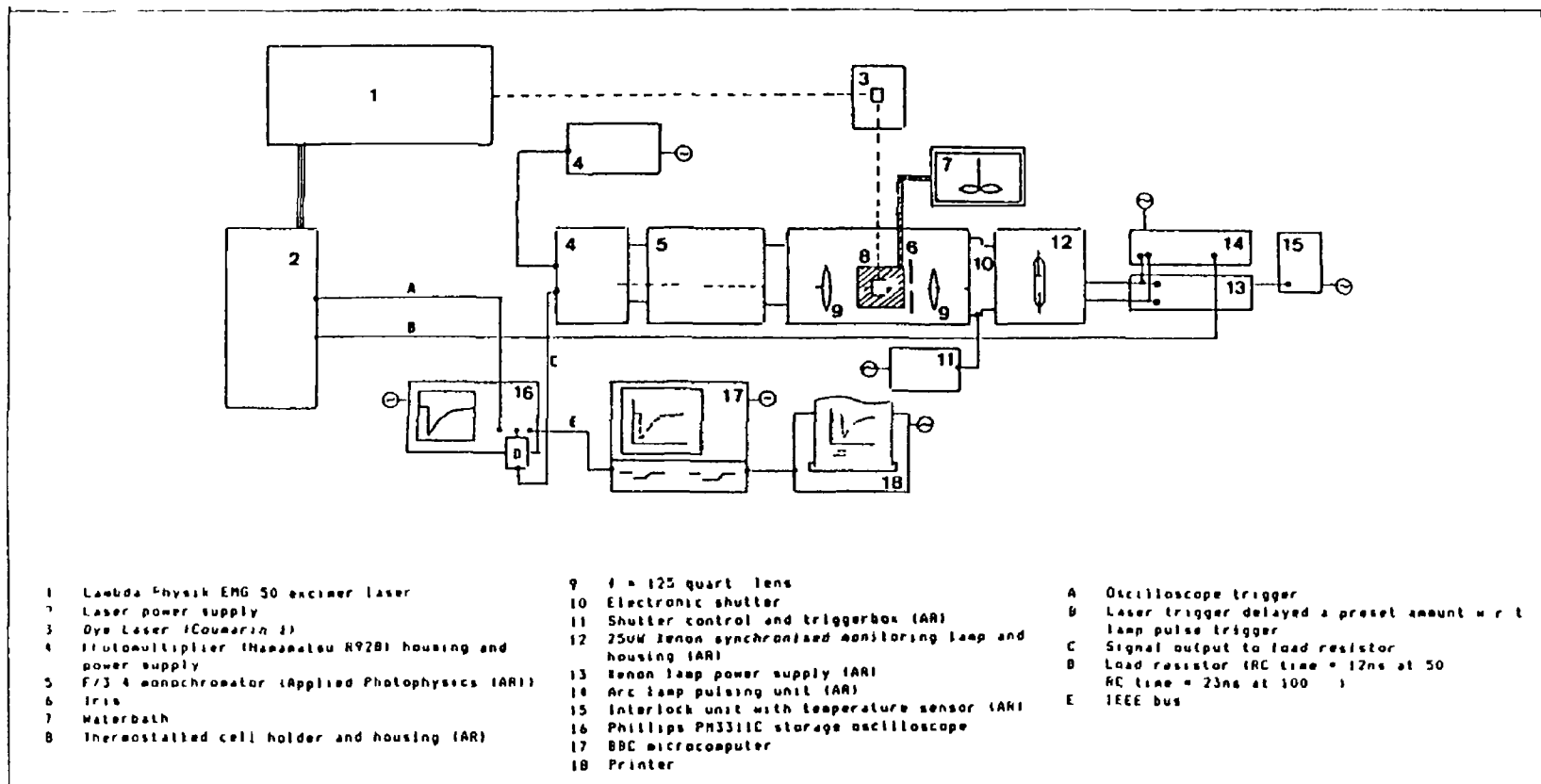
2.3.3.1 uv/vis Flash Photolysis System

The flash photolysis system is set up as a nanosecond kinetic spectrometer with a noble gas (excimer) laser as excitation source and a xenon arc lamp as monitoring light source in a right angle geometry (Figure 2.3.3.1) A Lambda Physik EMG 50 laser was used in these experiments. This laser can be filled with different gas mixtures and will give (with a XeCl gas mixture) pulses of about 40mJ and a halfwidth of about 15ns i.e. 2mW/pulse. The XeCl emission is at 308nm. The laser light is transformed via an inverted telescope from its original 26x10mm² dimensions to a rectangle of 10.8x4.2mm² (width x height) which is directed onto the surface of a quartz cell.

The monitoring light source was a water cooled 250 watt xenon arc lamp. The lamp output was focused on the front surface of the cell and recollimated onto the slit of a F/34 monochromator. The light detector was a Hamamatsu R928 photomultiplier wired for nanosecond response time. The optimum voltage for the photomultiplier was 850 volts. The signal output was connected via a variable load resistor to the transient analyser.

The digital transient analyser was a Philips PM3311 oscilloscope. This oscilloscope works on a CCP principle with a sampling speed of 125MHz (maximum of 8ns per sample point in single shot). The apparatus had an IEC/IEEE computer interface and was via this interface coupled and partially controlled by a BBC microcomputer (B+ series). Transient data obtained on oscilloscope can be read in to the computer and subsequently stored on disc.

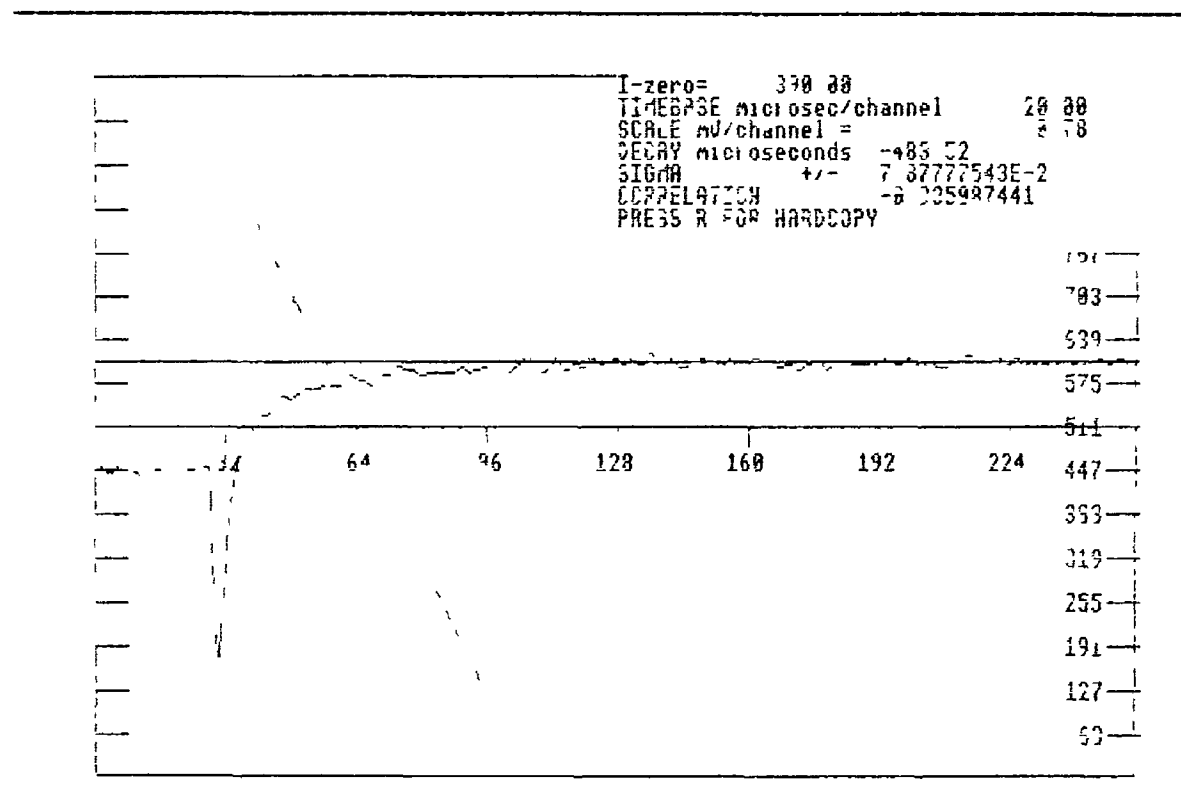
Figure 2.3.3.1: uv/vis Flash photolysis system.



The programme which allows the kinetic traces to be recorded, stored and analysed is listed in Appendix 2 (courtesy of Dr. Wil Van der Putten). A basic outline of the program will be given here.

Initially I_0 , the amount of light being transmitted through the solution before the laser flash, is recorded. This is accomplished by recording the voltage corresponding to that light detected by the photomultiplier tube when the electronic shutter (see Figure 2.3.3.1) is open, less the voltage generated by stray light. I is directly proportional to this voltage. The laser is fired with the shutter open and the firing of the laser triggers the oscilloscope. Thus the resulting trace shows the change in voltage with time which corresponds to the change in optical density of the sample as species are formed or decay away. A typical trace is shown in Figure 2.3.3.2.

Figure 2.3.3.2: Typical kinetic trace recorded with flash photolysis system given in Figure 2.3.3.1.



This trace is then stored, together with the timebase and voltage settings of the oscilloscope. These values allow the numerical calculation of I_t (the amount of light being transmitted through the solution at any time t) at a later date. A discussion of the treatment of this stored data is given further on.

2.3.3.2. trir Flash Photolysis System

The time resolved infrared flash photolysis system used in these series of experiments was developed and is in current use in Nottingham University (see Figure 2.3.3.3). A detailed description of the apparatus can be found in reference 38. Below is given a broad outline of the photolysis set-up.

The infrared solution cell (CaF_2 windows, 1.4mm PTFE spacers) is of conventional design modified with short lengths of stainless steel tubing. It is connected to a vacuum pump, argon and carbon monoxide cylinders and to a solution flow system, made of glass and PTFE with manually operated greaseless taps. The solution is changed between laser shots rather than flowing continuously to allow for any sample decomposition. Typically ca. 50cm^3 of solution are required per experiment. The uv source is a Lumonics Hyperex-440 excimer laser operating on XeCl (308nm, 8-12ns, ca. 100mJ per pulse) with an Applied Photophysics power supply and trigger unit (7KV, 2uF). The design of the infrared cell means that the uv laser beam and ir probe must necessarily be colinear. The angle between ir and uv beams in Figure 2.3.3.3 is grossly exaggerated. The uv laser is triggered by an Edinburgh Instruments laser modulation unit, which also provides the trigger pulse for the transient digitizer.

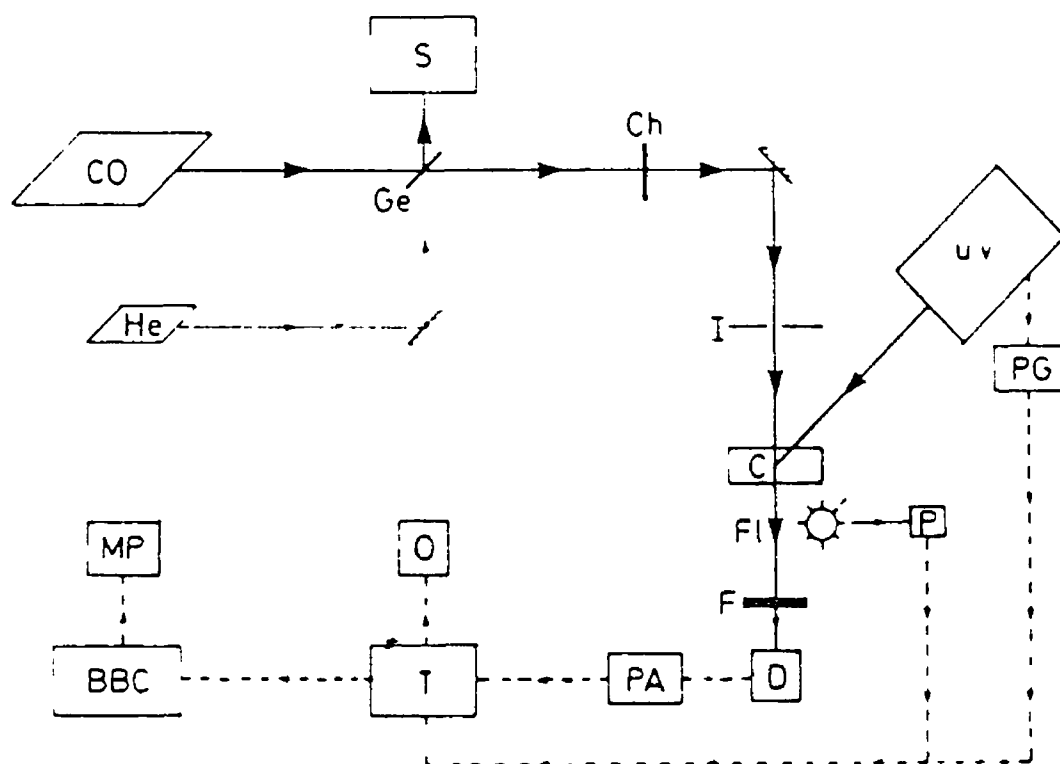
An Edinburgh Instruments PL3 line tunable c.w. CO laser with a semi-sealed tube is used with passive stabilisation. The cooling system uses FCCl_3 at 173K which is in turn cooled with liquid nitrogen. However the coolant pump must be switched off to reduce vibration when recording traces. Ir laser action within a particular $\nu \rightarrow \nu'$ manifold of CO occurs at frequencies nominally 4cm^{-1} apart but when run at full power lasers of this type have a tendency to give multiline output by operating on more than one $\nu \rightarrow \nu'$ transition simultaneously i.e. when laser is detuned.

Usable laser powers can be obtained over the range 2020 to 1700cm^{-1} . Extra frequencies within this range can be obtained by using ^{13}CO in the laser. A polished uncoated germanium beam splitter is used both to deflect part of the ir beam into an ir spectrophotometer for wavenumber calibration (Perkin Elmer 283B, single beam mode, accuracy $\pm 0.5\text{cm}^{-1}$) and also to provide a colinear alignment beam from a He-Ne laser.

The ir detector is a photoconductive HgCdTe detector (Infrared Associates Inc. HCT 100, area 1mm^2 , liquid nitrogen cooled). This is coupled to a pre-amplifier ($\times 6\%$ amplification rise time $< 1\mu\text{s}$, "roll off" ca. 10 Hz). The detector has a germanium bandpass filter placed immediately in front of the window of the detector. The ir laser beam was attenuated with an iris diaphragm which can be adjusted to compensate for absorption by the solvent. The adjustment was carried out for each laser line.

As with the uv system, firing the excimer laser triggers the transient digitizer (either Datalab DL 902 8-bit 1 MHz or DL 8-bit 20MHz) and the resulting kinetic trace is recorded. This data is then transferred to a BBC B+ microcomputer with relevant experimental data and stored on floppy disc.

Figure 2.3.3.3: trir Flash photolysis system.



Schematic diagram of the apparatus. Solid lines represent light paths, which have been somewhat simplified. Broken lines are electrical connections. Note that the angle between the *ir* and *uv* beams is exaggerated, in reality the angle is *ca* 5-10°. The components are labelled as follows: BBC, microcomputer; C, *ir* solution cell; Ch, chopper (for alignment and I_0 measurements); CO, *cw* *ir* laser; D, HgCdTe *ir* detector; F, *ir* bandpass filter; Fl, Xe flash lamp; Ge, germanium beam splitter; He, He-Ne alignment laser; I, iris diaphragm; MP, matrix printer (for printing spectra *etc*); O, oscilloscope; P, photodiode to trigger digitizer; PA, preamplifier with battery power supply; PG, pulse generator to trigger the *uv* laser and digitizer; S, *ir* spectrometer for laser calibration; T, transient digitizer; *uv*, XeCl excimer laser.

2.3.3.3 D.C.U. uv Flash Photolysis System

This experimental set-up is described in Section 3.3.

2.3.4 Treatment of Data

2.3.4.1 Kinetic measurement

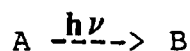
First order plots for species decaying away are made by plotting the natural log of the concentration versus time, t , and the slope of the plot gives first order rate constant k . In flash photolysis studies the only way to measure concentration is via the optical density of the species. The programmes used in these studies initially allow for calculation of absorbance values.

For example.

$I_0=175$ millivolts and corresponds to an arbitrary channel of 32 on the computer's scale. The computer screen is divided into so many millivolts per channel. It has 256 channels on the screen and there are 10 divisions on the oscilloscope each of which corresponds to 10mV. Then if a transience species has a channel value of 58 at time t , I_t , the measured intensity is proportional to $(58-32)/100 \text{ mV} = x$

Thus (Abs) at time $t = I_0/I_0-x = I_0/I_t$

For a reaction;



Optical density of the solution before the laser flash (Abs.)₀ is given by

$$(Abs.)_0 = \text{Log } I_0/I_t = E_a C_a^* L$$

At time t, after the flash the optical density is given by (Abs.)_t

$$(Abs.)_t = \text{Log } I_0/(I_t + \Delta I) = E_a C_a L + E_b C_b L$$

$$C_a + C_b = C_a^*$$

Therefore

$$(Abs.)_t = (E_a(C_a^* - C_b) + E_b C_b)L$$

$$(Abs.)_t - (Abs.)_0 = (-E_a C_b + E_b C_b)L$$

$$Abs. = C_b L (E_b - E_a)$$

$$C_b = Abs. / [(E_b - E_a)/L]$$

A plot of Ln C_b versus time is equivalent to a plot of Ln Abs. versus time as (E_b - E_a) and L are constant values.

E_a and E_b are the extinction coefficients of A and B. C_a and C_b are the concentrations of A and B at any time t. C_a^{*} is the initial concentration of A.

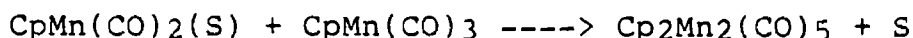
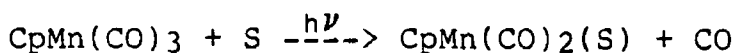
These calculations are the basis of both programmes used in these experiments for kinetic analysis. Calculation of absorbance values is also central to the programmes for generating transient spectra. The absorbance values are calculated from the data files on disc in the manner shown above. The time of the recorded spectra is determined by

which channel number is used in the calculations as each channel division corresponds to a certain time span. The calculated absorbance values are then plotted against corresponding wavenumber to generate spectra.

2.3.5 Determination of reaction rates

The rate of reaction of $\text{CpMn(CO)}_2(\text{S})$, $\text{ArCr(CO)}_2(\text{S})$ and $\text{CbFe(CO)}_2(\text{S})$ with ligand X (X= PPh_3 , 4-vinylpyridine, 4-picoline, 1-hexene, CO, or N_2) was determined by measuring the observed rate of grow-in of the dinuclear species in the presence and absence of the ligand. The concentration of N_2 and CO was assumed to be saturation in cyclohexane i.e. $6.34 \times 10^{-2} \text{ mol dm}^{-3}$ and $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ respectively. The difference in the rate is due to the reaction of the dicarbonyl fragment with the ligand. To find the true rate of reaction the rate of grow in of the dimer in the absence of ligand is subtracted from that in the presence of ligand and divided by the concentration of the ligand. For example in the case of the reaction of $\text{CpMn(CO)}_2(\text{S})$ with ligand;

In absence of ligand,



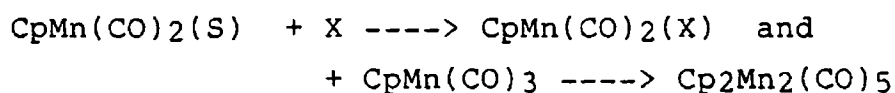
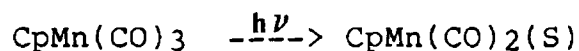
$$\frac{-d[\text{CpMn(CO)}_2(\text{S})]}{dt} = \frac{d[\text{Cp}_2\text{Mn}_2(\text{CO})_5]}{dt}$$

$$= k_1[\text{CpMn(CO)}_3] [\text{CpMn(CO)}_2(\text{S})]$$

$$= k_{\text{obs}}[\text{CpMn(CO)}_2(\text{S})]$$

as $[\text{CpMn(CO)}_3]$ is constant.

In presence of ligand X,



$$-d[\text{CpMn(CO)}_2(\text{S})] = d[\text{Cp}_2\text{Mn}_2(\text{CO})_5]$$

dt

dt

$$\begin{aligned} &= k_1[\text{CpMn(CO)}_3][\text{CpMn(CO)}_2(\text{S})] + \\ &\quad k_2[\text{CpMn(CO)}_2(\text{S})][\text{X}] \end{aligned}$$

$$= (k'_{\text{obs}} + k_2[\text{X}])[\text{CpMn(CO)}_2(\text{S})]$$

$$= k'_{\text{obs}}[\text{CpMn(CO)}_2(\text{S})]$$

$$k_{\text{obs}} = k'_{\text{obs}} + k_2[\text{X}]$$

$$k'_{\text{obs}} - k_{\text{obs}} = k_2[\text{X}]$$

$$k_2 = (k'_{\text{obs}} - k_{\text{obs}})/[\text{X}]$$

In cases where the temperature of the reaction was varied the corresponding k_{obs}' for the formation of the dimer was used in the calculation

2.3.6 Determination of Arrhenius and Eyring Plots.

Arrhenius and Eyring plots were determined for the reaction of the dicarbonyl species with various ligands X (X = PPh₃, hexene, 4-picolene, 4-vinylpyridine and CpMn(CO)₃) by varying the temperature of the photolysis solution and measuring the rate of grow-in of the dimer for a wide range of temperatures.

The Arrhenius equation is given by

$$\ln k_{\text{obs}} = E_{\text{act}}/(RT) + \ln(A)$$

Therefore a plot of $\ln k$ versus $1/T$ gives a slope of E_{a}/R .

T = temperature in Kelvin

E_{a} = Activation energy in J/mol

R = the gas constant

The Eyring equation is given by

$$\ln(k_{\text{obs}}/T) = -(\Delta H^\ddagger/RT) + (\Delta S^\ddagger/R) + \ln[(kT/h)]$$

Therefore a plot of $\ln k_{\text{obs}}/T$ versus $1/T$ gives a slope of $-\Delta H^\ddagger/R$ and an intercept of $(\Delta S^\ddagger/R + \ln[(kT/h)])$

2.3.7 Attempted Synthesis of Cp₂Mn₂(CO)₅

When a degassed solution of CpMn(CO)₃ in n-hexane was photolysed at 180K a red compound was observed almost instantaneously but disappeared after approximately 2 minutes. An infrared spectrum obtained after 30 seconds, showed depletion of the bands which could be assigned to parent tricarbonyl (2026 and 1943cm⁻¹). Photolysis was

continued for one hour during which two bands appeared at 1950 and 1895 cm^{-1} . The origin of these bands is unknown at present. A brown insoluble residue was isolated from the photolysis solution. This residue was assumed to be due to decomposition of the CpMn(CO)_3 photolysis products (e.g. to yield oxides of manganese).

The above experiment was repeated using MeCpMn(CO)_3 . A red compound was initially formed but this time the photolysis product was stable for 30-45 minutes. An infrared spectrum taken at room temperature during this experiment showed the disappearance of the parent compound i.e. the bands at 2026 and 1943 cm^{-1} , with the appearance of two bands at 1905 and 1960 cm^{-1} .

Irradiation of a sample of CpMn(CO)_3 , on a cold finger which was continuously purged with argon yielded only a brown oxidation product of manganese. Irradiation of a sample of CpMn(CO)_3 in solid pentane at liquid nitrogen temperatures under vacuum, appeared to have no effect. Upon warming the solution slightly to above the melting point of the solvent, a red complex was seen to form which was stable in the refrozen pentane for up to 1 hour.

2.3.8 A Study of the Variation in Absorbance of the Photogenerated Species with Laser Flash Intensity.

In order to determine if the initially observed species was due to a multiphoton event a study of the variation in yield of this species versus laser flash intensity was undertaken. This was accomplished by measuring the absorbance of the species when filters, of varying absorptivity at 308nm, were placed in front of the sample. A linear relationship indicates that the first observed species was formed as a result of a single photon event.

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Section 3

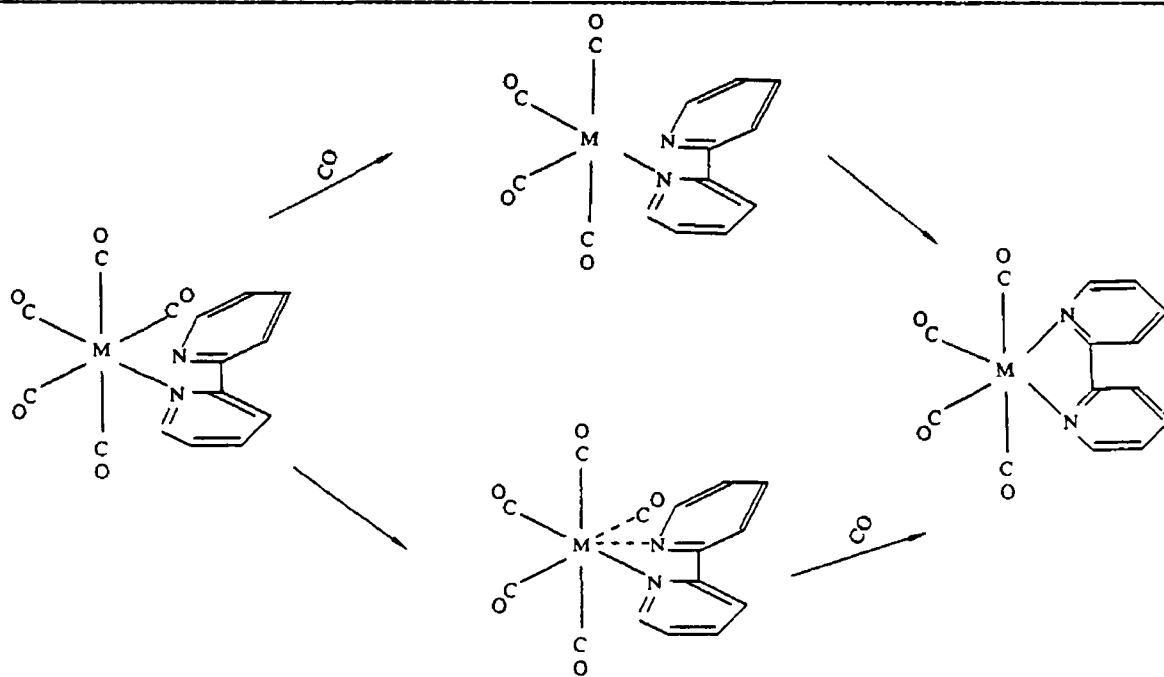
SPECTROSCOPIC INVESTIGATIONS OF THE CHELATION REACTIONS OF CHROMIUM CARBONYL COMPLEXES CONTAINING MULTIDENTATE LIGANDS

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3.1 INTRODUCTION

The generation of a vacant co-ordination site in a molecule has been suggested as the most important step in a catalytic cycle. Metal carbonyls have been central to the study of catalytic processes because of the ease of removal of the carbon monoxide ligands (by thermal or photochemical means) to generate highly reactive 16 valence-electron species. Simon *et al.* have shown that photogenerated $\text{Cr}(\text{CO})_5$ complexes with methanol on a picosecond timescale.^{1a} We have been interested in studying the chelation reactions of multidentate metal carbonyl complexes. In chelation reactions involving bidentate ligands such as is shown in Figure 3.1 1 ring closure may occur via two processes;

Figure 3.1.1: Ring closure mechanisms in chelation reactions.



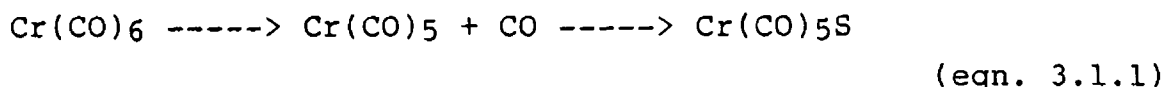
In the upper process, the intermediate stage involves a 16 valence-electron species. Studies on the formation of chelate products and ligand substitution reactions have led

to a greater understanding of the kinetic and thermodynamic parameters governing such reactions. The properties of the intermediates and transition states of such reactions are of importance to the development of a detailed understanding of homogenous catalytic processes for which the active species is co-ordinatively unsaturated. Understanding such chelation processes may allow one to determine methods of generating a 16 valence-electron species from stable 18 valence-electron chelate products. Binding such molecules to insoluble supports would allow a highly efficient heterogeneous catalyst which could be activated by electrochemical, thermal or photochemical means

Many of the studies on chelation reactions have been carried out with diimine ligands and we have been interested in the chelation processes of such ligands at metal hexacarbonyl centres, particularly $\text{Cr}(\text{CO})_6$. The efficiency of bipy and other diimine ligands as chelating ligands stems from both their chelating ability and a balance between their σ donor and π -acceptor properties which can be adjusted to the electronic requirement of the complexed metals (by varying the substituents on the ligands)

3 1.1 Ligand Substitution Reactions of Metal Hexacarbonyls

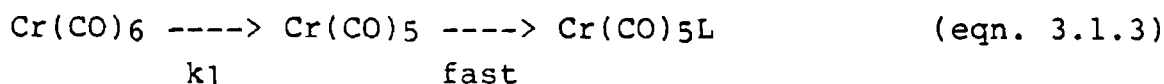
The primary photoreaction of $\text{Cr}(\text{CO})_6$ has been shown by a number of workers to be dissociation of CO, and it is likely that $\text{Cr}(\text{CO})_5$ is the primary product of thermal reactions also.¹ If the reaction takes place in a solvent with donor properties, such as pyridine, thf, or acetonitrile, the 16 valence-electron, co-ordinatively unsaturated pentaco-ordinate species forms a solvent stabilised complex (equation 3.1 1) (S = solvent).

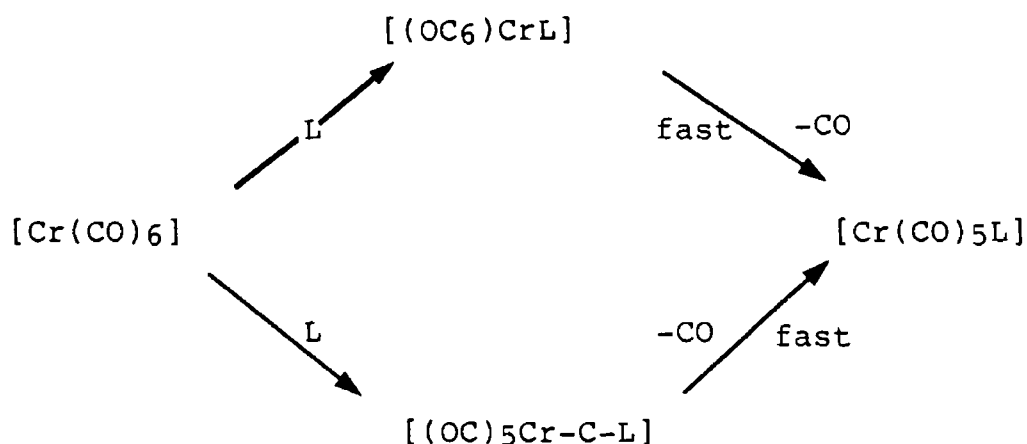


In solvents with poor donor ability, experiments indicate that the Cr(CO)_5 intermediate is very reactive; flash photolysis studies have shown that in carbon monoxide saturated cyclohexane, the recombination rate constant is approximately $3 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. Competition ratio studies have shown that the Cr(CO)_5 species has a low discriminatory ability. The solvent-chromium interaction is usually weak and the solvent can be readily displaced by a better ligand. Subsequent reactions can displace another CO or the ligand.

The substitution reactions of Cr(CO)_6 can usually be encompassed within a two term rate law (equation 3.1.2). The ligand independent first order path described by k_1 is consistent with carbonyl dissociation to form a five co-ordinate intermediate as the rate determining step (equation 3.1.3). The ligand dependent path described by k_2 could involve attack at the ligand L at either the carbonyl carbon or chromium atom of Cr(CO)_6 (Scheme 3.1.1).

$$\frac{-d[\text{Cr(CO)}_6]}{dt} = k_1[\text{Cr(CO)}_6] + k_2[\text{Cr(CO)}_6][\text{L}] \quad (\text{eqn. 3.1.2})$$





0

Scheme 3.1.1

In nonpolar solvents it is quite likely that the ligand independent path is dominant and in such cases it has been argued that the process approaches dissociative (D) behaviour. A consequence of D behaviour is that the enthalpies of activation should closely relate to the first (not mean) carbonyl bond dissociation energy and the M-C force constants for $M(CO)_6$ ($M = Cr, Mo, \text{ or } W$).³⁻⁵ The order of activation energy for dissociative ligand independent substitution reactions for $M(CO)_6$ species are in agreement with the M-C force constants. Graham *et al.* measured the activation parameters for the reaction of group 6 metal carbonyls with phosphine and phosphite ligands and showed them to be consistent with equation 3.1.3⁶

Further studies on the substitution reactions of group 6 metal hexacarbonyls have been carried out. Angelici studied the replacement of a carbonyl group in $Cr(CO)_6$ by a pyridine ligand.⁸ They found that the chromium π bonding to the remaining five carbonyls was increased rendering the Cr-CO bond stronger. ^{1r} Studies showed

substitution of one carbonyl by pyridine resulted in the strengthening of the Cr-CO bonds and therefore pyridine could stabilise the transition state in the proposed CO dissociation mechanism.

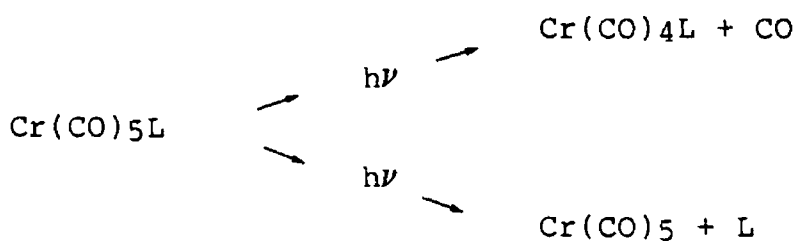
Although the majority of group 6 metal carbonyls proceed via a ligand independent path, as the concentration of the entering ligand and/or polarity of the solvent is increased the second order reaction becomes more important.⁶ Other factors that favour the second order reaction are increasing size of the central atom and increasing nucleophilicity and π -acceptor ability of the entering ligand. There is evidence which indicates that both paths of Scheme 3.1.1 are important for strong nucleophiles. The upper path could proceed via an associative(A) or interchange(I) process, but since the associative process would involve a 20 valence-electron intermediate, the interchange process is much more probable.⁷

For the interchange process (Scheme 3.1.1 upper) the associative and dissociative modes are possible. It is quite likely that the interchange process is dissociative as a comparison of the enthalpies of activation for both the first and second order processes for $L = \text{PBu}_3$ substitution show little change.⁷ Thus although some involvement of the entering ligand in the transition state was observed the process primarily involves bond breaking. The dissociative process is also more in keeping with the notion that 16 and 18 electron states are more probable than 20 electron states

3.1.2 Substitution Reactions of Metal Pentacarbonyl Ligand Complexes

An understanding of the parameters governing the formation of $\text{M}(\text{CO})_4\text{L}$ from $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Mo}, \text{Cr}, \text{or W}$; $\text{L} =$

bidentate ligands) may be obtained from a study of the substitution reactions of the pentacarbonyl complexes. The derivatives of chromium hexacarbonyl, particularly the monosubstituted complexes of the type $\text{Cr}(\text{CO})_5\text{L}$, exhibit reactivity patterns and kinetics similar to chromium hexacarbonyl itself. Of course the presence of one or more non-carbonyl ligands alters properties to some extent. The photolysis of $\text{Cr}(\text{CO})_5\text{L}$ can result in the loss of either CO or L (Scheme 3.1.2).



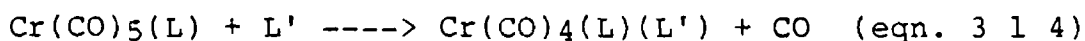
Scheme 3.1.2

In the presence of added ligand L, the upper path could generate either cis- or trans- $\text{Cr}(\text{CO})_4(\text{L})_2$ while the lower path would simply regenerate $\text{Cr}(\text{CO})_5\text{L}$. The upper path becomes more important as the strength of the Cr-L bond increases, even though excitation energies are high enough to cause loss of CO or L. Thus, for strong ligands (good σ -donors/ π -acceptor complexes), complete replacement of the carbonyl ligands can occur, while for ligands such as thf, $\text{Cr}(\text{CO})_5(\text{thf})$ is the principal product. The wavelength of excitation light also influences the relative efficiencies of the paths in Scheme 3.1.2, as higher energy irradiation preferentially causes CO dissociation.⁹

Thermal substitution reactions of group 6 carbonyl derivatives often follow kinetics similar to those of the photolysis reaction above. As for the reactions of

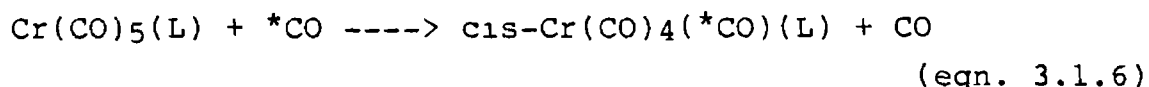
Cr(CO)₆, substitution reactions usually proceed via loss of CO. The rate law for equation 3.1.4 usually consists of two terms (equation 3.1.5) and is similar to the rate law for Cr(CO)₆ substitution reactions. However the nature of the ligand L in Cr(CO)₅(L) complexes greatly influences the reaction rate especially the magnitude of k₁, the rate constant for the ligand independent term. In virtually all cases the substitution reaction rate is larger when L is any ligand other than CO.^{10,11} The ligands with good

σ-donor ability but poor π-acceptor ability show significantly faster rates than those ligands closer to CO in bonding, the π-acceptor ligands.¹²⁻¹⁴



$$\frac{-d[\text{Cr(CO)}_5(\text{L})]}{dt} = k_1[\text{Cr(CO)}_5(\text{L})] + k_2[\text{Cr(CO)}_5(\text{L})][\text{L}'] \quad (\text{eqn. 3.1.5})$$

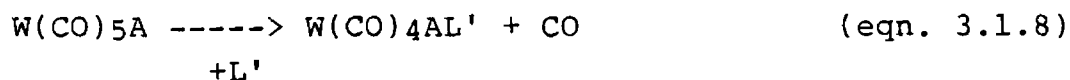
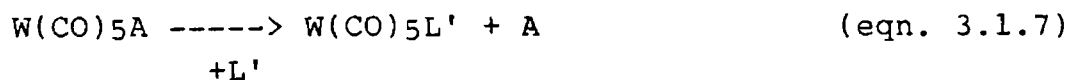
The labilisation of Cr(CO)₅(L) by L is invariably of the carbonyl ligands cis to L, thus it is probable that the incoming ligand is initially in the cis position. However this may not always be the case, as rearrangement about the central atom may occur. The cis-labilisation of Cr(CO)₅(L) could be due to the strengthened Cr-C bond trans to L, especially for poor π-acceptor ligands. Alternatively, the five co-ordinate intermediate species Cr(CO)₄(L) could be stabilised by poor π-acceptors occupying a basal position in a square pyramidal intermediate, thereby facilitating the reaction. The existence of such a intermediate is shown by equation 3.1.6, where by microscopic reversibility, since the entering CO occupies a cis position the outgoing CO must have left a cis-position. Thus if the entering ligand is L', a cis-derivative is initially formed, although trans-Cr(CO)₄(L)(L') might eventually be formed because of greater thermodynamic stability.



It has been noted that as the electron density on the metal increases, more π -back-bonding occurs, and the Cr-C bond distance decreases and the C-O bond distance increases. In chromium carbonyl derivatives, ligands that have a high ratio of σ -donor to π -acceptor ability tend to increase electron density at the chromium and consequently the remaining carbonyl ligands are bound more tightly to the metal than the carbonyls in Cr(CO)_6 or other derivatives with ligands with low σ -donor/ π -acceptor ratios (see Section 4).

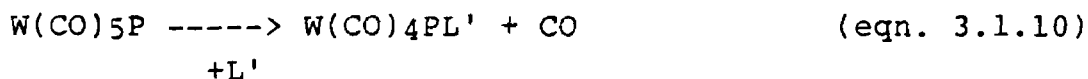
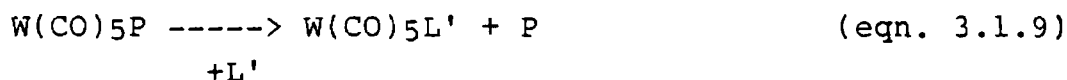
A great deal of work has been carried out on amine substitution in $\text{M(CO)}_5\text{(amine)}$ complexes. The most complete of these by Dahlgren and Zink was an investigation of the effects of a diverse array of unique ligands on the photochemistry of $\text{W(CO)}_5\text{(L)}$ (L = acetonitrile, NH_3 , cyclohexylamine, pyridine, piperidine, PPh_3 , PBr_3 , PCl_3 , Ph_3 , P(n-Bu)_3 , methoxymethoxycarbonyl, phenylmethoxycarbonyl, CS, or Br-).¹⁵ The bonding properties of the unique ligand L, in these $\text{W(CO)}_5\text{(L)}$ complexes perturb the nature of the lowest excited state and as such give rise to a mechanism by which this state may be fine tuned to provide a variety of photochemical consequences. Variation of L leads to three contrasting modes of photosubstitution reactivity.

Class 1 reactivity.



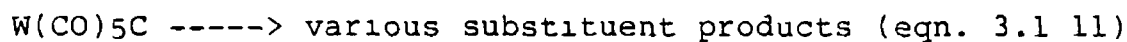
A = acetonitrile, cyclohexamine, NH_3 , piperidine, or pyridine; ϕ_1 ca. 0.5; $2 < 10^{-2}$.

Class 2 reactivity:



P = PPh_3 , PBr_3 , PCl_3 , Ph_3 , or P(n-Bu)_3 ; $\phi_1 = \phi_2 = 0.3$

Class 3 reactivity:



C = methoxymethoxycarben, phenylmethoxycarben, CS, or Br^- ;
 $\phi_1 \leq 10^{-2}$

In all cases the experimental evidence suggested that the primary photochemical step was dissociative in character.

3.1.3 Studies of Chelation Reactions of Metal Pentacarbonyl Compounds co-ordinated to Phosphorus and Sulphur Bidentate Ligands

Connor and co-workers have studied the chelation reactions of a number of bidentate phosphorus and sulphur ligand complexes of metal hexacarbonyls.¹⁶ They investigated the chelation reactions of $M(CO)_5(\text{chelate})$ ($M = \text{Cr}$ or Mo), (chelate = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dpp), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe) or $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe)). The principal enthalpy requirement for activation was found to be M-CO bond stretching, although 'strain' in the bending of the chelate ring contributes, especially in the formation of small rings. The principal entropy contribution was determined to be the statistical advantage enjoyed by the donor atom at the 'free' end of a short chelate chain, although steric effects also contribute here. The mechanism was considered as concerted, in that the stretching of a M-CO bond must be accompanied by the 'appearance' of an incoming donor atom in the right orientation. Factors which increase the probability of this occurrence increase the rate of the chelation reaction.

In a further study by these workers, they showed that chelation was a concerted process in which enthalpy made the largest contribution to the overall free energy.¹² Whereas the mean Mo-CO bond energy in Mo(CO)_6 is substantially greater than the mean Cr-CO bond energy in Cr(CO)_6 , the enthalpy of activation for chelation for molybdenum complexes was significantly less than in their chromium analogues. In addition, they noted that the enthalpy of activation, in the case of the chromium complexes was greater than the mean Cr-CO bond energy whereas the reverse was true for molybdenum complexes. They determined that the entropy of activation for the formation of $M(CO)_4(\text{chelate})$ largely discriminated between rates of chelation of ligands containing similar donor atoms. Their

observations suggested that although the mechanism of chelation is concerted in both cases, it has a greater dissociative component in the case of chromium. This may reflect the larger size of molybdenum which reduces the need for the M-CO bond to stretch in order to accommodate the incoming donor atom in the transition state.¹²

In another study by these workers on the chelation reactions of $M(CO)_5(L)$ ($M=Cr, Mo$; $L = RSCH_2CH_2SR$; $R = CMe_3(bte), H(pte),$ or $NMe_3(dte)$), they showed the importance of electronic substituent effects in the ring closure step.¹⁷ The observation of steric hindrance (bte chelated more slowly than pte) and acceleration by electron density (dte chelated more rapidly than pte) suggested that the associative contribution to the chelation process is of greater importance for sulphur donor chelating ligands than for the phosphorus analogues. In the latter case steric acceleration is observed which is consistent with a dissociative process.

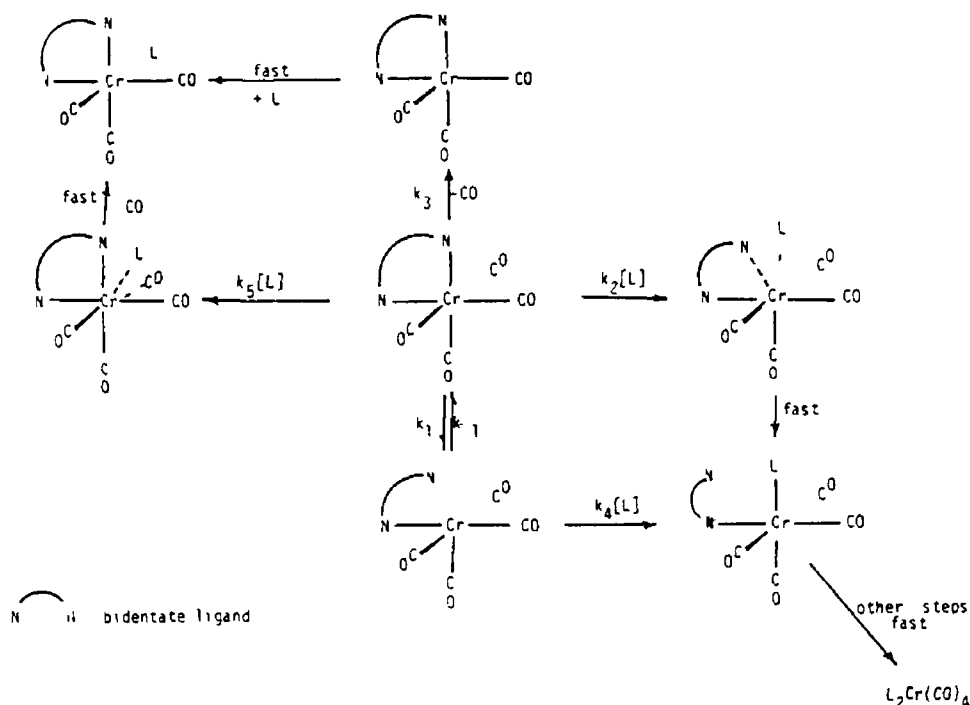
3.1.4 Ligand Substitution Reactions of Metal Tetracarbonyl Ligand Complexes

Chromium compounds which contain α -alpha diimine ligands are examples of σ -donor/ π acceptor ligands. These ligands accept π -electron density from the chromium into the $C=N \pi^*$ -orbitals, and are considered to be moderately good π -acceptors. These ligands are strong enough π acceptors to displace CO completely from $Cr(CO)_6$ although these compounds might better be regarded as $Cr(III)$ complexes of $bipy^-$ or $phen^-$ anions.

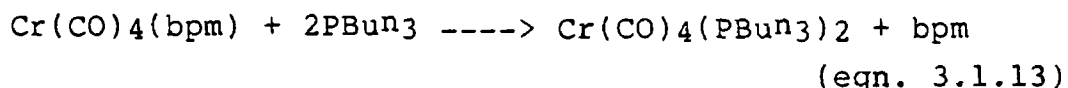
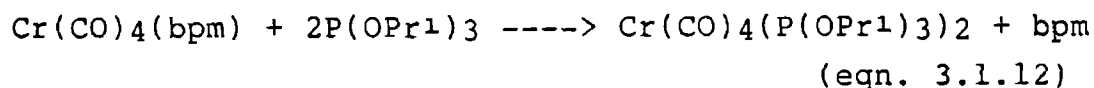
In a study by Dobson et al. the ligand substitution reactions of $M(CO)_4(chelate)$ complexes were studied¹⁸ These workers have postulated that, in systems in which the chelating ring possesses some degree of rigidity such as

in $M(CO)_4(bipy)$ ($bipy = 2,2'$ -bipyridyl), the chelating ligand is retained in most instances. There is some evidence that the chelate ring does open when the carbonyl ligand is lost from $M(CO)_4(bipy)$.^{20,21} If ring rigidity is not a factor, loss of the chelating ligand is the predominant pathway e.g. in $M(CO)_4(tmen)$ complexes ($tmen = N,N,N',N'$ -tetramethylenediamine)²² or bpm ($bpm = 2,2'$ -bis(pyridyl)methane).²⁰

The contrast in mechanism in $Cr(CO)_4(bpm)$ given in equations 3.1.12 and 3.1.13, to that for the related $Cr(CO)_4(bipy)$ which proceed via the path governed by k_3 (Scheme 3.1.3) underscores the dramatic effect on mechanism on the presence of a six-membered rather than a five-membered chelate ring. In the latter system, ring displacement is not observed although evidence for a ring opening path leading to expulsion of CO in this system has been detailed.



Scheme 3.1.1



The rate data for both ligands are consistent with the rate law

$$\frac{-d[\text{Cr(CO)}_4(\text{bpm})]}{dt} = k_1.[\text{Cr(CO)}_4(\text{bpm})] + k_2.[\text{Cr(CO)}_4(\text{bpm})].[L]$$

(eqn. 3.1.14)

Another significant observation, however is that the rates of reaction in $\text{Cr(CO)}_4(\text{bipy})$ and $\text{Cr(CO)}_4(\text{bpm})$ are not greatly different relative to the rates of reaction in $\text{Cr(CO)}_4(\text{tmen})$ and $\text{Cr(CO)}_4(\text{tmpa})$ ($\text{tmpa} = \text{N,N,N',N',-tetramethyl-1,3-diaminopropane}$). The bpm reacts approximately an order of magnitude faster. By contrast rates of reaction for $\text{M(CO)}_4(\text{tmpa})$ with L versus those for $\text{M(CO)}_4(\text{tmen})$ ($\text{M} = \text{Cr or W}$) are some three or more orders of magnitude faster.^{22,23} These differences cannot, at least for the W results, be attributed to a drastic decrease in the k_4/k_1 ratio in the six membered ring system, but are attributable instead to a much greater ease of W-N bond breaking for the six-membered ring system. The lack of such pronounced effects in the bpm system were attributed to a residual ring-rigidity in the bpm complex such that there is an inhibition of M-N motion colinear with the bond axis.

Reactions of $\text{M(CO)}_4(\text{chelate})$ ($\text{M} = \text{Cr, Mo, or W}$) with a ligand L result in one of three complexes, (i) $\text{M(CO)}_3(\text{L})(\text{chelate})$, (ii) $\text{M(CO)}_4(\text{L})_2$ or (iii) $\text{M(CO)}_3(\text{L})_3$. Which of these three types of compound forms depends upon the nature of the chelate ligand, as the

stronger ligands (bipy, phen, or dppe) tend to be retained and $M(CO)_3(L)(\text{chelate})$ complexes formed, while weaker ligands are displaced and $M(CO)_4(L)_2$ complexes formed. The rate law for such reactions can be generalised in equation 3.1.15. The reaction proceeds via one of three mechanisms; (i) associative ($M = Mo$ or W only) (ii) dissociative or (iii) chelate ring opening. For chelate = phenanthroline (phen), bipy etc. complexes, the dissociation of carbon monoxide forms a five co-ordinate complex which reacts with L to form product.^{13,24,26} Evidence strongly indicates dissociation occurs from carbonyl positions cis to the phen or bipy chelating ligand. Similarly, substitution can occur in the opposite direction, indicating the reversibility of the reaction.²⁷

$$\text{rate} = (k_1 + k_2[L])([M(CO)_4(\text{chelate})]) \quad (\text{eqn. 3.1.15})$$

These studies show that bipy, phen and other ligands that are weaker π -acceptors than CO labilise octahedral carbonyl complexes towards dissociative loss from positions cis to these ligands. This cis-labilisation results in reaction substitution rates several orders of magnitude larger for these chelate complexes than for $Cr(CO)_6$. The loss of CO from a cis position does not necessarily result in fac-geometry for the product $Cr(CO)_3(L_2)(L')$, as the five co-ordinate intermediate is often partially fluxional and in several cases fully fluxional on the time scale of the substitution reactions.²⁶

In a study by Connor and co-workers the consequences of steric influences upon chemical reactivity were investigated.²⁸ Steric acceleration was observed, unambiguously indicating that the dissociative process is the dominant pathway of chelation. These workers showed the greater importance of bond breaking relative to bond making in $Cr(CO)_4(\text{chelate})$ complexes (chelate = dpe, dmpe, or dcpe). They found that in many instances the formation and reactions of these and similar complexes correlate better

with the steric requirement of the substituent groups rather than the basicity of the the ligand as measured by pK_a .

S Dobson et al. have recently studied the kinetics and mechanism of displacement of dtd (dtd = 2,2,9,9-tetramethyl-3,8-dithiadecane) and dtu (dtu = 2,2,10,10-tetramethyl-3,9-dithiaundecane) from $W(CO)_4(dta)$ (dta = dithiaalkane).²⁹ dtd and dtu form seven- and eight-membered rings respectively, and are displaced by Lewis bases to give $W(CO)_4L_2$ and dta or dtu. Reaction are biphasic, proceeding through non-steady-state intermediates $cis-(dta)(L)W(CO)_4$ after initial reversible ring opening. These workers found that the dominant influences on reactivity were rates of chelate ring opening which increased with increasing ring size. The rates of W-S bond breaking in the $cis(ndta)(L)W(CO)_4$ intermediates produced after chelate ring opening increased with increasing steric demand.

3.1.5 Chelation Reactions of $M(CO)_5(diimine)$ Complexes as Monitored by Fast Spectroscopic Techniques

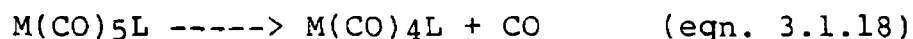
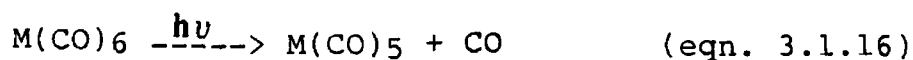
Section 3.1.3 has summarised the chelation reactions of metal pentacarbonyl complexes co-ordinated in a monodentate fashion to phosphorus and sulphur bidentate ligands. The isolation of similar diimine type complexes proved to be more difficult because of the greater reactivity and labile nature of these species. Thus the initial studies of these complexes focused on the formation of the pentacarbonyl diimine complexes in situ. The reactions were photochemically initiated and the subsequent thermal reactions were monitored by fast spectroscopic techniques.

The development in the last decade in rapid scanning spectroscopic techniques (e.g. Ft-ir and uv/vis diode array spectrophotometers) has enabled the study of chelation reactions of metal carbonyl diimine complexes. A great deal of these studies have been carried out by Lees and co-workers,^{30,31} who initially studied the reaction kinetics and behaviour of intermediates produced in the photolysis of $M(CO)_6$ ($M = Cr, Mo, \text{ or } W$) solutions containing 1,4-di-tert-butyl-1,4-azabutadiene (1,4-dab) ligand. Electronic absorption data were recorded on a microprocessor controlled diode-array spectrophotometer at short time intervals (typically a few seconds), following the photolysis of $M(CO)_6$ in benzene containing 1,4-dab. These spectra illustrated the rapid formation of a primary reaction intermediate, assigned as a $M(CO)_5(\text{solvent impurity})$ species, which subsequently formed $M(CO)_5(1,4\text{-dab})$. The identification of the $M(CO)_5(1,4\text{-dab})$ species was based on its similarity to $M(CO)_5(\text{piperidine})$ and $M(CO)_5(\text{pyridine})$ complexes. The assumed $M(CO)_5(1,4\text{-dab})$ complex extruded CO by a relatively slow first order process to form $M(CO)_4(1,4\text{-dab})$. Rates of chelation for 1,4-dab were compared with literature values for phen and bipy. The differences in reaction rates were explained by consideration of the stereochemistry of the ligand (L) in $M(CO)_5(L)$ complexes. Phen chelated more rapidly as the N donor atoms are co-strained to be co-planar in this molecule, in contrast to the possible s-trans conformation of the 1,4-dab in solution.

Lees' study on the kinetics and mechanism of a photogenerated $W(CO)_5(L)$ intermediate where $L = 2\text{-pyridinal-imine}$ ligand yielded similar conclusions.³² The rate data obtained for the formation of $W(CO)_4(L)$ (equation 3.1.18) indicated that a substantial contribution to the CO extrusion reaction is made by the associating ligand when it is already co-ordinated in a monodentate

fashion. The nature of the substituents on the 2-pyridinal-imine ligand determined the degree of the associative component of the reaction.

Lees also carried out a series of similar studies on the photoinitiated reactions of $M(CO)_6$ ($M = Cr, Mo, \text{ or } W$) in benzene solution containing the diimine ligands ,phen, bipy and 1,4-dab. Equations 3.1.16 to 3.1.18 are consistent with the spectral observations:



The spectrum of $M(CO)_5(L)$ was almost identical to the spectrum of $M(CO)_5(2\text{-phenylpyridine})$. The rates of reaction were found to be independent of ligand concentration over the concentration range 1×10^{-3} to 1×10^{-2} mol dm^{-3} . and to depend on the nature of the diimine ligand. The observed rate of chelation was greater than the thermal substitution of either L or CO in $M(CO)_5(L)$ in which L is an amine.^{33,34} Lees suggested that the more rapid chelation was because of the effect of the diimine being already bound to the metal carbonyl in a monodentate fashion. The dependence of the reaction rate with diimine was interpreted as an indication of a substantial associative contribution in the overall chelation step. The rates of reaction were ordered $Mo > Cr > W$ as is the order of the M-C force constants. Lees concluded that extrusion of CO from $M(CO)_5L$ is a major factor in controlling the rate of overall chelation mechanism. In addition the lowering of the activation barrier for CO extrusion from $M(CO)_5L$ as against $M(CO)_6$ indicated the associative character of diimine ligand when it is already co-ordinated in a monodentate fashion. Lees

carried out further studies on the chelation reaction of $M(CO)_5(\text{pyridine } 2\text{-carbaldehyde imine})$ ligand with similar results.^{35,36}

Wrighton et al. studied the chelation reaction of intermediates produced upon photolysis of $M(CO)_6$ ($M = Mo, Cr$ or W) solution containing 4,4'-dialkyl-2,2'-bipyridyl ligands, via rapid-scan Fourier transform ir spectroscopy.³⁵ These results were consistent with the reaction scheme outlined in equations 3.1.16 to 3.1.18. The rate of formation of $M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bipy})$ was compared with the formation of $M(CO)_4(\text{pyridine})$ from $M(CO)_5(\text{pyridine})$ and pyridine, and the significant increase in rate of CO loss in $M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bipy})$ was attributed to an overwhelming contribution from the associative ligand replacement reaction.

In all of the experiments so far described a number of factors should be considered.

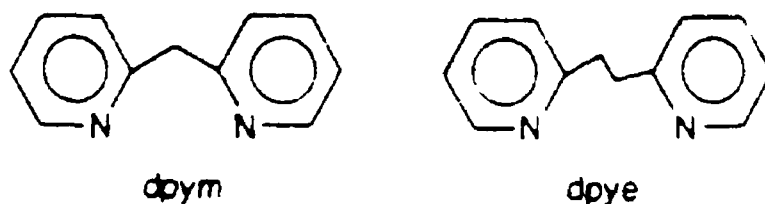
(i) an excess of ligand was always present in the reaction solution

(ii) the intermediate species was never isolated and characterised. Its identity was determined by comparison with spectra of similar compounds.

Several attempts have been made to isolate bidentate ligand complexes which are co-ordinated in a monodentate fashion. Isolation of $M(CO)_5(\text{dipyridylalkane})$ ($M = Cr, Mo$ or W) species indicated that these type of complexes do not necessarily undergo chelation via a spontaneous ring closure mechanism³⁸ The absence of chelation was attributed to poor σ overlap between the σ orbital of unco-ordinated N atom and the metal d orbital in $M(CO)_5(\text{dipyridylalkane})$ It appeared as if addition of bridging C atoms to bpy skeleton to generate

di-2-pyridylmethane (dpym) and 1,2-di-2-pyridylethane (dpve) (Figure 3.1.2) reduces M-N overlap. The stability of these complexes could also be due to a decreased interaction between the rings and the increase in the number of atoms in final chelate ring. Both of these factors have been shown by other workers to have considerable effect on the chelation process.

Figure 3.1.2:



$M(CO)_5(en)$ ($M = Cr, Mo, \text{ or } W$; $en = \text{ethylenediamine}$) complexes undergo chelation via a first order process to form $M(CO)_4(en)$ and CO .³⁹ The order for the reaction rates for the formation of these complexes are consistent with the calculated M-C force constants of $M(CO)_6$ complexes in solution. The reduced reaction rate relative to bipy was attributed to reduction of ligand orbital overlap that is necessary to bring about chelation and to diminished affinity of the ligand electrons for the metal centre.

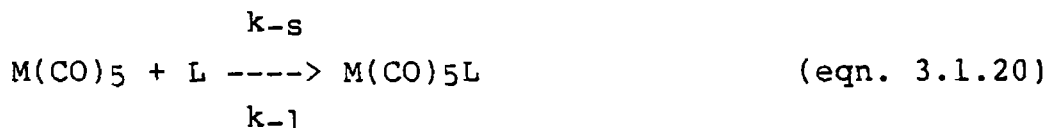
3.1.6 Investigation of the Chelation Reactions of $M(CO)_5(\text{diimine})$ Complexes Generated via Flash Photolysis Techniques

Isolation of monodentate α/α -diimine ligands has proven difficult as the chelation reactions of these complexes

occur on fast timescales. Both of these facts have encouraged the study of the chelation reactions via flash photolysis techniques. Observations of the formation of an intermediate pentacarbonyl species in the formation of $M(CO)_4(\text{diimine})$ compounds indicates that in such cases elimination of the second carbonyl does not take place in a concerted fashion with initial co-ordination of the ligand. Furthermore it has been shown that in the case of diimine that can take a conformation where the direction of the second co-ordination is not suitable for co-ordination $M(CO)_5L$ (L ligates in a monodentate fashion) was isolated.

Oishi carried out a study on the laser flash photolysis of photochemical substitution in $M(CO)_6$ ($M = \text{Cr, Mo, or W}$) with phen.⁴⁰ The two N's of phen must be on the same side therefore his study would determine if co-ordination was concerted when the N's are constrained. Upon flash photolysis of $\text{Cr}(CO)_6$ and phen in benzene, a solvated pentacarbonyl species is formed which in turn forms a new species ($\lambda_{\text{max}} = 440\text{nm}$) via first order kinetics. This new species was assigned as a pentacarbonyl $\text{Cr}(CO)_5(\text{phen})$ and its rate of formation depended on the substituents on phen indicating ligand co-ordination through N. The absorption maximum at 440nm is at a longer wavelength than the corresponding absorption in $\text{Cr}(CO)_5(\text{pyridine})$ (absorption maximum at 405nm in benzene). Distortion because of overcrowding was discounted as the absorption maximum for the assumed $\text{Cr}(CO)_5(\text{bpy})$, observed by Lees et al., was 410nm. The difference was attributed to an electronic interaction between non-co-ordinated nitrogen and Cr thereby giving rise to distortion from a typical octahedral co-ordination

Oishi detailed the following reaction scheme (given in equations 3.1.19 and 3.1.20) to explain his experimental observations:



if $[M(CO)_5]$ is constant (steady state approximation);

$$\frac{d[M(CO)_5S]}{dt} = \frac{-k_{-s}.k_1.[L]}{k_s.[S] + k_2.[L]} [M(CO)_5S] \quad (\text{eqn. 3.1.21})$$

If $k_s.[S] \gg k_1.[L]$

$$\frac{d[M(CO)_5S]}{dt} = -k_{app}[L].[M(CO)_5S] \quad (\text{eqn. 3.1.22})$$

$$k_{app} = (k_{-s}.k_1)/(k_s.[S])$$

The second order rate constant k_{app} , obtained from the plot of pseudo first order rate constant k_{obs} versus $[L]$, consists of a term involving the equilibrium of solvent co-ordination and the real rate constant for the co-ordination of L, k_1 .

$$k_{obs} = \frac{k_{-s}.k_1.[L]}{k_s.[S] + k_1.[L]} \quad (\text{eqn. 3.1.23})$$

Increased values for k_{app} for phen over pyridine indicates that rate enhancement was due to the additional nitrogen. In case of bipy, k_{app} is smaller than pyridine because of the steric hindrance caused by the protons of C3' and C3. The rate of dissociation of the second carbonyl (k_{co}) in $M(CO)_5(\text{phen})$ ($M = Mo, Cr, \text{ or } W$) were considerably greater (by at least a factor of 1000) than those for $M(CO)_5(\text{bipy})$. In addition the ordering of k_{co} ($Mo > W > Cr$) clearly differs from that of dissociative

reactivity for $M(CO)_6$ and $M(CO)_5L$. This suggested that there was a strong electronic interaction between the nonco-ordinated nitrogen of phen and metal, especially Mo and W.

In a recent study by Kalyanasundaram the dynamics of photoinduced formation of $M(CO)_4(\text{polypyridyl})$ ($M = Mo, Cr, \text{ or } W$) complexes were investigated.⁴¹ Laser photolysis of the metal hexacarbonyl containing various polypyridyl ligands yield initially the solvent co-ordinated pentacarbonyl species which reacted with the ligand in solution to form $M(CO)_5(\text{polypyridyl})$ complexes. The growth rate and final yield of $M(CO)_5(\text{polypyridyl})$ depended on the concentration of the ligand. The rate of formation of the complexes follows the order $Mo > Cr > W$. The formation of the final product (in the cases of Mo and W compounds) involving unimolecular extrusion of CO, showed good first order kinetics and the growth rate was independent of ligand concentration.

As has been stated in section 3.1.5 the chelation reactions of $M(CO)_5(\text{diimine})$ ($M = Mo, Cr, \text{ or } W$) in solution have always been studied in the presence of excess ligand. We were interested in synthesising monodentately co-ordinated $Cr(CO)_5(\text{diimine})$ complexes with a view to studying the reactions of these complexes in aromatic and alkane solvents. In our attempts to synthesise these compounds we prepared the following compounds ($Cr(CO)_5)_2(\text{dmbipy})$, ($Cr(CO)_5)_2(\text{bipy})$ and $Cr(CO)_5(\text{trpy})$. The reactions of these species in solution were monitored by uv/vis and ir spectroscopy. These studies have yielded valuable information on the nature of the chelation process at metal carbonyl centres.

3.2 RESULTS AND DISCUSSION

3.2.1 The Synthesis and Characterisation of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (dmbipy = 4,4'-dimethyl-2,2'-bipyridyl) and its Reactions in Toluene Solution

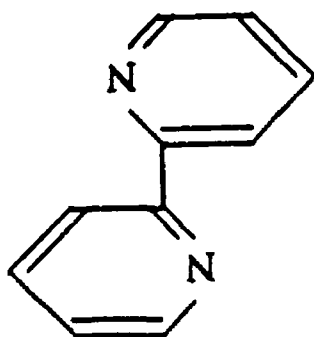
3.2.1.1 The Isolation of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

The use of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ in the preparation of $\text{Cr}(\text{CO})_5(\text{X})$ derivatives (X = nucleophilic ligands) was first documented by Skibbe and Grevels.⁴² They found that $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ was labile with respect to loss of cis-cyclooctene in solution at temperatures greater than 243K and therefore could be used as a source of $\text{Cr}(\text{CO})_5$ at temperatures above this. We were interested in synthesising monodentately co-ordinated $\text{Cr}(\text{CO})_5(\text{diimine})$ complexes with a view to studying the reactions of such complexes in solution (see Section 3.1).

The reaction of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ with dmbipy (in a 1:2 molar ratio to favour formation of the monosubstituted product) was therefore expected to yield $\text{Cr}(\text{CO})_5(\text{dmbipy})$. dmbipy is a relatively non-polar ligand and is soluble in non-polar solvents such as pentane. Upon co-ordination to $\text{Cr}(\text{CO})_6$ the resulting $\text{Cr}(\text{CO})_5(\text{dmbipy})$ complex was expected to be considerably more polar and thus would be insoluble in non-polar solvents. However surprisingly the reaction of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ with dmbipy in pentane resulted in the formation of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in high yield. Initial co-ordination of one $\text{Cr}(\text{CO})_5$ moiety to the dmbipy ligand has been suggested to activate the second pyridyl to produce the bridging species. In addition studies have shown that bipy

exists in solution in an s-trans conformation (see Figure 3.2.1.1).⁴³⁻⁴⁵ Such a conformation would require rotation about the C-C' bond and thus hinder the formation of the chelate product, to allow the formation of the bridging species.

Figure 3.2.1.1: s-trans conformation of bipy in solution.



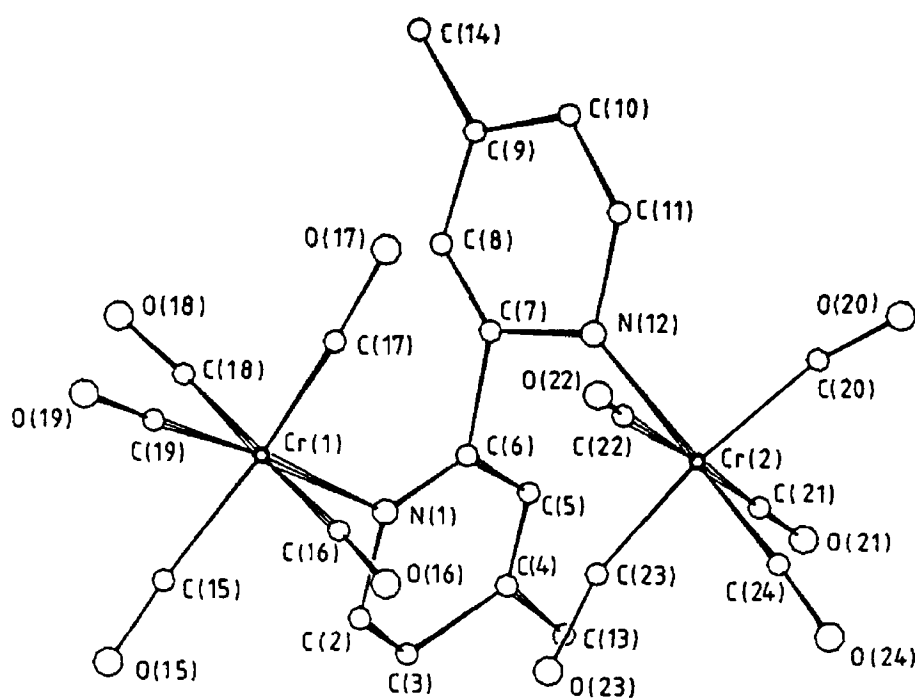
However it is thought likely in this bridging complex the presence of two metal pentacarbonyl moieties on the dmbipy ligand prevents chelation by mutually blocking the second binding site on the ligand. It is possible that the formation of the bridging complex was as a result of a purely physical effect i.e. its low solubility in pentane.

The molecular formula of this complex was confirmed by elemental analysis. Determination of the crystal structure for this complex showed that $(Cr(CO)_5)_2(dmbipy)$ contained a bridging dmbipy ligand as shown in Figure 3.2.1 2 (see Section 4.2 for full crystal structure determination), in which the two pyridyl rings are twisted by ca. 90° relevant to each other.

As yet bipyridyl complexes of group 6 metal hexacarbonyls, in which the bipyridyl ligand co-ordinates in a monodentate fashion, have not been isolated in a pure state, (though many workers claim to have observed such species in

solution),³⁰⁻³² as the formation of the chelate product occurs rapidly. Complexes of the type $M(CO)_5(dipyridylalkane)$, in which the ligand is co-ordinated in a monodentate fashion, have been isolated.³⁸ The absence of chelation has been attributed to poor σ overlap between the σ orbital of the unco-ordinated N atom and the metal d orbital in $M(CO)_5(dipyridylalkane)$.

Figure 3.2.1.2: The molecular structure of $(Cr(CO)_5)_2(dmbipy)$



3.2.1.2 ir Spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

Figure 3.2.1.3 shows the ir spectral bands of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ at 2068(w), 1937(s), 1921(s) and 1905(m,sh) cm^{-1} in toluene solution. An additional band at 1983 cm^{-1} can possibly be assigned to a small amount of $\text{Cr}(\text{CO})_6$ formed upon decomposition of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (vide infra). Figure 3.2.1.4 shows the ir bands in carbonyl stretching region for $\text{Cr}(\text{CO})_5(2\text{-phenylpyridine})$ in toluene with bands at 2066, 1921, and 1907 cm^{-1} .³⁵ In addition the ir spectral bands recorded 5s after irradiation of a solution of $\text{Cr}(\text{CO})_6$ and 4,4'-n($\text{C}_{19}\text{H}_{34}$)₂-2,2'-bipyridyl in methylcyclohexane were given as 2069, 1925, and 1915 cm^{-1} .³⁵ The number and positions of these bands are concordant with a pentacarbonyl species of pseudo C_{4v} symmetry in which the ligand is co-ordinated in a monodentate fashion.

Figure 3.2.1.3: The ir spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (ν_{co} region), in deoxygenated toluene solution.

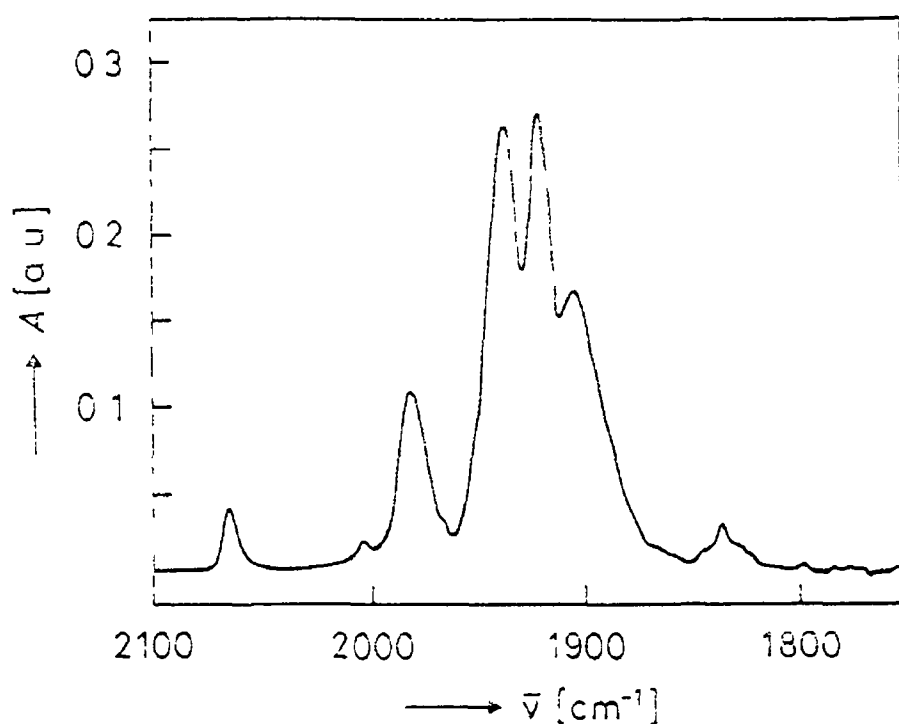
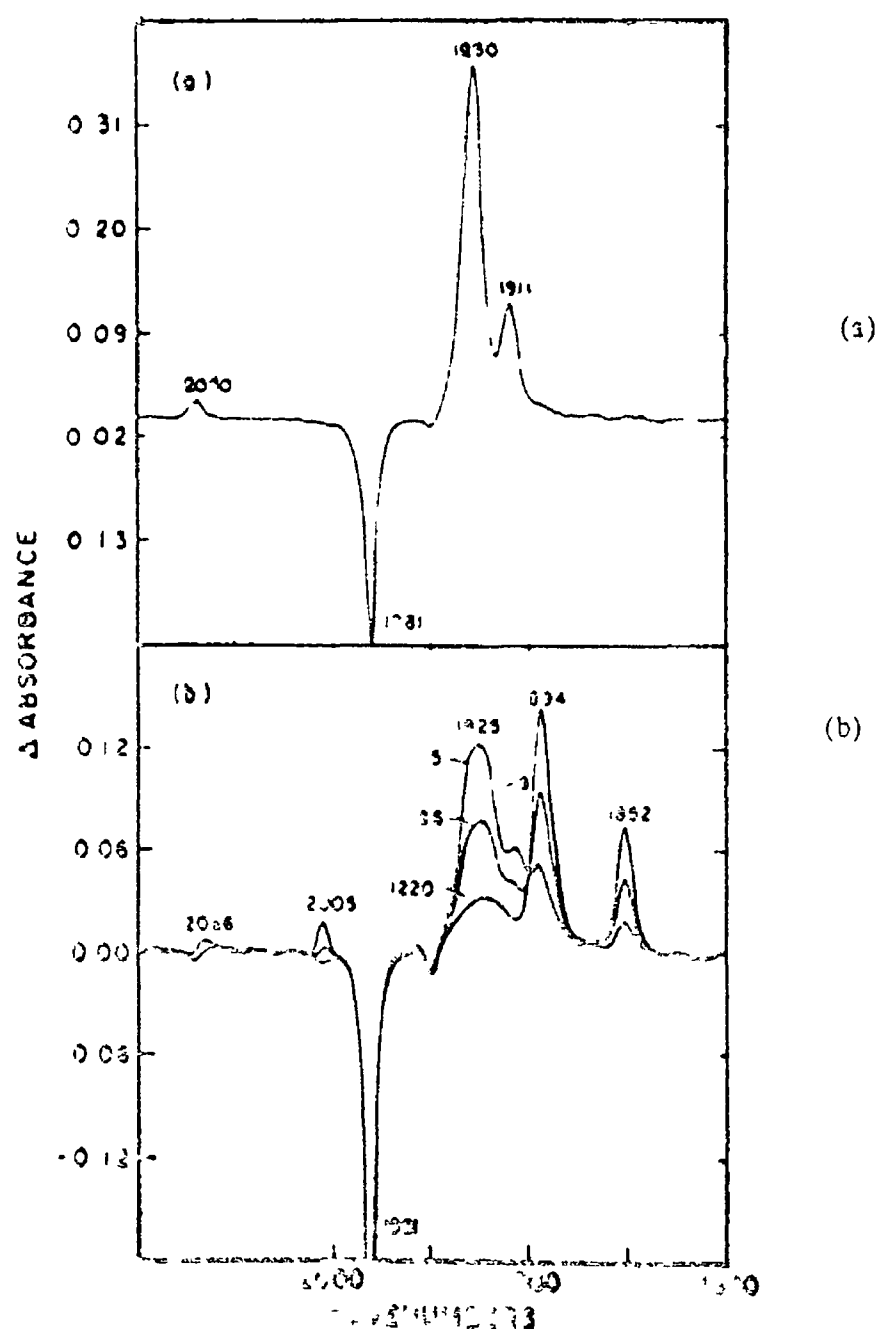
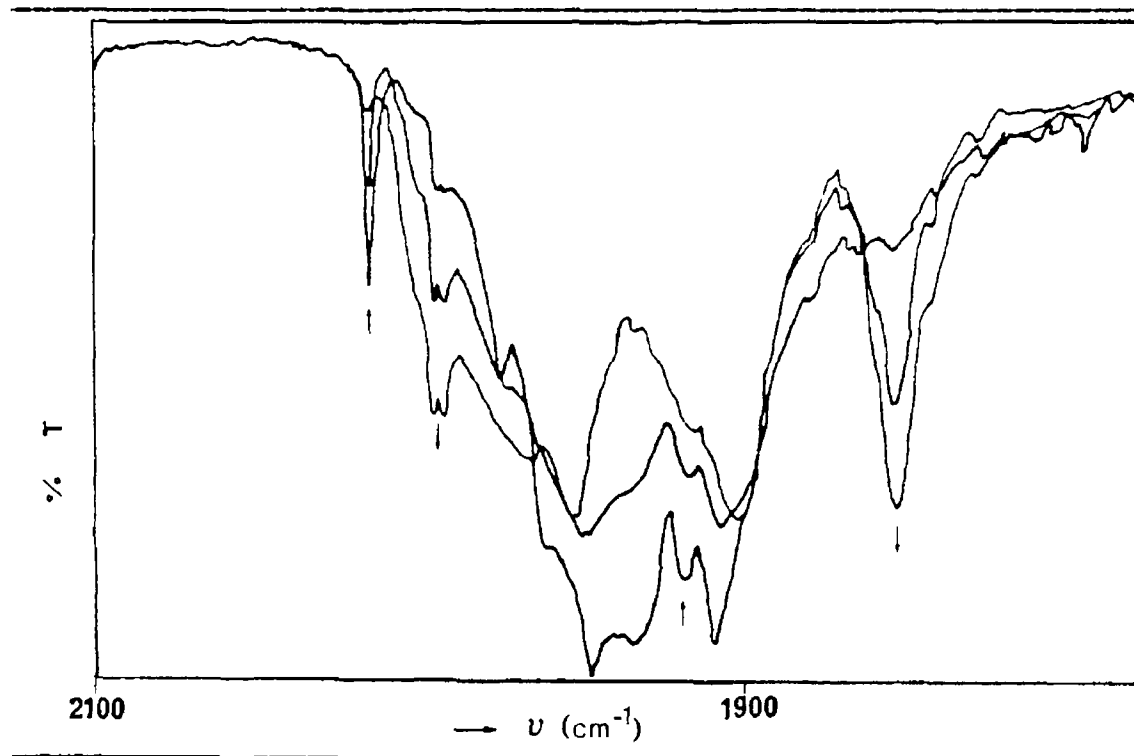


Figure 3.2.1.4: The ir spectra (ν_{CO} region) of $Cr(CO)_5(2\text{-phpy})$ in deoxygenated toluene solution (a); the ir difference spectrum recorded upon photolysis of $W(CO)_6$ in benzene solution containing an excess of 4,4'-($C_{19}H_{39}$)₂-bipy ligand (b).



The four bands of the bridging complex at 2068, 1937, 1921, and 1905 cm^{-1} correspond to the A_1 , E_1 (the 'E' mode is split in the spectrum i.e. at 1937 and 1921 cm^{-1}) and A_1^2 modes of a pseudo C_{4v} molecule respectively. The ir bands of the bridging complex in KBr are given in Figure 3.2.1.5. It is noted that the enhanced intensity of the normally forbidden B_1 mode (at ca. 1980 cm^{-1}) implies that the symmetry of the molecule about the metal carbonyl centre is reduced (this band is masked in the spectrum of the bridging complex in toluene solution by the presence of the T_{1u} band of $\text{Cr}(\text{CO})_6$ vide infra). This phenomena has been reported in $\text{M}(\text{CO})_5(\text{dipyridylalkane})$ complexes ($M = \text{Mo}, \text{Cr}, \text{or W}$),³⁸ and has been attributed to the asymmetry of the dmbipy ligand, which reduces the the overall symmetry of the molecule from pseudo C_{4v} to C_s . In addition the perturbation of the local C_{4v} symmetry is indicated by the removal of the degeneracy of the E mode (resulting in two bands at 1937 and 1921 cm^{-1}).

Figure 3.2.1.5: ir spectral changes (ν_{CO} region) recorded upon heating a KBr disc of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$, at 343K at 15 minute intervals.



3.2.1.3 uv/vis Spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

The uv/vis spectrum recorded upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in degassed toluene (recorded ca. 1 minute after dissolution) is given in Figure 3.2.1.6. The spectrum exhibits a low energy absorption band in the visible region centred at 410nm ($\epsilon = 5149 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) and further stronger bands in the uv region. These bands together with those measured for similar compounds by Zulu and Lees are given in Table 3.2.1.1.47 These workers assigned the transitions outlined in Table 3.2.1.1 to the observed bands based on the behaviour of these bands in a variety of solvents.

Figure 3.2.1.6: The uv/vis spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in deoxygenated toluene solution at 296K.

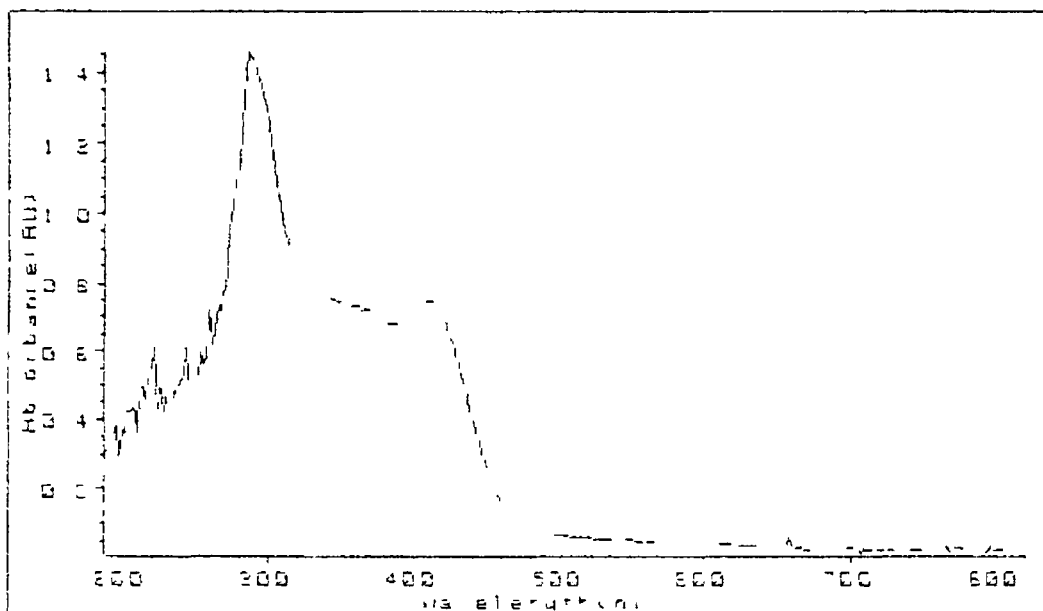


Table 3.2.1.1: Electronic absorption data and spectral assignments for $W(CO)_5(L)$ and $(M(CO)_5)_2(L)$ ($M = Cr$ or W) in benzene at 293K

Compound	$\max(nm)$ ($10^4 E, mol^{-1} dm^3 cm^{-1}$)	
	$1A_1 \rightarrow 1E$	MLCT
$(W(CO)_5)_2(pyz)a$	397 (0.55)	510 (1.20)
$(W(CO)_5)_2(4,4'bipy)b$	404 (1.18)	438 (1.08)
$(W(CO)_5)_2(bpe)c$	404 (1.07)	450 (1.55)
$W(CO)_5(pyr)$	398 (0.71)	d
$W(CO)_5(4,4,-bipy)$	400 (1.03)	d
$W(CO)_5(bpe)$	402 (0.36)	440(sh)
$(Cr(CO)_5)_2(dmbipy)$	410 (0.52)	d

(a) pyr = pyrazine, (b) 4,4'bipy = 4,4'-bipyridine (c) bpe = trans-1,2-bis(4-pyridylethylene)
(d) overlaps with LF band

Thus the band at 410nm in the spectrum of $(Cr(CO)_5)_2(dmbipy)$ in toluene can be attributed to a $1A(e4b22) \rightarrow 1E(e3b22a11)$ LF transition while those in the uv region can be assigned to a combination of $1A(e4b22) \rightarrow 3E(e3b22a11)$ LF and MLCT transitions.

The $1A_1 \rightarrow 1E$ absorption bands are similar in both the mononuclear and dinuclear complexes (Table 3.2.1.1), which would indicate that the local C_{4v} symmetry of the carbonyl ligands was essentially unperturbed on forming the ligand bridged dimers. The conformation of these ligands would not be expected to change upon co-ordination as they are very symmetrical in structure. bipy has been shown to exist in solution as a s-trans isomer and yet in the crystal structure of $(Cr(CO)_5)_2(dmbipy)$ the two pyridyl rings were twisted by 90° relative to each other. This would suggest that co-ordination of the ligand to $Cr(CO)_5$ moiety could significantly perturb the overall symmetry of the molecule.

The position of the MLCT band can be used to assess the energy of the ligand π^* -acceptor orbitals. When $L = 4,4'$ -bipy or bpe, the MLCT band is lower in energy than the LF band in both the mononuclear and dinuclear complexes. The ligand π^* orbitals appear to be stabilised to a small extent. In the pyrazine complex, the energy level was substantially lowered. In general the more π^* -conjugation present in the system the lower the energy of the π^* orbital of the ligand. The absence of a MLCT band at higher wavelength (i.e. above 410nm) in the spectrum of $(Cr(CO)_5)_2(dmbipy)$ indicates that there is little π^* conjugation in the molecule. This would suggest that the pyridyl rings are not coplanar in solution (as is the case in the solid structure shown in Figure 3.2.1.2). In addition the absence of an absorption band at 290nm normally assigned to a $\pi \rightarrow \pi^*$ transition in bipyridyl complexes, suggests that the energy of the bipy based π^* energy level in $(Cr(CO)_5)_2dmbp$ is higher than in either the free ligand or $Cr(CO)_4dmbp$. This implies that the two pyridyl ring systems in the bridging complex are not coplanar precluding efficient overlap of the π systems on the two rings.

Previous workers have shown that photolysis of $\text{Cr}(\text{CO})_6$ in benzene containing excess bipy ligand showed the growth of a band at 410nm which was assigned to a $\text{Cr}(\text{CO})_5(\text{bipy})$ complex.³³ This species was not isolated from solution but its spectral bands are very similar to those assigned to $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$.

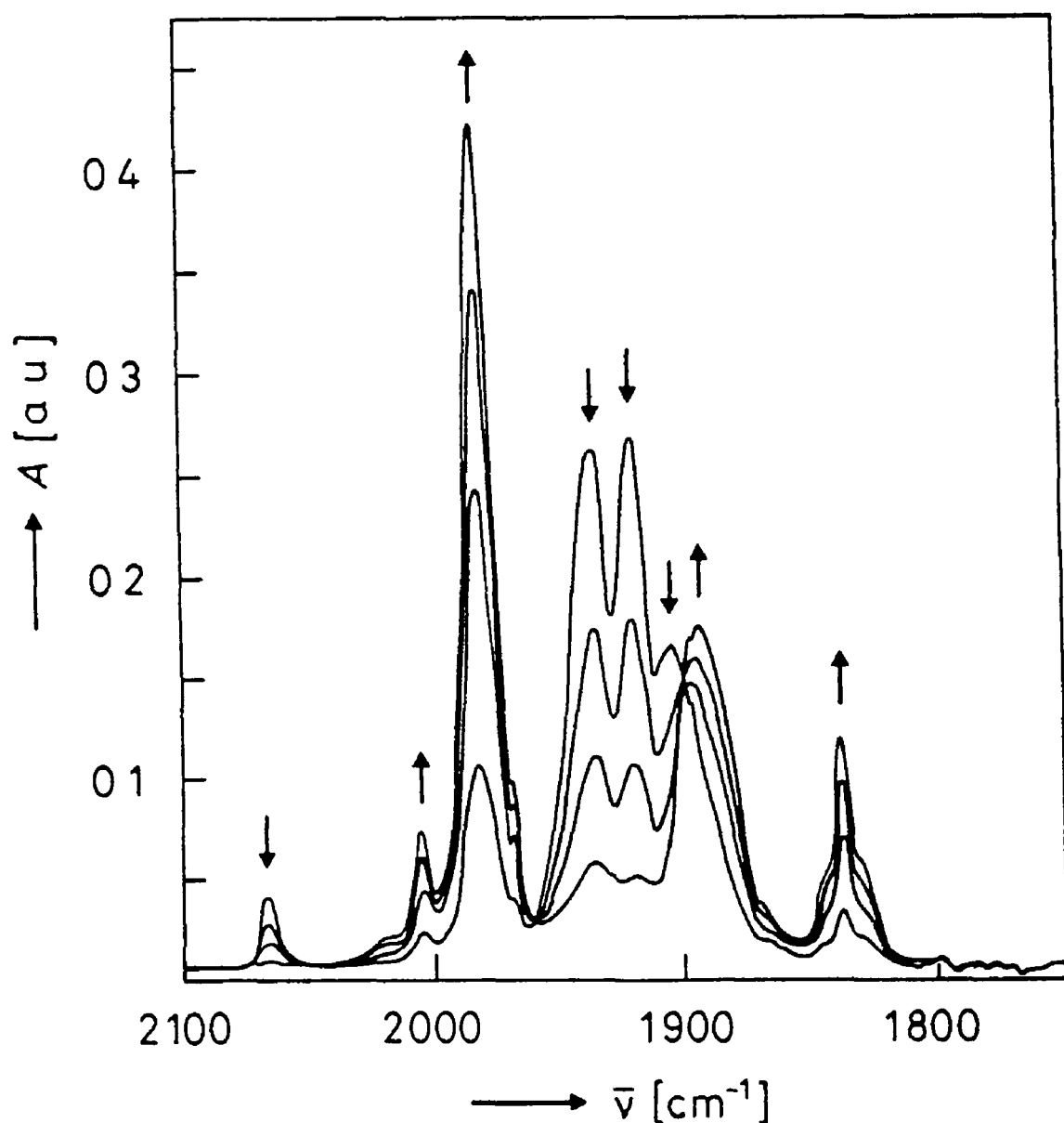
3.2.1.4 The Thermal Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in the Solid Phase

The formation of a chelate product $\text{Cr}(\text{CO})_4(\text{dmbipy})$ from $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was observed in the solid phase. The ir spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in a KBr disc at room temperature is given in Figure 3.2.1.5, together with spectra recorded at various time intervals after the KBr disc has been heated to 343K. The ir band at 2061cm^{-1} is seen to diminish as does the band at 1905cm^{-1} and new bands at 2000 and 1800cm^{-1} formed. These bands have been identified as the A_1 and B_2 ir modes of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ by comparison with those of an authentic sample (for preparation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ experimental section).

3.2.1 5 Monitoring, by ir Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in Toluene Solution at ambient temperature

An arbitrary amount of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was added to a nitrogen purged toluene solution in a sealed ir cell, under a nitrogen atmosphere, and the ir spectral changes which occurred upon standing of this solution are shown in Figure 3.2.1.7. The intensity of the four bands, which have been previously assigned to the $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ complex, diminished upon standing, with the concomitant growth of bands at $2007(\text{w})$, $1896(\text{s})$ and $1839(\text{s})\text{cm}^{-1}$.

Figure 3.2.1.7: The ir spectral changes (ν_{CO} region) recorded upon standing of a solution of $(Cr(CO)_5)_2(dmbipy)$ ($3.1 \times 10^{-3} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 0, 1,500, 3,600 and 6960s at ambient temperature.



These bands were assigned to the A₂, B₁ and B₂ vibrational modes of a C_{2v} tetracarbonyl Cr(CO)₄(dmbipy) species and confirmed as such by comparison with an authentic sample (see experimental section). A weak band at ca. 1860cm⁻¹, which overlaps with the band at 1896cm⁻¹, was assigned to the A₁ vibrational mode.

A strong band at 1980cm⁻¹ which can be assigned to Cr(CO)₆ (based on comparison with authentic sample) was also formed. The maintenance of isosbestic points throughout the reaction indicated that the formation of hexacarbonyl and Cr(CO)₄(dmbipy) was via a process uncomplicated by side or subsequent reactions. The stoichiometry of this reaction was confirmed by determining the ratio of [Cr(CO)₆] to [Cr(CO)₄(dmbipy)] throughout the reaction. The results in Table 3.2.1.2 show this ratio to remain constant, within experimental error.

Table 3.2.1.2: Absorbance values for $\text{Cr}(\text{CO})_6^{\text{a}}$ and $\text{Cr}(\text{CO})_4(\text{dmbipy})^{\text{b}}$ measured at various times, n , following dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in toluene solution.

Compound	Time(s)						
	300	2100	3420	4080	4980	6180	8580
$\text{Cr}(\text{CO})_6$	.0470	.1521	.2194	.2706	.3141	.3585	.4054
$\text{Cr}(\text{CO})_4$	.0128	.0410	.0580	.0734	.0860	.0989	.0113
Ratio ^c	3.73	3.96	3.32	3.45	3.44	3.30	

a Absorbance of $\text{Cr}(\text{CO})_6$ measured at 1983cm^{-1}

b Absorbance of $\text{Cr}(\text{CO})_4\text{dmbp}$ measured at 1836cm^{-1}

c $\text{Abs. of } \text{Cr}(\text{CO})_6_{t=n+1} - \text{Abs. of } \text{Cr}(\text{CO})_6_{t=n}$

$\text{Abs of } \text{Cr}(\text{CO})_4(\text{dmbipy})_{t=n+1} - \text{Abs. of } \text{Cr}(\text{CO})_4(\text{dmbipy})_{t=n}$

Determination of the extinction coefficient of $\text{Cr}(\text{CO})_6$ ($\epsilon = 14,505 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ at 1983cm^{-1}), $\text{Cr}(\text{CO})_4(\text{dmbipy})$ ($\epsilon = 3670 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ at 1836cm^{-1}) in toluene solution (see Tables 3.2.1.3) confirmed a 1:1 molar ratio of $\text{Cr}(\text{CO})_6$ to $\text{Cr}(\text{CO})_4(\text{dmbipy})$ is maintained throughout the reaction.

Table 3.2.1.3: Data for the determination of ϵ for extinction coefficients for $\text{Cr}(\text{CO})_4(\text{dmbipy})$ and $\text{Cr}(\text{CO})_6$.

Compound	Concentration (mol dm ⁻³)	Absorbance (A.U.)	ϵ (mol ⁻¹ dm ³ cm ⁻¹)

$\text{Cr}(\text{CO})_6$	9.54×10^{-4}	.1426	14,947
	7.73×10^{-4}	.1097	14,191
	5.53×10^{-4}	.0799	14,442

=> $\epsilon = 14,505 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$

$\text{Cr}(\text{CO})_4(\text{dmbipy})$			
	1.60×10^{-3}	.0611	3,818
	3.44×10^{-3}	.1222	3,552
	3.44×10^{-3}	.1232	3,581
	3.60×10^{-3}	.1342	3,728

=> $\epsilon = 3,670 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$

The determination of the extinction coefficient of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ ($\epsilon = 1,250 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ at 2065cm^{-1}) indicated that the stoichiometry of the reaction to be as given in equation 3.2.1.1 (see Table 3.2.1.4).

$(\text{Cr}(\text{CO})_5)_2(\text{dmbipy}) \quad \text{---->} \quad \text{Cr}(\text{CO})_6 + \text{Cr}(\text{CO})_4(\text{dmbipy})$

(eqn. 3.2.1.1)

Table 3.2.1.4: Determination, at various time intervals, of the number of moles of $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_4(\text{dmbipy})$ produced and number of moles of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ consumed during the chelation reaction.

Moles of carbonyl complex formed in time interval ($t_{n+1} - t_n$) ($\times 10^5$)			
$t_{n-1} - t_n$	$\text{Cr}(\text{CO})_4(\text{dmbipy})$	$\text{Cr}(\text{CO})_6$	$(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$
2100 - 300	7.9	7.7	-7.2
3420 - 2100	4.6	4.6	-6.0
4080 - 3420	3.5	4.2	-4.2
4980 - 4080	3.0	3.4	-3.7
6180 - 4980	3.1	3.8	-3.4
8580 - 6180	3.2	3.8	-4.0
8580 - 300	25	27	-28

n has same meaning as in Table 3.2.1.2.

The stoichiometry was confirmed by repeating the reaction on a large scale. A known amount of $(\text{Cr}(\text{CO})_5)_2(\text{dmbp})$ in nitrogen purged toluene solution was left overnight under an nitrogen atmosphere. The solvent and any hexacarbonyl formed were removed by vacuum pumping and the residual orange compound analysed by elemental analysis. The results are summarised below;

Element	Theoretical % in cmpd.	% found in cmpd.
Carbon	55.17	58.02
Hydrogen	3.44	4.39
Nitrogen	8.04	7.52

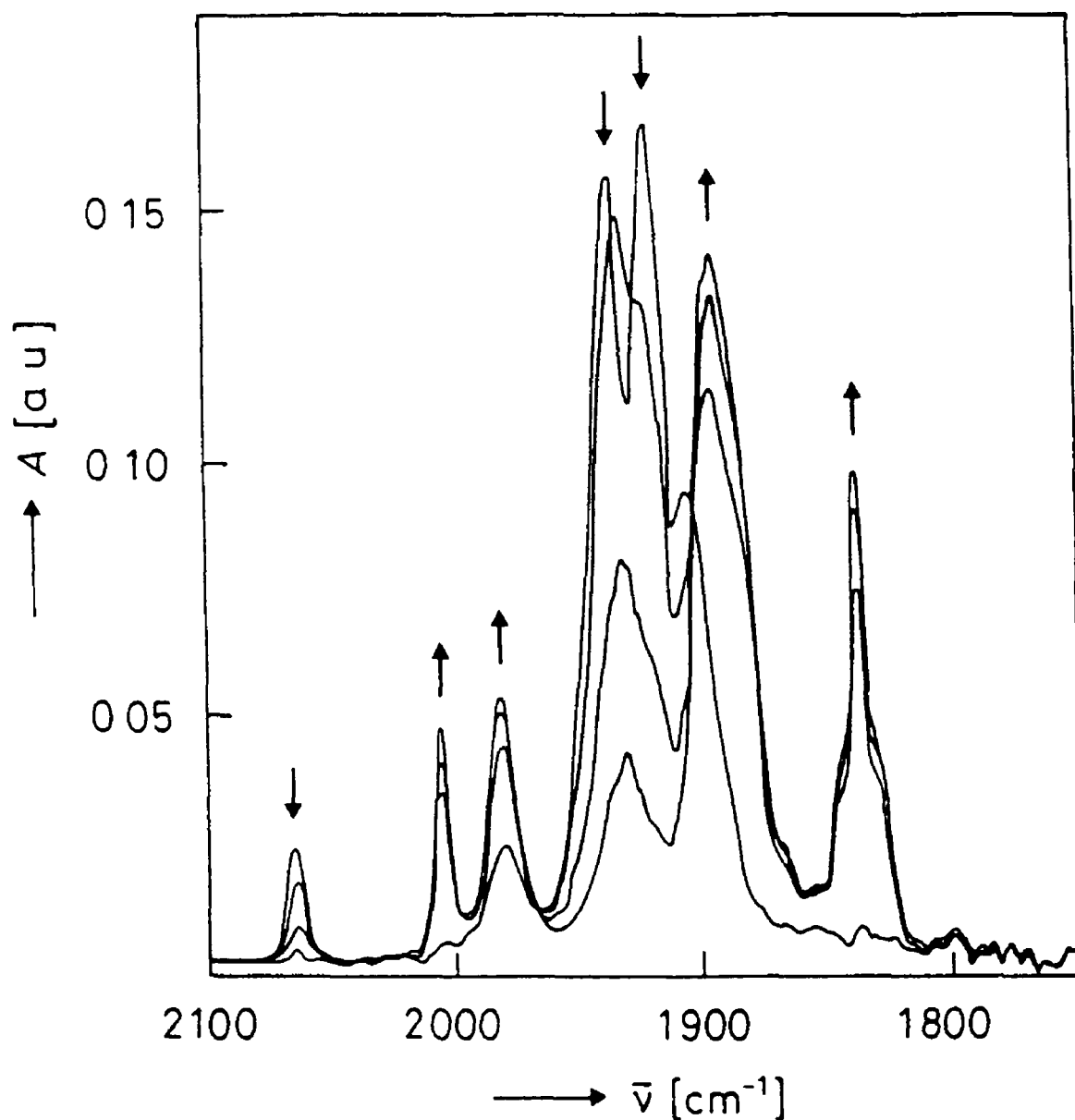
Thus while the sample was not completely pure it was of sufficient quality to conclude that a molar equivalent of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ was formed from $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (equation 3.2.1.1).

3.2.1.6 Monitoring, by ir Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in Toluene Solution Containing Excess dmbipy Ligand, at Ambient Temperature

The overall stoichiometry of the reaction as given in equation 3.2.1.1 shows one molecule of both $\text{Cr}(\text{CO})_4(\text{dmbipy})$ and $\text{Cr}(\text{CO})_6$ was formed from one molecule of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$. It was not apparent from the above experiments if the chelation reaction was an associative intramolecular rearrangement process or a dissociative process. Therefore the chelation reaction was studied under varying experimental conditions, including those in which excess dmbipy ligand was added to the reaction solution. The ir spectral changes recorded upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in toluene, in the presence of excess dmbipy, are shown in Figure 3.2.1.8.

Table 3.2.1.5 shows the absorbance values and corresponding molar equivalents for $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$, $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\text{dmbipy})$ at various time intervals throughout the chelation reaction when, excess dmbipy was present.

Figure 3.2.1.8: The ir spectral changes (ν_{CO} region) occurring upon standing a solution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ ($1.8 \times 10^{-3} \text{ mol dm}^{-3}$) and dmbipy ($1.3 \times 10^{-1} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 120, 900, 2,220, and 11,520s at ambient temperature.



While the overall stoichiometry of the reaction is approximately 1:2 ($\text{Cr(CO)}_5)_2(\text{dmbipy})$):($\text{Cr(CO)}_4(\text{dmbipy})$) the absorbance changes at 2065cm^{-1} ($\text{Cr(CO)}_5)_2(\text{dmbipy})$ and 1834cm^{-1} ($\text{Cr(CO)}_4(\text{dmbipy})$) shows this stoichiometry is not maintained throughout the reaction. ($\text{Cr(CO)}_5)_2(\text{dmbipy})$ is seen to disappear quite rapidly in the initial stages of the reaction but it does not yield a 2 molar equivalent of $\text{Cr(CO)}_4(\text{dmbipy})$. However one must be cautious when attaching significance to these observations as the absorbance values of ($\text{Cr(CO)}_5)_2(\text{dmbipy})$ are quite low at the analysis wavelength (thus errors in these values could be quite large).

The presence of dmbipy in solution inhibits the formation of Cr(CO)_6 from the bridging complex, while the yield of $\text{Cr(CO)}_4(\text{dmbipy})$ is almost doubled, relative to that when there is no excess ligand present. The effect of excess ligand on the yield of Cr(CO)_6 indicates that the reaction mechanism is not as simple as that given in equation 3.2.1.1. If such were the case the effect of adding excess ligand would be negligible.

A most interesting feature of Figure 3.2.1.8 is the nature of the E mode of the bridging species (1930cm^{-1}); the degeneracy of the E mode being restored relatively soon after the reaction begins. These results are consistent with the bridging molecule forming an intermediate species which in turn forms $\text{Cr(CO)}_4(\text{dmbipy})$. The position and intensity of these bands indicate that this intermediate species is also a pentacarbonyl molecule and its spectrum is similar to $\text{Cr(CO)}_5(2\text{-phpy})$ (2-phpy = 2-phenylpyridine). It was also noted that the chelation reaction occurred on a much faster timescale than in the absence of any excess ligand.

The reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in toluene solution were further studied by uv/vis spectroscopy. The use of a fast scanning diode array spectrophotometer allowed the determination of the kinetics and thermodynamics of the chelation reaction.

3.2.1.7 Monitoring, by uv/vis Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in Toluene Solution at 295K

The spectral changes, shown in Figure 3.2.1.9(a), were recorded upon standing of a degassed solution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in toluene. The LF band of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ at 410nm was seen to decay with a concomitant growth of a band in the visible region centred at 518nm. The maintenance of an isosbestic point at ca. 470nm indicates that the reaction is uncomplicated by side or subsequent reactions. The final spectrum recorded, given in Figure 3.2.1.9(b), shows three bands, at 518nm(w), 387nm(sh) and 330nm(sh), which are characteristic of a $\text{Cr}(\text{CO})_4(\text{dmbipy})$ complex.^{48,49} These bands are identical to those of an authentic sample of $\text{Cr}(\text{CO})_4(\text{dmbipy})$. They have been assigned by a number of workers as being;

MLCT	at 518nm
$^1\text{A} \rightarrow ^1\text{E}$	at 387nm
$^1\text{A} \rightarrow ^3\text{E}$	at 327nm

The rate constant for the formation of the chelate product was determined from the grow-in of the MLCT band of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ at 518nm. A plot of $\ln[(A - A_0)/(A - A_t)]$ versus time exhibited linearity with correlation coefficients typically about 0.99. The slope of the plotted line is equal to the rate constant for the reaction k_{obs} which in this case was $3.33 \times 10^{-4} \text{ s}^{-1}$ at 296K. Figure 3.2.1.10 shows the absorbance at 518nm versus time for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ (dotted line) and a single exponential is fitted to this curve.

Figure 3.2.1.9: (a) The uv/vis spectrum of $\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ ($1.2 \times 10^{-4} \text{ mol dm}^{-3}$) in degassed toluene solution at 296K, and the spectral changes occurring upon standing of this solution for 500, 1250, and 4000s. (b) uv/vis Spectrum recorded upon completion of the chelation reaction.

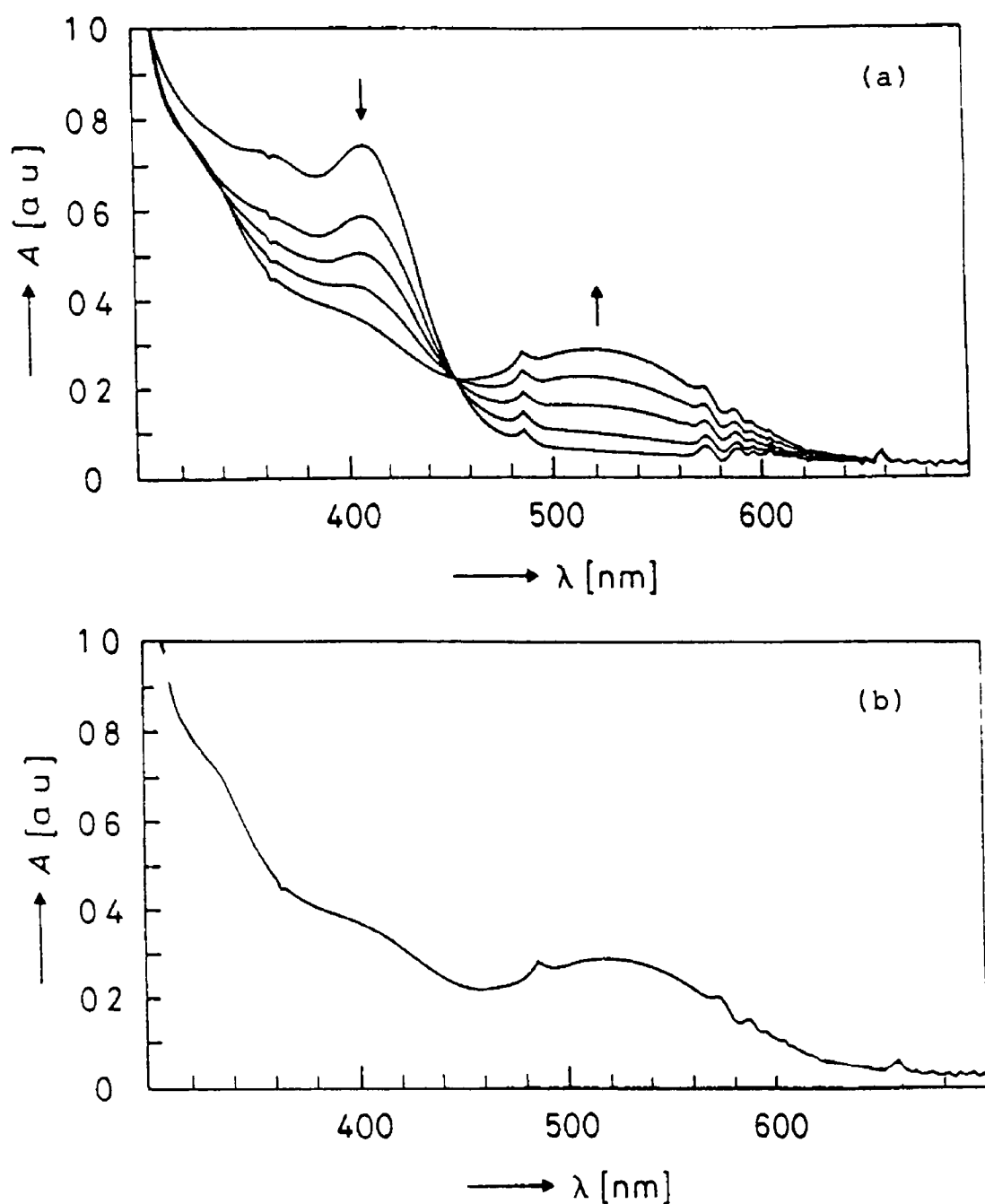
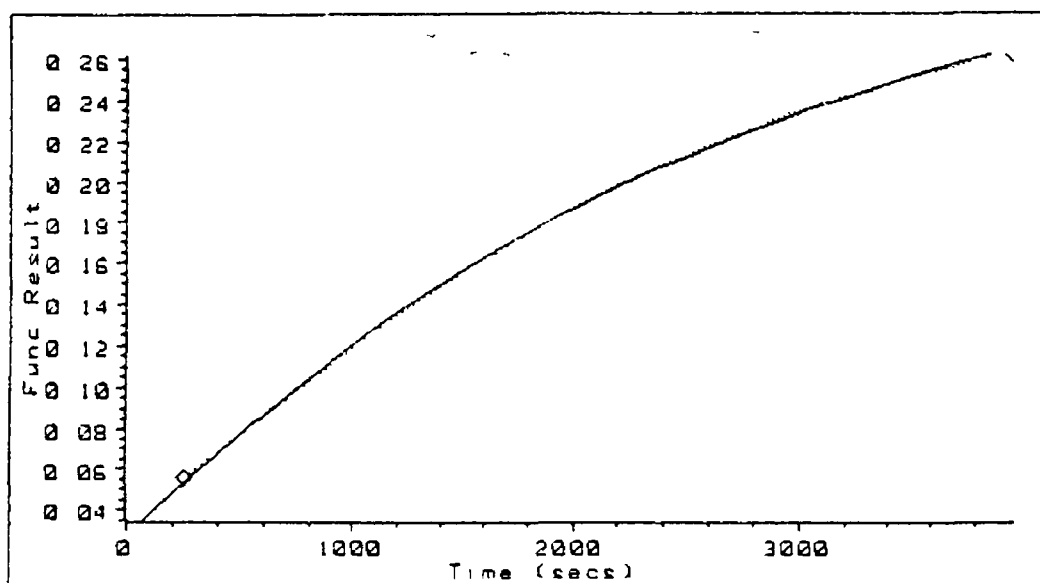


Figure 3.2.1.10: A plot of the variation of the absorbance at 518nm for the reaction of $\text{Cr(CO)}_5)_2(\text{dmbipy})$ to form $\text{Cr(CO)}_4(\text{dmbipy})$ and Cr(CO)_6 (only $\text{Cr(CO)}_4(\text{dmbipy})$ absorbs at 518nm).



The only similar experiment, to date, has been the monitoring by uv/vis diode-array spectroscopy of the chelation reaction of $\text{M(CO)}_5(\text{en})$ to form $\text{M(CO)}_4(\text{en})$ and CO ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$, $\text{en} = \text{ethylenediamine}$) ³⁹ kobs for the formation of $\text{Cr(CO)}_4(\text{en})$ at 323K was given as $3 \times 10^{-4} \text{s}^{-1}$ (in chloroform solution). The rate of formation of $\text{Cr(CO)}_4(\text{dmbipy})$ is considerably greater than the substitution reaction of pyridine with $\text{Cr(CO)}_5(\text{pyridine})$ to form the disubstituted tetracarbonyl species. Wrighton has attributed this to a substantial contribution to CO extrusion by the ligand being already co-ordinated in a monodentate fashion.³⁶

3.2.1.8. Monitoring, by uv/vis Spectroscopy, of the Behaviour of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in Toluene Solution, Containing Excess dmbipy Ligand, at 295K

The uv/vis spectral changes observed upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in toluene solution containing excess dmbipy ligand are shown in Figure 3.2.1.11. The intensity of the product MLCT band at 518nm at the end of the chelation reaction (A_p), relative to the LF band at 410nm (corresponding to $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ at the start of the reaction) (A_r), increased upon addition of excess dmbipy ligand.

Table 3.2.1.6: Determination of the relative yield of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ (i.e. relative to initial concentration of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$), in the presence and absence of excess dmbipy.

Concentration of dmbipy mol dm^{-3}	$(A_p)/(A_r)$
0.00	0.51
0.00	0.48
1.40×10^{-2}	0.93
4.10×10^{-2}	0.88
1.33×10^{-1}	0.88

Figure 3.2.1.11: uv/vis Spectral changes occurring upon standing a solution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ ($1.4 \times 10^{-4} \text{ mol dm}^{-3}$) and dmbipy (0.13 mol dm^{-3}) in degassed toluene solution at 296K, for 150, 375, 675, 1000, 1550, and 3775s.

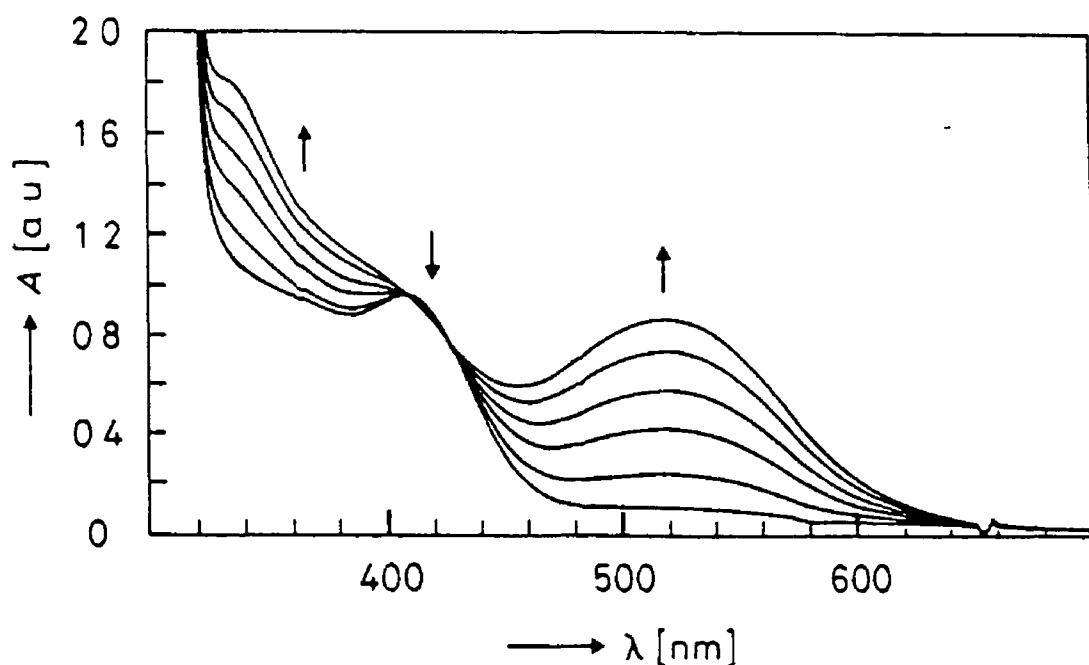
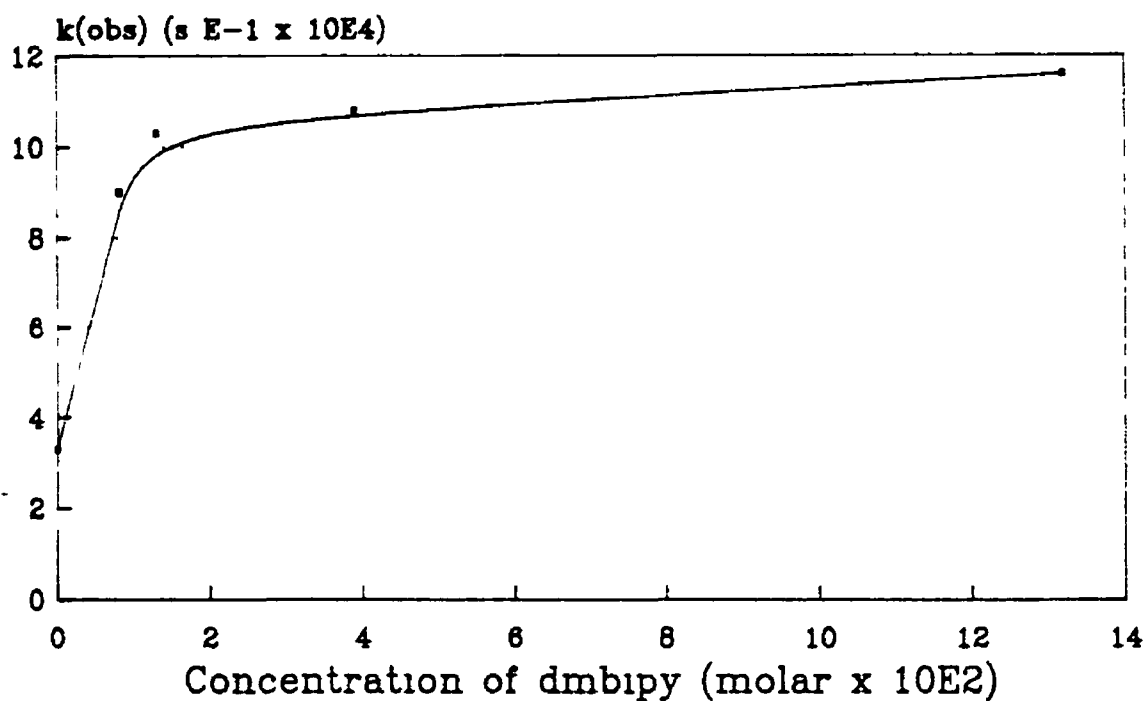


Table 3.2.1.6 shows the relative yield of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ from $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in the presence and absence of ligand. These results are consistent with the reaction stoichiometry given in equation 3.2.1.2. Determination of the exact stoichiometry of all species in solution is difficult because of the overlap of spectral bands.

The presence of excess dmbipy had a considerable effect on the rate of chelation. The rate constant for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ at various concentrations of dmbipy are given in Table 3.2.1.7 and shown graphically in Figure 3.2.1.12.

Figure 3.2.1.12: The dependence of k_{obs} (s^{-1}), for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$, on the concentration of added dmbipy.



The presence of ligand increases the observed rate constant to a maximum value of $1.14 \times 10^{-3} \text{ s}^{-1}$. The plateau effect, evident in Figure 3.2.1.12, is typical of equilibrium processes, but could also indicate that the reaction course was altered by the addition of excess ligand.

Table 3.2.1.7: The variation in k_{obs} , for the formation of the chelate product, with concentration of dmbipy in solution

Concentration of dmbipy (mol dm ⁻³)	k_{obs} (s ⁻¹)
0.00	3.33×10^{-4}
6.52×10^{-3}	8.56×10^{-4}
1.40×10^{-2}	9.58×10^{-4}
4.10×10^{-2}	1.03×10^{-4}
1.33×10^{-1}	1.14×10^{-3}

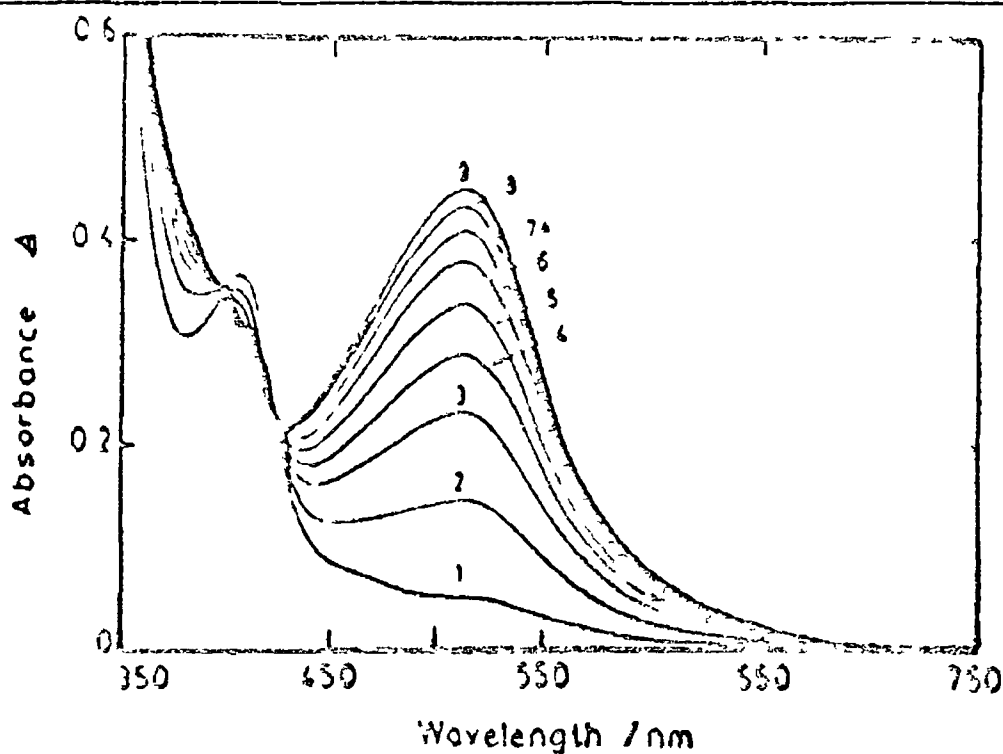
This experiment is essentially similar to a great deal of others which have been carried out by Lees et al.³¹⁻³⁵ Figure 3.2.1.13 shows the spectral changes recorded following the ca. two second irradiation of a solution of 5×10^{-4} moldm⁻³ W(CO)₆ in benzene at 293K, containing 10^{-2} moldm⁻³ 2,2'-bipyridine (2,2'-bipy).³² Table 3.2.1.8 gives the first order rate constant for this reaction and similar reactions with other diimine ligands.

The rate of formation of W(CO)₄(diimine) depended on the nature of the diimine ligand. This dependence was interpreted as an indication of an associative process. In this particular work and in many other studies the rate of chelation appeared to be independent of ligand concentration. This was attributed to the fact that these workers always monitored the chelation reactions in the 'plateau' region of free ligand concentration.

Table 3.2.1.8: First order rate constant for the formation of $W(CO)_4(\text{diimine})$ in benzene at 293K.

diimine	$K_{\text{obs}} \text{ (s}^{-1}\text{)}$
2,2'-bipy	3.86×10^{-2}
4,4'-(CH ₃) ₂ -bipy	3.51×10^{-2}
4,4'-(C ₄ H ₉) ₂ -bipy	1.58×10^{-2}
4,4'-(C ₆ H ₅) ₂ -bipy	1.98×10^{-2}

Figure 3.2.1.13: uv/vis Spectral changes recorded following ca. 2s photolysis with a 200 W Hg lamp of a solution of $W(CO)_6$ ($5 \times 10^{-4} \text{ mol dm}^{-3}$) and bipy ($10^{-2} \text{ mol dm}^{-3}$) in benzene at 293K. Curve 1 is the initial spectrum recorded within 4 s after photolysis. Curves 2-9, spectra at 15s intervals.



3.2.1.9. Behaviour of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in CO Saturated Toluene

Saturation of the toluene with carbon monoxide prior to dissolving $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$, resulted in a rapid reduction in intensity of the band at 410nm ($k_{\text{obs}} = 1.7 \times 10^{-1} \text{ s}^{-1}$); see Figure 3.2.1.14. Only a small yield of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ was detected under these conditions (< 20% of that obtained in the absence of both carbon monoxide and added dmbp); k_{obs} for the production of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ was $1.8 \times 10^{-1} \text{ s}^{-1}$. This implies that the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ from $\text{Cr}(\text{CO})_5(\text{dmbipy})$ competes with the dissociation of $\text{Cr}(\text{CO})_5(\text{dmbipy})$ into $\text{Cr}(\text{CO})_5$ and dmbp. CO reacts with $\text{Cr}(\text{CO})_5$ to generate $\text{Cr}(\text{CO})_6$. This result is in contrast to that in reference 35, in which $\text{W}(\text{CO})_5(4,4'-(\text{C}_{19}\text{H}_{39})-2,2'\text{-bipy})$ does not appear to be labile to loss of $4,4'-(\text{C}_{19}\text{H}_{39})-2,2'\text{-bipy}$. however this latter result was obtained in the presence of an excess of $4,4'-(\text{C}_{19}\text{H}_{39})-2,2'\text{-bipy}$ which would compete with CO for the pentacarbonyl complex. The presence of carbon monoxide would also suppress the reformation of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ from $\text{Cr}(\text{CO})_5(\text{dmbipy})$ and $\text{Cr}(\text{CO})_5$.

An additional experiment confirmed that $\text{M}(\text{CO})_5(\text{N-ligand})$ complexes are labile to loss of the N-ligand when the N-ligand contains a bulky group alpha to the co-ordinating ligand. Figure 3.2.1.15 shows the spectral changes observed when $\text{Cr}(\text{CO})_5(2\text{-phpy})$ was dissolved in thf solution. These spectral changes are consistent with the following reactions;

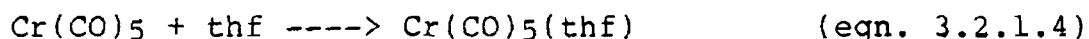


Figure 3.2.1.14: uv/vis Spectral changes observed following dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in CO saturated toluene solution at 296K.

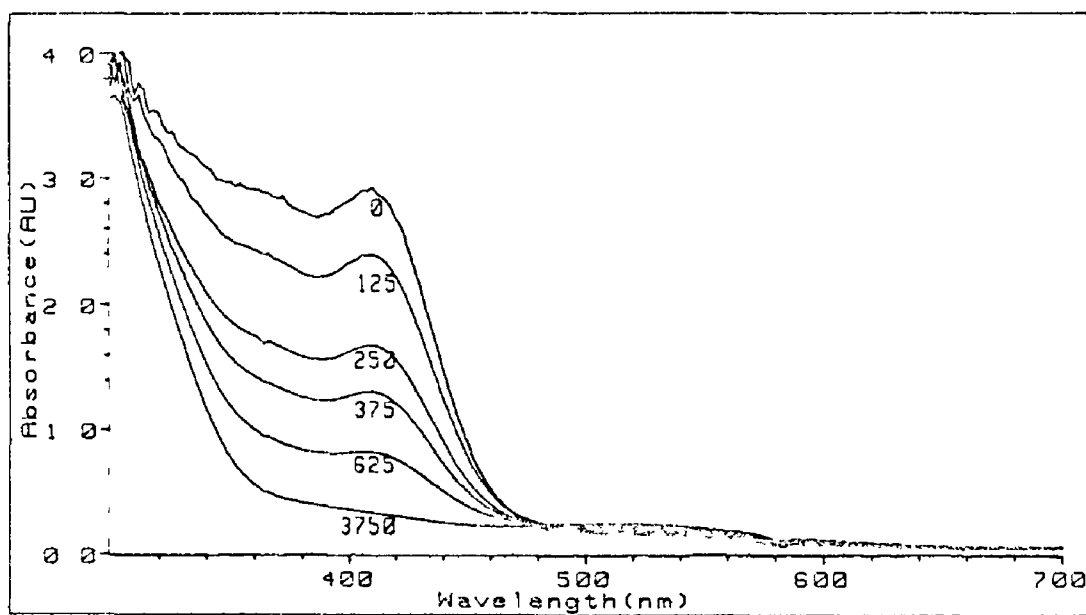
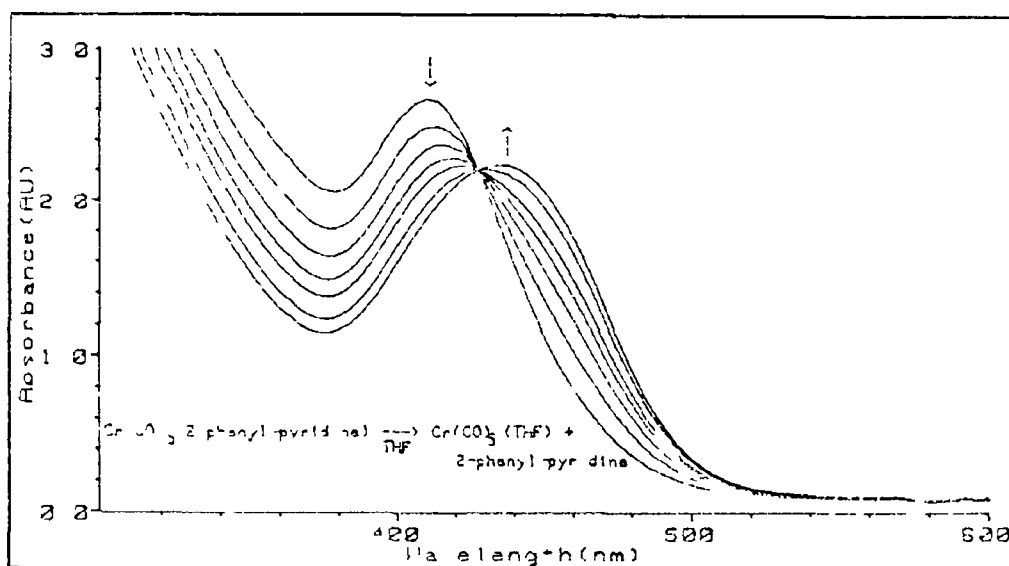


Figure 3.2.1.15: uv/vis Spectral changes observed upon dissolution of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in degassed thf solution.



3.2.1.10 The Activation Parameters for the Formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$, in the Presence and Absence of Excess dmbipy

The activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ were measured in the presence and absence of excess dmbipy and the results given in Tables 3.2.1.9 and 3.2.1.10 (see also Figures 3.2.1.16 and 3.2.1.17).

Table 3.2.3.9: Experimental data for the determination of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ in the absence of any excess ligand.

Temperature (K)	$\ln(R)_a$	$\ln(R_t)_a$
315	-5.24	-10.99
309	-6.53	-12.27
305	-6.66	-12.38
303	-7.26	-12.98
296	-8.06	-13.75

Arrhenius Plot.

Slope = $-13,224 \pm 1365$

Int. = $36.56 \pm .22$

Corr. coeff. = .979

Eyring Plot.

Slope = $-12,929 \pm 1386$

Int. = $29.87 \pm .22$

Corr. coeff. = .998

$\Rightarrow E_a = 110 \pm 11 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 107.5 \pm 11 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = 51 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

(a) $\ln(R)$ and $\ln(R_t)$ have the same meaning as defined in Section 2.2

(b) Errors in S values are larger than might be indicated from the corr. coeff as the temperature range used to determine $\Delta S^\ddagger$ is very small

Table 3.2.1.10: Experimental data for the determination of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ in the presence of excess dmbipy ligand.

Temperature (K)	$\text{Ln}(\text{R})$	$\text{Ln}(\text{R}_t)$
311	-5.40	-11.14
309.5	-5.60	-11.33
306	-5.86	-11.58
303	-6.44	-12.16
300	-6.78	-12.48
297	-7.07	-12.76

Arrhenius Plot.

Slope = $-11,351 \pm 658$

Int. = $31.10 \pm .09$

Corr. coeff. = .993

Eyring Plot.

Slope = $-11,043 \pm 677$

Int. = $24.37 \pm .10$

Corr. coeff. = .993

=> $E_a = 94.4 \pm 5.5 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 91.8 \pm 5.6 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = 5.15 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Figure 3.2.1.16: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ in the absence of excess ligand.

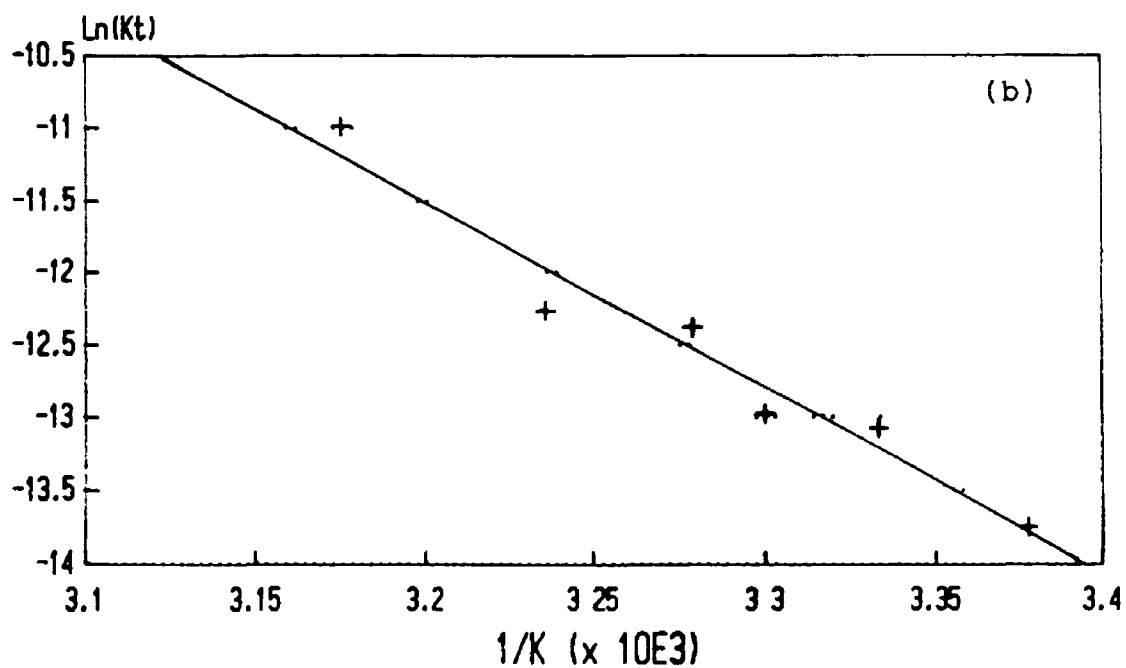
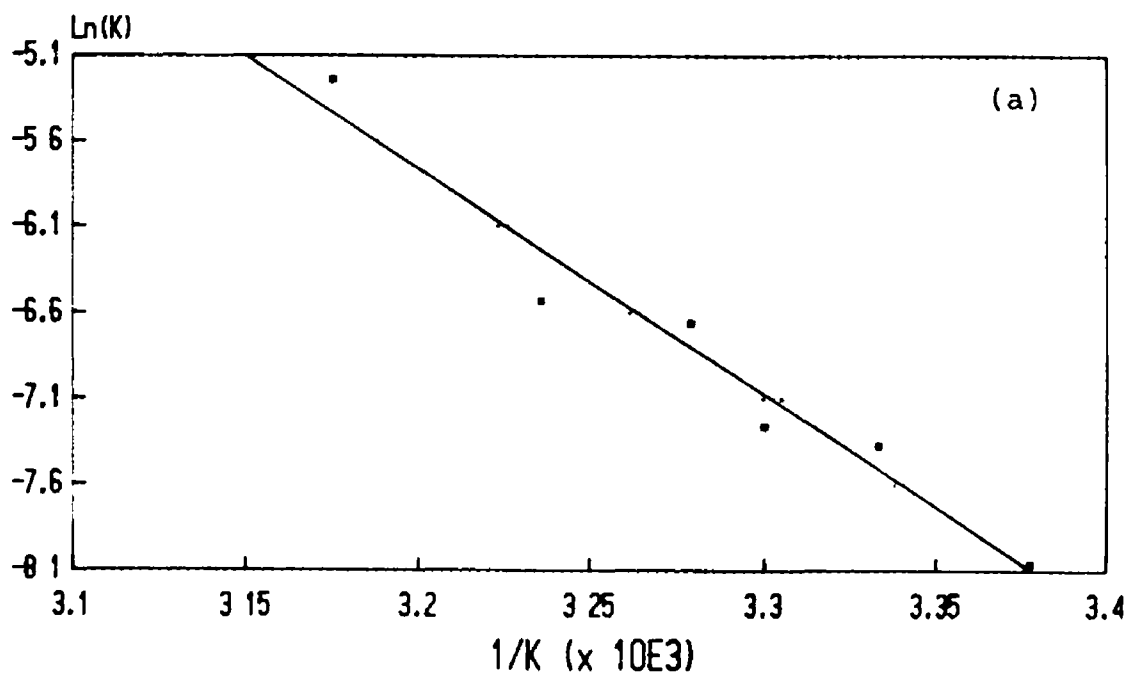
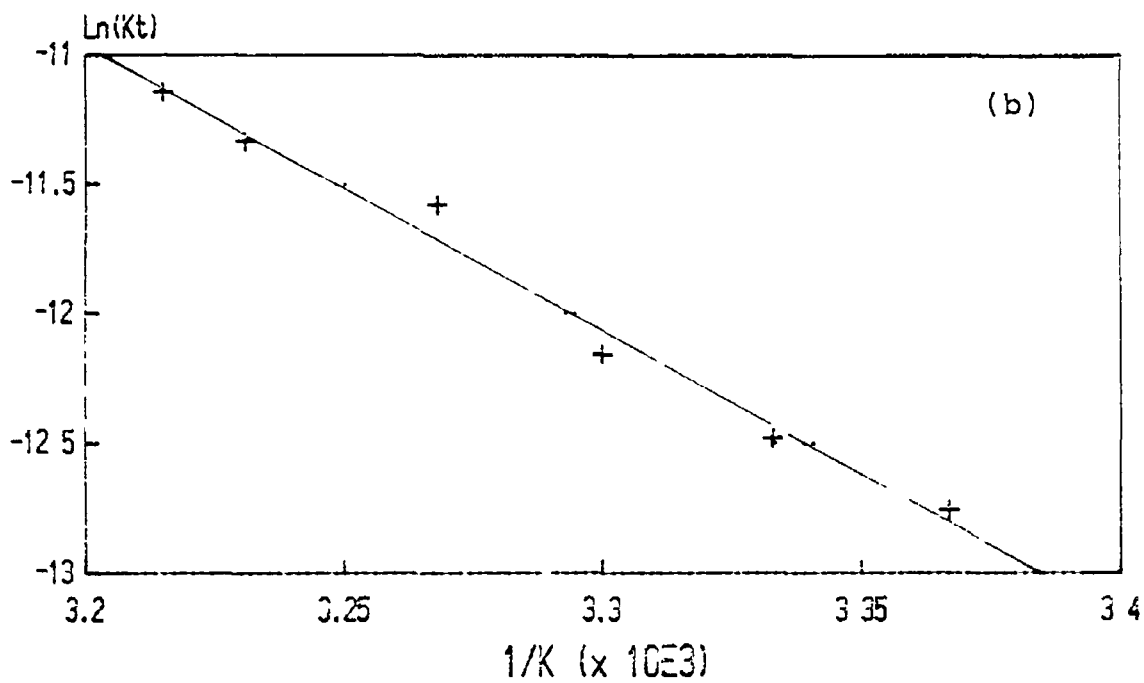
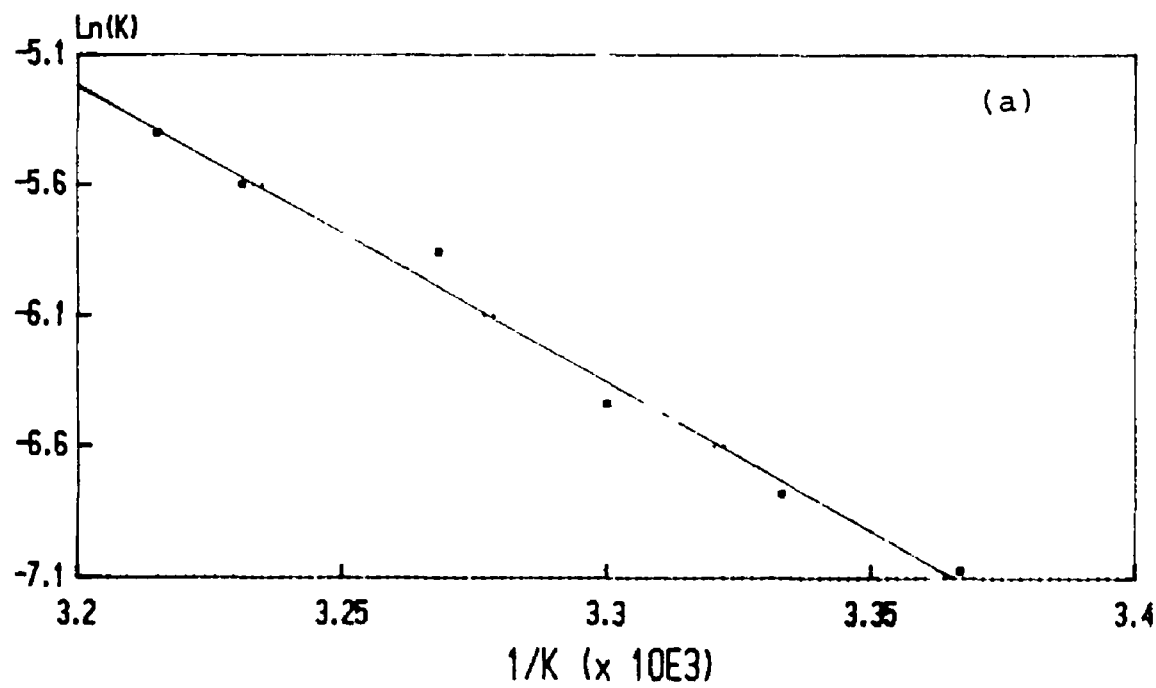


Figure 3.2.1.17: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ in the presence of excess dmbipy ligand.



The differences in parameter values in the two cases indicate that the rate determining step was not identical. Arrhenius plots of k_{obs} over the temperature range 295K to 308K allowed an estimate of the activation energy for the formation of $Cr(CO)_4(dmbipy)$ of $110KJmol^{-1}$, in the absence of ligand, and $94.7KJmol^{-1}$, in the presence of excess ligand. These values are very much greater than the activation energy for the breaking of Cr-CO bond.⁶ The activation enthalpy for the $Cr(CO)_5(pyridine)$ dissociative process is $122.2 KJmol^{-1}$ in hexane which is similar to the above values. This would suggest that the breaking of the Cr-N bond is the rate determining step in the reaction. The activation parameters for the formation of a number of chelate diimine products in the presence of excess diimine are given in Table 3.2.1.11.

Table 3.2.1.11: Calculated activation parameters for the formation of $M(CO)_4(diimine)$ ($M = Cr, Mo$ or W) in the presence of excess diimine ligand.

Ligand	Metal	$\Delta H^\ddagger (KJmol^{-1})$	$\Delta S^\ddagger (Jmol^{-1}K^{-1})$
2,2'-bipy	W	80.3	2.1
4,4'-(CH ₃) ₂ -bipy	W	69.0	-37.7
4,4'-(C ₄ H ₉) ₂ -bipy	W	71.1	-36.0
4,4'-(C ₃ H ₇) ₂ -dab)a	Cr	80.3	-46.9
4,4'-(C ₃ H ₇) ₂ -dab)a	Mo	77.0	-42.3
4,4'-(C ₃ H ₇) ₂ -dab)a	W	87.4	-37.2

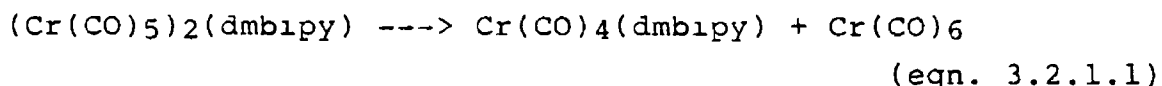
a reference 33

The values of activation enthalpy for the different ligands are in the order $\text{Mo} < \text{Cr} < \text{W}$ which would indicate that perhaps the breaking of the M-CO bond was the rate determining step. The negative values for $\Delta S^\ddagger$ indicate the associative nature of the transition state. The small value of $\Delta S^\ddagger$ for the formation of $\text{W(CO)}_4(4,4'\text{-bipy})$ is similar to our value ($\Delta S^\ddagger = 5.5 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$) for formation of $\text{Cr(CO)}_4(\text{dmbipy})$ (both reactions being carried out in the presence of excess ligand). The rate determining step in the absence of ligand is a dissociative process. This result is consistent with those of Dobson et al. who found that the chelation reactions of $\text{M(CO)}_5(\text{LL})$ where LL was a bidentate phosphorus or arsenic donor ligand proceeded via a largely dissociative mechanism.

3.2.1.11 Concluding Remarks

The results of section 3.2.1.1 to 3.2.1.11 can be summarised as follows:

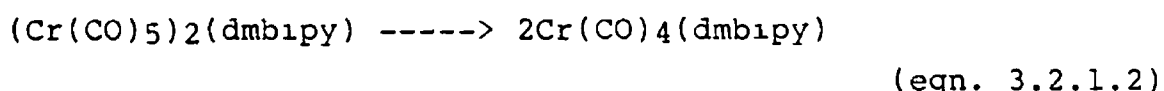
(1) the overall stoichiometry of the chelation reaction in the absence of any excess ligand is given in equation 3.2.1.1;



The stoichiometry of the reaction has been confirmed by measurement of the ir absorbance values for $(\text{Cr(CO)}_5)_2(\text{dmbipy})$, $\text{Cr(CO)}_4(\text{dmbipy})$ and Cr(CO)_6 at various time intervals during the reaction;

(11) the presence of excess dmbipy in solution changes the overall stoichiometry of the reaction (equation 3.2.1.2). This process involves the formation of an intermediate

species and this was shown by measurement of the ir absorbance values and also by the changes observed in the E mode of the $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ complex during the chelation reaction. These results are consistent with the formation of $\text{Cr}(\text{CO})_5(\text{dmbipy})$ when excess dmbipy is present in solution.



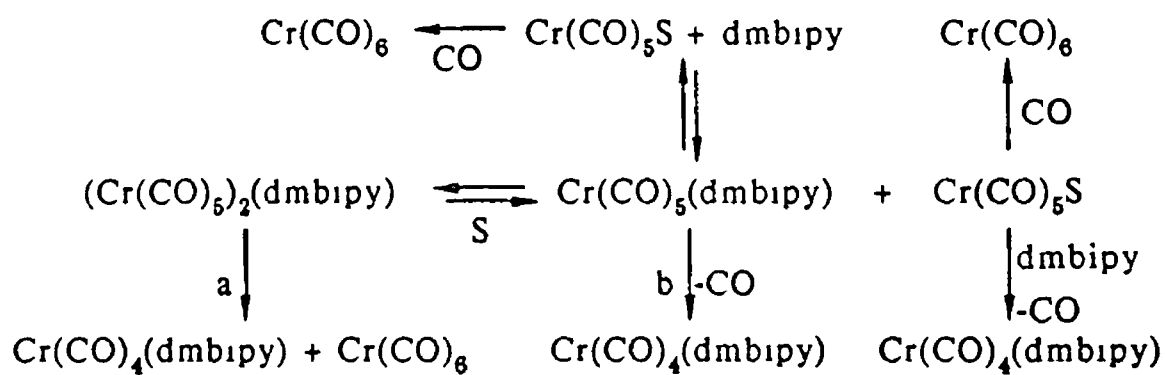
(iii) saturating the toluene solution with carbon monoxide decreases the yield of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ with a correspondingly large increase in the formation of $\text{Cr}(\text{CO})_6$. Such results indicate that $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ is labile to loss of a $\text{Cr}(\text{CO})_5$;

(iv) the measurement of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ indicated that;

- in the absence of ligand the rate determining step in the formation of the chelate product is dissociative in nature;
- in the presence of excess ligand the entropy of the system changes little in the rate determining step.

These results are consistent with the reaction mechanism given in Scheme 3.2.1.1. In the absence of excess ligand the equilibrium in reaction c lies largely to the left and the rate determining step corresponds to reaction a. In the presence of excess ligand the concentration of $\text{Cr}(\text{CO})_5(\text{dmbipy})$ is greatly increased (because the back reaction of $\text{Cr}(\text{CO})_5$ and dmbipy is suppressed) and the rate determining step is b. This reaction scheme also explains the effect of carbon monoxide on the observed reactions.

PROPOSED MECHANISM



S = TOLUENE

Scheme 3 2.1.1

3.2.2 The Synthesis and Characterisation of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ and its Reactions in Toluene Solution

3.2.2.1 The Isolation of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$

The preparation of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ was identical to that of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (see Experimental Section 3.3.3.3), with the product crystallising from an argon purged solution of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ containing bipy ligand. The molecular formula of this complex was confirmed by elemental analysis. The crystal structure of this complex has not been determined as yet because of failure to grow crystals of sufficient quality. The ir and uv/vis spectroscopic properties of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ are similar to those of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (vide infra).

3.2.2.2 ir and uv/vis Spectra of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$

Figure 3.2.2.1(a) shows the ir spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in nitrogen purged toluene solution at 293K. The spectrum exhibits four bands in the CO stretching region at 2060(w), 1936(s), 1920(s) and 1905(m,sh) cm^{-1} . There is an additional band at 1983 cm^{-1} which was assigned to a small amount of $\text{Cr}(\text{CO})_6$ formed upon decomposition of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$. However this band is also present in the ir spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in KBr disc (Figure 3.2.2.1(b)). Depending on the ligand attached to the pentacarbonyl fragment, the C_{4v} local symmetry may be severely perturbed. In such cases the formally forbidden B₁ mode gains some intensity and in addition the degeneracy of the E mode may be lifted. This is the case in the $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ and its dmbipy analogue.

Figure 3.2.2.1: (a) The ir spectrum (ν_{co} region) of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in deoxygenated toluene solution; (b) the ir spectrum (ν_{co} region) of $(\text{Cr}(\text{CO})_5(\text{bipy}))$ in KBr disc.

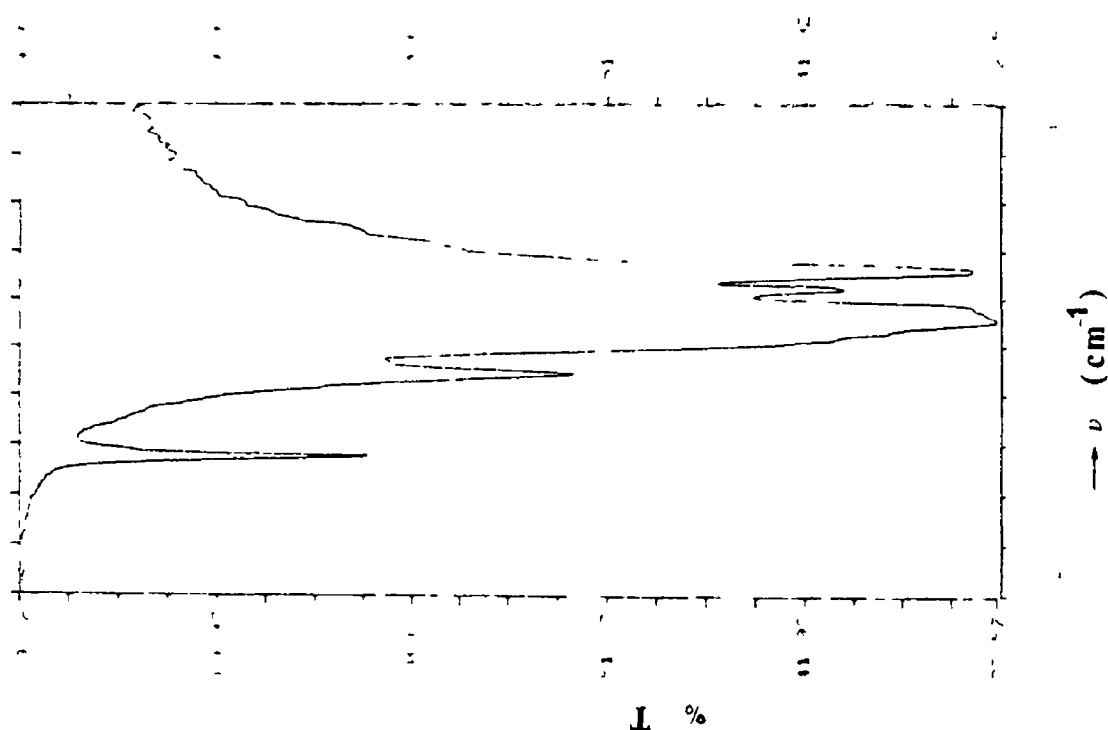
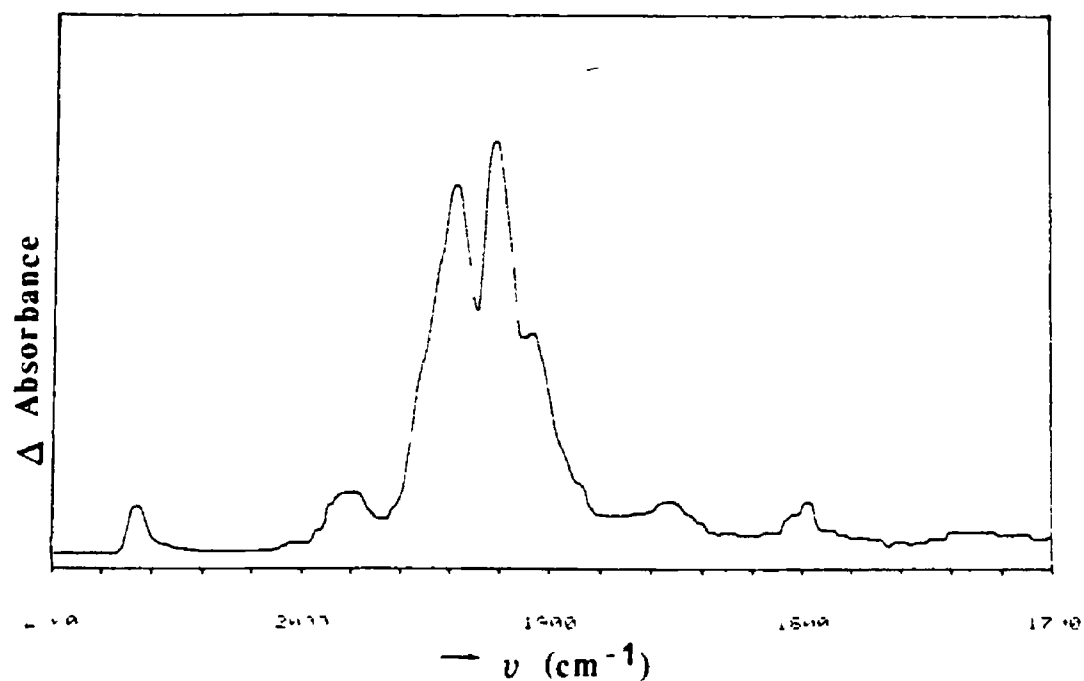
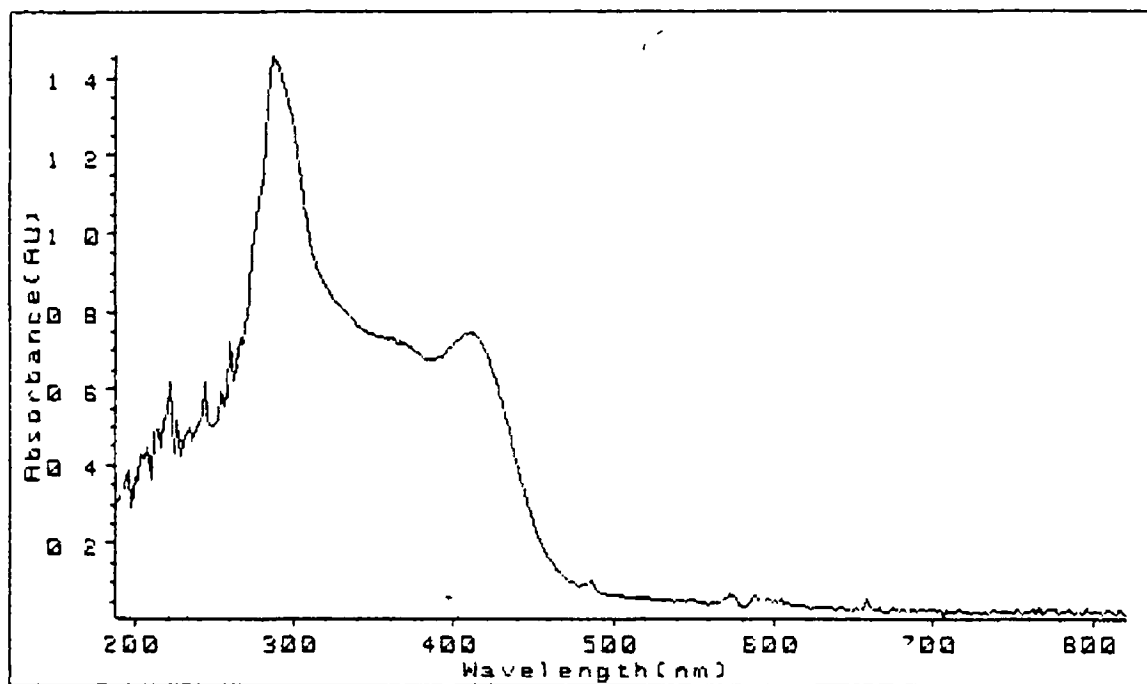


Figure 3.2.2.2: The uv/vis spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in degassed toluene solution at 297K.



The uv/vis spectrum of the bipy bridging species is given in Figure 3.2.2.2(a). The spectrum exhibits bands almost identical to those of $\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$; a low energy absorption band in the visible region centred at 410nm and further stronger bands in the uv/vis region. In addition the spectrum is identical to that observed by Lees *et al.* on the photolysis of a deaerated solution of $\text{Cr}(\text{CO})_6$ and bipy in benzene solution. The spectral assignments of these bands as a LF (at 410nm) and overlapping LF and MLCT bands (uv region) therefore seem valid. The position of these bands can be compared to those of $\text{Cr}(\text{CO})_5(2\text{-phpy})$. The position of the LF bands of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ is almost identical to that of the 2-phpy complex (Figure 3.2.2.2(b)), indicating that the further perturbation of the local symmetry is minimal on forming a bridging

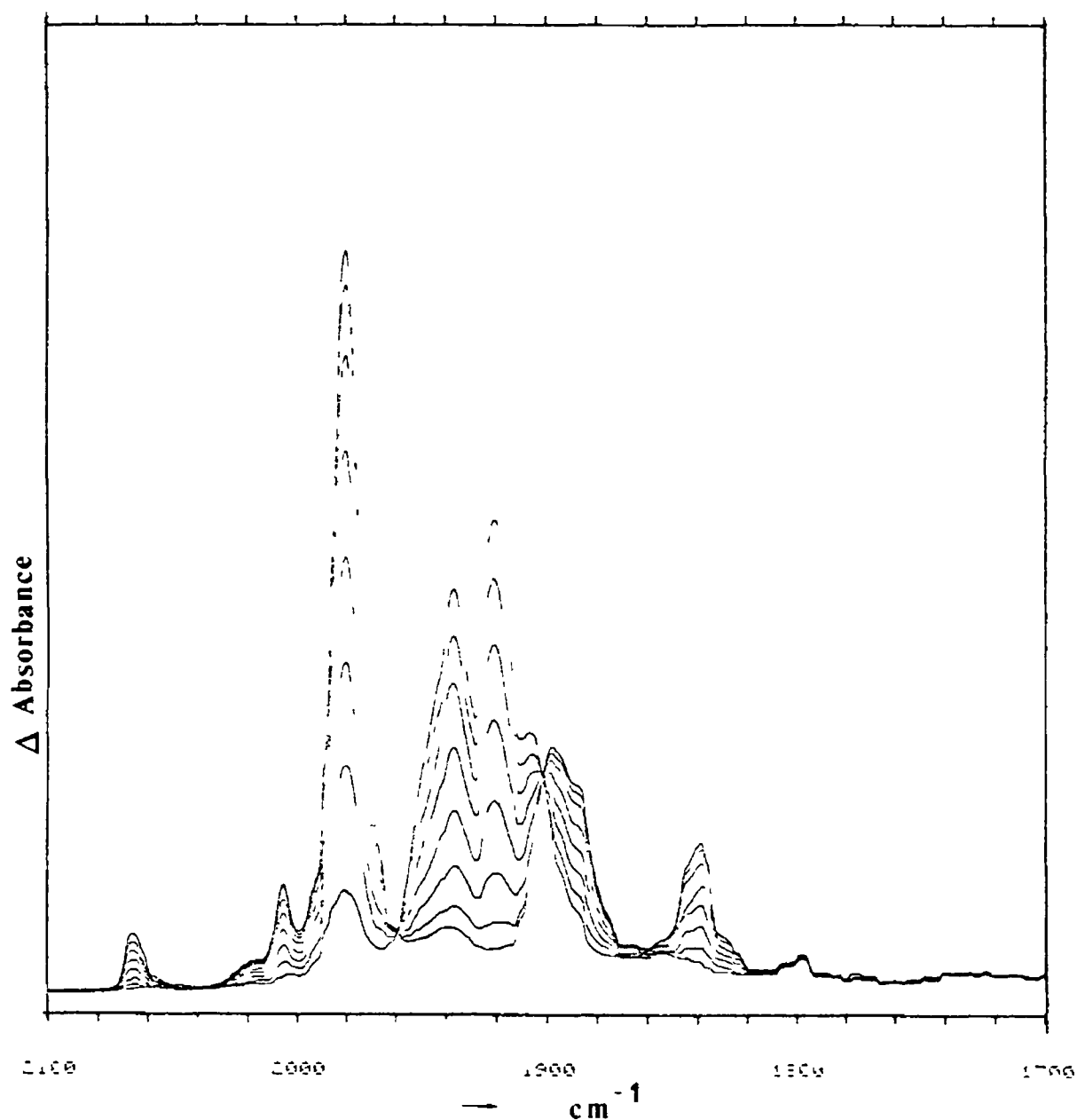
species. However as has been stated in Section 3.2.1.3 the position of the MLCT band at low wavelengths indicates that there is little π^* conjugation in the molecule. This would suggest that the conformation of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in solution is similar to that of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$, i.e. the two pyridyl rings are not coplanar.

3.2.2.3 Monitoring, by ir Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in Toluene Solution at ambient temperature

The ir spectral changes recorded upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in a nitrogen purged toluene solution at 293K are shown in Figure 3.2.2.3. The bands at 2060, 1936, 1920 and 1905 cm^{-1} , assigned to the $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ species are seen to diminish, with a concomitant growth of bands at 2006(w), 1896(s) and 1839(s) cm^{-1} . It was expected that these bands were as a result of the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$, based on the results of the analogous dmbipy complex. Comparison of these bands with those of an authentic sample of $\text{Cr}(\text{CO})_4(\text{bipy})$ confirmed this assumption. These spectral bands and a further weak shoulder band at 1860 cm^{-1} were assigned to the A_2 , B_1 , B_2 and A_1 modes of the C_{2v} $\text{Cr}(\text{CO})_4(\text{bipy})$ species respectively.

As with the dmbipy complex, $\text{Cr}(\text{CO})_6$ was seen to form concurrently with the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ (identified by its characteristic absorption band at 1980 cm^{-1}). The formation of the tetracarbonyl and hexacarbonyl products were uncomplicated by side or subsequent reactions as indicated by the maintenance of an isosbestic point throughout the reaction. Thus, the chelation reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ appeared to be very similar in nature to those of the analogous dmbipy complex.

Figure 3.2.2.3: The ir spectral changes (ν_{CO} region) recorded upon standing of a solution of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ ($2.8 \times 10^{-3} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 120, 720, 1320, 1920, 2520, 3120, 3720 and 4320s at ambient temperature.



Measurement of the changes in the moles of $\text{Cr}(\text{CO})_4(\text{bipy})$, $\text{Cr}(\text{CO})_6$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ during various time intervals of the chelation reaction further confirmed this observation (Table 3.2.2.1). Table 3.2.2.2 gives the data for the determination of the extinction coefficients of $\text{Cr}(\text{CO})_4(\text{bipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$.

Table 3.2.2.1: Data for the determination of the extinction coefficients for $\text{Cr}(\text{CO})_4(\text{bipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ (.1mm pathlength).

Concentration (mol dm^{-3})	Absorbance (A.U.)	ϵ ($\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)
(a) $\text{Cr}(\text{CO})_4(\text{dmbipy})$		
1.41×10^{-3}	.0435	3,085
4.17×10^{-3}	.1362	3,266
7.81×10^{-4}	.0304	3,894
$\Rightarrow \epsilon = 3,412 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$		

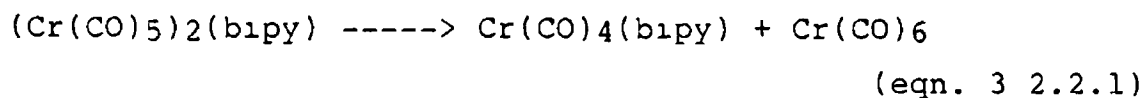
(b) $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

1.61×10^{-3}	.0193	1,198
3.25×10^{-3}	.0398	1,225
$\Rightarrow \epsilon = 1,200 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$		

Table 3.2.2.2: The number of moles of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\text{bipy})$ produced, and the number of moles of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ consumed during various time intervals of the chelation reaction.

Time interval (s) $t_{n-1} - t_n$	Moles of carbonyl complex formed (or consumed) in that time interval ($\times 10^6$)		
	$\text{Cr}(\text{CO})_4(\text{bipy})$	$\text{Cr}(\text{CO})_6$	$(\text{Cr}(\text{CO})_5)_2(\text{bipy})$
720 - 120	2.27	5.5	4.46
1320 - 720	3.73	4.53	4.22
1920 - 1320	3.82	4.7	4.46
2520 - 1920	3.54	4.53	4.46
3120 - 2520	3.45	4.1	4.46
6120 - 120	22.7	28	26.5

The overall stoichiometry of the chelation reaction can therefore be given by equation 3.2.2.1;



3.2.2.4 Monitoring, by ir Spectroscopy the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in Toluene Solution Containing Excess bipy Ligand, at Ambient Temperature

The behaviour of the bipy bridging species in toluene solution mirrored closely that of the dmbipy complex. A study of the reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in the presence of excess bipy was also expected to follow the behaviour of the $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ complex. Figure 3.2.2.4 shows the ir spectral changes recorded upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in nitrogen purged toluene solution. It can be seen that the behaviour of this complex does indeed mimic that of the $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$;

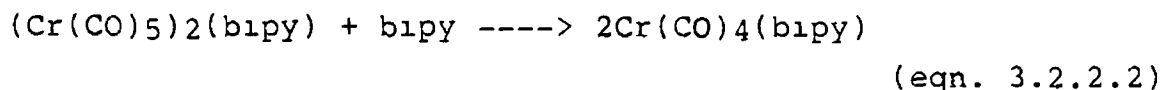
(a) the yield of $\text{Cr}(\text{CO})_4(\text{bipy})$ is almost doubled in the presence of excess ligand (see Table 3.2.2.3) as compared to the case when no ligand is present.

(b) the formation of $\text{Cr}(\text{CO})_6$ is suppressed.

(c) the reaction proceeds at an increased rate when excess ligand is present.

(d) the degeneracy of the E mode was restored, soon after the reaction began.

The overall stoichiometry of the reaction can therefore be given by equation 3.2.2.2



The stoichiometry given in equation 3.2.2.2 was maintained throughout the course of the chelation reaction. The reactions were further studied by uv/vis diode-array spectroscopy to determine their thermodynamic and kinetic parameters.

Figure 3.2.2.4. The ir spectral changes (ν_{CO} region) occurring upon standing a solution of $(Cr(CO)_5)_2(bipy)$ ($9.2 \times 10^{-4} \text{ mol dm}^{-3}$) and $bipy$ ($1.4 \times 10^{-1} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 120s and 300s intervals thereafter, at ambient temperature.

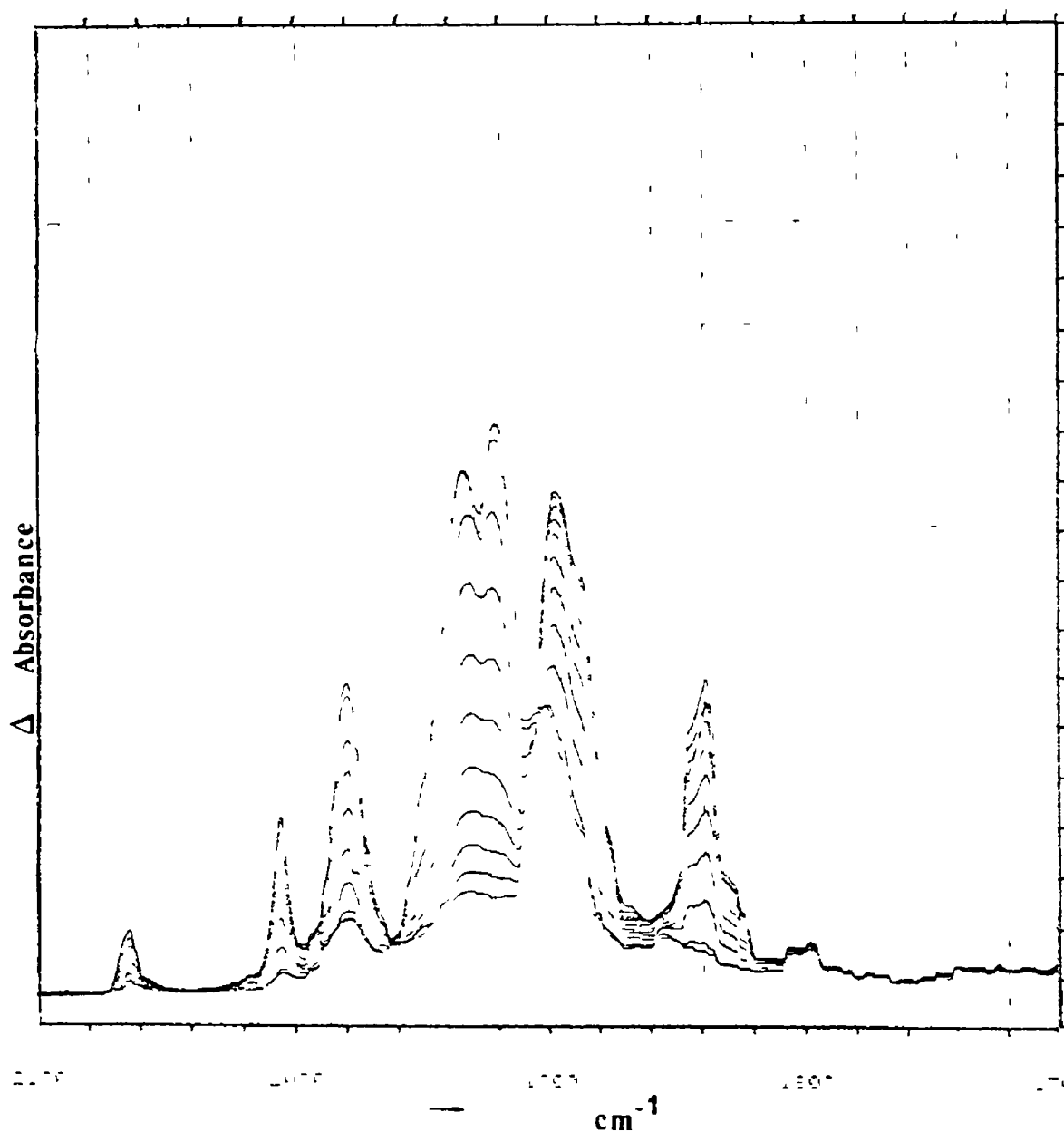


Table 3.2.2.3: Moles of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\text{bipy})$ produced and moles of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ consumed at various time intervals during the chelation reaction in the presence of excess ligand.

Time interval	Moles of carbonyl complex formed (or consumed) in corresponding interval ($\times 10^6$)		
$t_{n-1} - t_n(\text{s})$	$\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$	$\text{Cr}(\text{CO})_6$	$\text{Cr}(\text{CO})_4\text{dmbipy}$

Sample 1:

420 - 120	3.36	0.29	6.16
720 - 420	3.36	0.72	5.67
1020 - 720	2.69	0.94	4.93
1320 - 1020	2.86	0.89	4.20
1620 - 1320	1.68	0.97	3.08
3120 - 120	18.14	5.30	29.60

Sample 2:

390 - 90	2.69	0.17	6.16
690 - 390	2.86	0.79	5.67
990 - 690	2.18	0.98	5.23
1290 - 990	2.67	1.18	4.31
3090 - 90	18.48	6.95	33.90

3.2.2.5 Monitoring, by uv/vis Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in Toluene Solution

The spectral changes recorded upon dissolution of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in degassed toluene solution are given in Figure 3.2.2.5(a). The band, previously assigned as the LF $1\text{A} \rightarrow 1\text{E}$ absorption band at 410nm diminished upon standing of the solution and a band at 520nm was seen to form concomitantly. This latter band was assigned to a $\text{Cr}(\text{CO})_4(\text{bipy})$ based on its similarity with that of an authentic sample. The final spectrum displayed the three absorption bands characteristic of $\text{Cr}(\text{CO})_4(\text{diimine})$ complexes; MLCT at 520nm, $1\text{A} \rightarrow 1\text{E}$ at 390nm, and $1\text{A} \rightarrow 3\text{E}$ at 327nm.

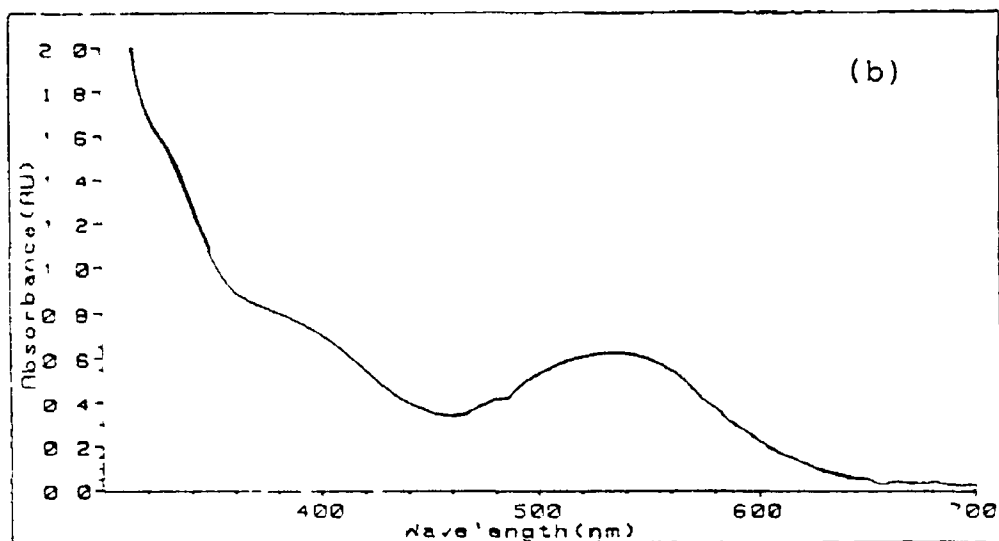
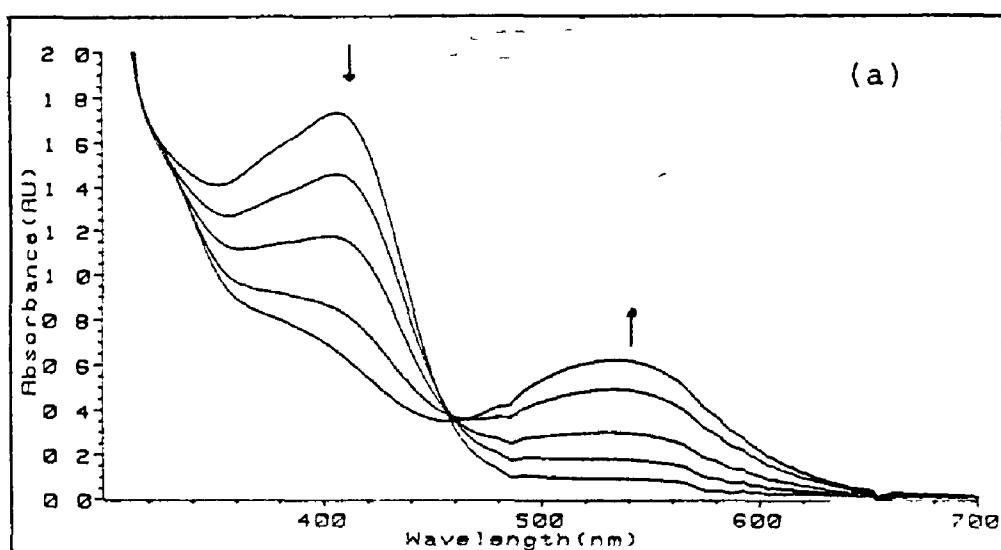
The profile of the chelation reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ have been shown to be very similar and it is reasonable to assume that the nature of the chelation reaction is identical in both cases. The rate constant for the formation of the chelate product was determined from the grow-in of this MLCT band at 520nm. At 293K k_{obs} was typically $8.33 \times 10^{-4} \text{ s}^{-1}$. This is approximately 2.5 times faster than the corresponding chelation reaction of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$. Differences in k_{obs} values in chelation reactions have been attributed to steric interactions between substituents on the diimine ring and the carbonyl moieties. The ligands differ only in the presence of a methyl group in the 4 position on the pyridyl ring. The order of reactivity measured in the time-resolved studies on the dynamics of photoinduced formation of $\text{M}(\text{CO})_4(\text{polypyridyl})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) followed the order phenanthroline $\gg$ bipy $>$ dmbipy. The differences in rate data were interpreted in terms of steric constraints and differences in basicity of the ligands. For the phen

ligand, the N atoms are held coplanar and this facilitates rapid chelation. In the $(Cr(CO)_5)_2(dmbipy)$ and $(Cr(CO)_5)_2(bipy)$ complexes the molecule must undergo rearrangement and loss of $Cr(CO)_6$ in order to form the chelate product. The presence of a methyl group on the 4 position of the pyridyl ligand may hinder this process.

If breaking of the Cr-N bond is the rate determining step then the observed rate constant should depend on the basicity of the ligand. This is seen to be the case (pK_a of $bipy = 4.5$, pK_a of $dmbipy = 5.45$). This may be confirmed in the future by measuring the rate of reaction of the chelate product from $(M(CO)_5)_2(bipy)$ ($M = Mo$ or W), as the M-N bond strength, and therefore the rate of reaction, will vary with M.

Connor et al. in their studies on the chelation reactions of $Cr(CO)_5(L)$ ($L = (cycloC_6H_{12})_2PCH_2)_2$ (dcpe), $(cyclo-Ph)_2PCH_2)_2$ (dpe) and $((cyclo-Me)_2PCH_2)_2$ (dmpe) found the rate of reaction to vary according to $dmpe > dpe > dcpe$. These and other workers found that the smaller the potential chelate ring, the faster the chelation reaction, and this was attributed to an entropy effect. In our studies the chelate ring size does not vary and would not explain the differences in reaction rate.

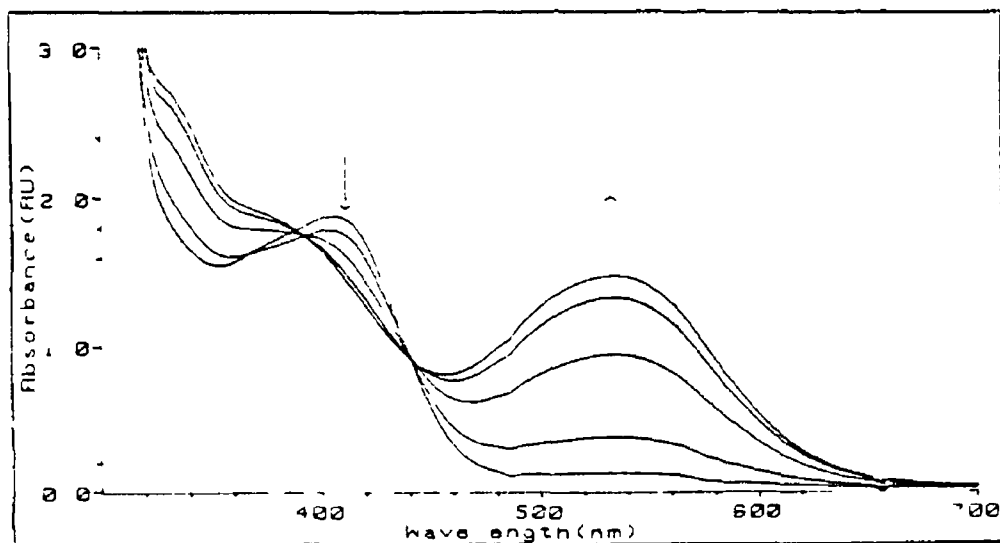
Figure 3.2.2.5: (a) The uv/vis spectrum of $\text{Cr}(\text{CO})_5)_2(\text{bipy})$ (ca. $1.8 \times 10^{-4} \text{ mol dm}^{-3}$) in degassed toluene solution at 296K, and the spectral changes occurring upon standing of this solution for 200, 600, 1200 and 2200s. (b) uv/vis Spectrum recorded upon completion of the chelation reaction.



3.2.2.6 Monitoring, by uv/vis Spectroscopy, of the Reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in Toluene Solution, Containing Excess bipy Ligand, at 295K

From Figure 3.2.2.6 the effect of excess bipy on the chelation reactions of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ can be seen to be practically identical to the analogous dmbipy complex.

Figure 3.2.2.6: uv/vis Spectral changes occurring upon standing a solution of $\text{Cr}(\text{CO})_5)_2(\text{bipy})$ (ca. $2 \times 10^{-4} \text{ mol dm}^{-3}$) and bipy ($1.3 \times 10^{-2} \text{ mol dm}^{-3}$) in degassed toluene solution at 296K, for 0, 180, 400, 900 and 2600s.



These effects can be summarised thus,

(a) the yield of $\text{Cr}(\text{CO})_4(\text{bipy})$ was doubled in the presence of excess ligand.

(b) the presence of excess ligand had a considerable effect on the rate of formation of $\text{Cr}(\text{CO})_4(\text{bipy})$. Figure 3.2.2.7 shows the variance in this rate with ligand concentration.

(c) Figure 3.2.2.8 shows the variation in the ratio of uv/vis absorbance values of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ to $\text{Cr}(\text{CO})_4(\text{bipy})$ with concentration of bipy. This plot confirms the overall stoichiometry of the reaction to be 1:2 ($(\text{Cr}(\text{CO})_5)_2(\text{bipy})$) : $(\text{Cr}(\text{CO})_4(\text{bipy}))$.

Figure 3.2.2.7: The dependence of k_{obs} (s^{-1}), for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$, on the concentration of added bipy (mol dm^{-3}).

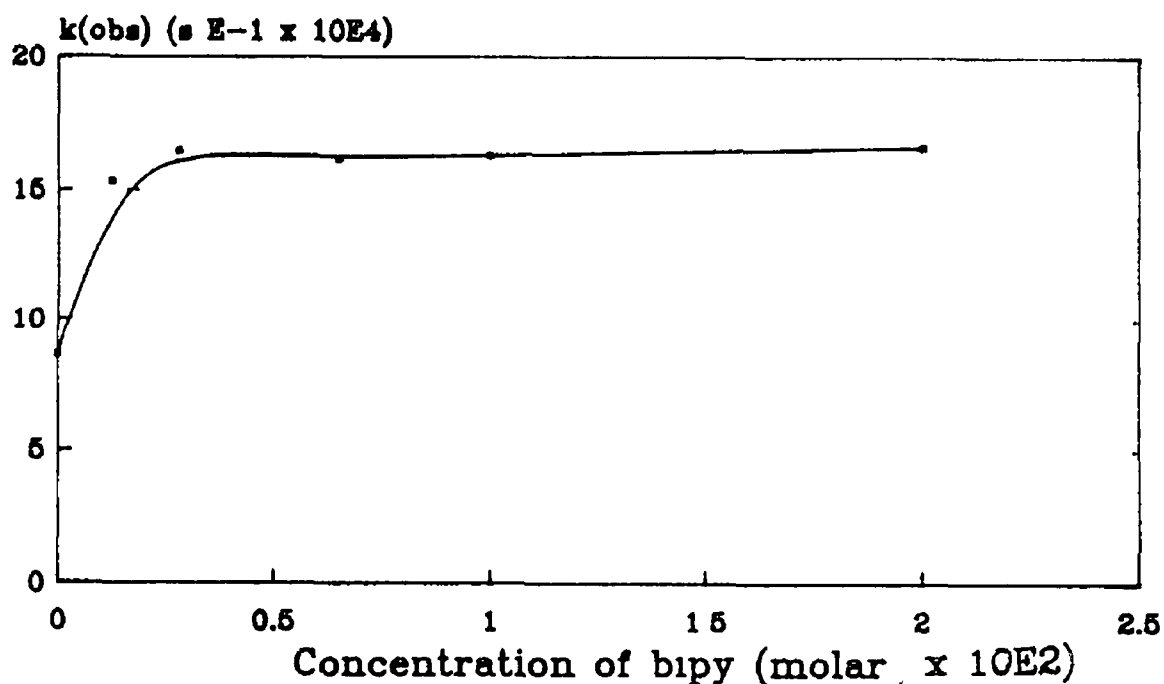
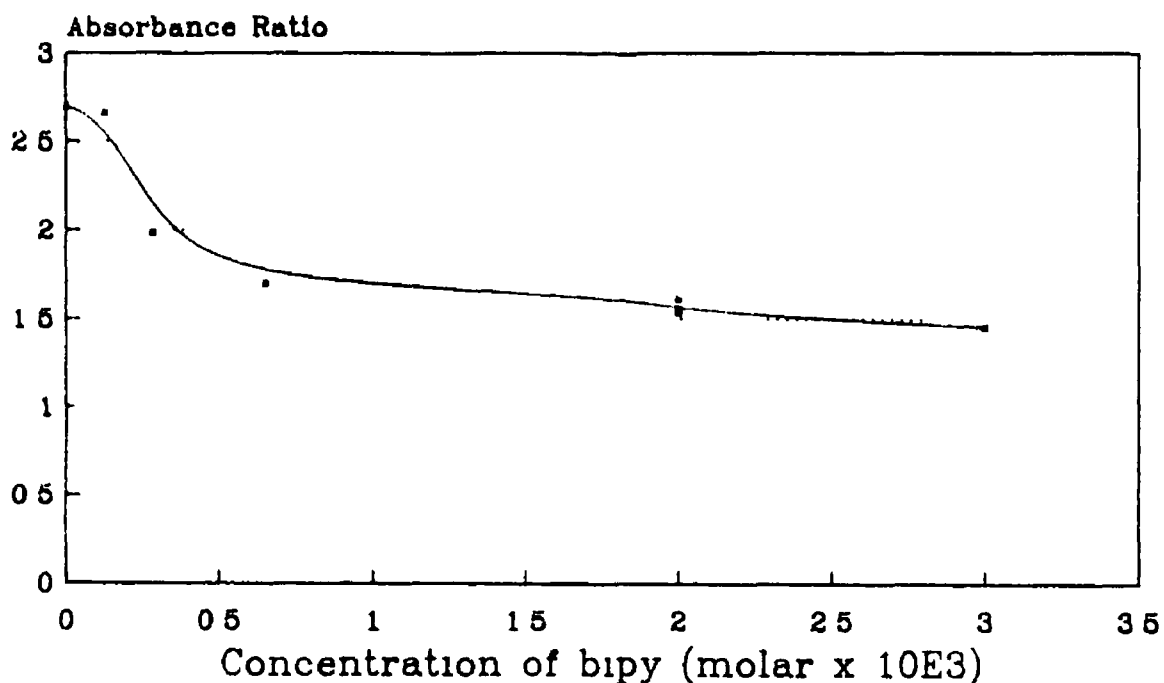


Figure 3.2.2.8: Plot showing the variation in the absorbance ratio (initial absorbance of at 410nm ($\text{Cr(CO)}_5)_2(\text{bipy})$) / final absorbance at 515nm ($\text{Cr(CO)}_4(\text{bipy})$) versus concentration of bipy (mol dm^{-3}).



3.2.2.7 Determination of the Activation Parameters for the Formation of $\text{Cr(CO)}_4(\text{bipy})$ in the Presence and Absence of Excess Ligand

Table 3.2.2 4 gives the variation in k_{obs} with temperature, for the formation of $\text{Cr(CO)}_4(\text{bipy})$ in the absence of excess bipy. The enthalpy of activation derived from this data correlate well with that for the formation of $\text{Cr(CO)}_4(\text{dmbipy})$. If the enthalpy of activation relates to the breaking of the Cr-N bond then one would expect the $\Delta H^\ddagger$ values to differ slightly in the two compounds (considering the pK_a values of the two ligands (pK_a of

bipy is 4.5 and pK_a of dmbipy is 5.45)). The lower value of the $\Delta H^\ddagger$ for the bipy complex, may be a reflection of the greater ease of breaking Cr-N bond ($\text{Cr(CO)}_5)_2(\text{bipy})$ molecule compared to its dmbipy analogue. As has been stated earlier (Section 3.2.2.5) if the breaking of the the M-N bond is the rate determining step then k_{obs} should vary with bond strength. The value of $\Delta S^\ddagger$ was also decreased relative to the dmbipy complex.

The activation parameters for the formation of the chelate product in the presence of excess ligand are detailed in Table 3.2.2.4 (and shown graphically in Figures 3.2.2.9 and 3.2.2.10). As with $(\text{Cr(CO)}_5)_2(\text{dmbipy})$, the enthalpy value is slightly smaller in the presence of excess ligand than in the absence of ligand, but there is a significant difference in the corresponding entropy values. This rate determining step could be the formation of a $\text{Cr(CO)}_5(\text{bipy})$ intermediate complex in which the bipy ligand is co-ordinated in a partially bidentate fashion (Figure 3.2.2.9).

Figure 3.2.2.9: Possible conformation of intermediate complex in the formation of $\text{Cr(CO)}_4(\text{bipy})$ from $(\text{Cr(CO)}_5)_2(\text{bipy})$.

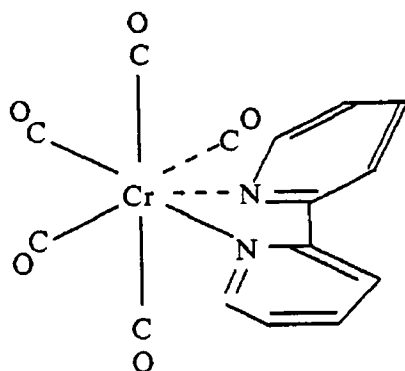


Table 3.2.2.4: Experimental data for the determination of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ in the presence and absence of excess bipy ligand).

(a) In the absence of excesss ligand:

Temperature (K)	$\text{Ln}(R)$	$\text{Ln}(R_t)$
296	-7.24	-12.93
298	-7.06	-12.77
300.5	-6.73	-12.43
303	-6.42	-12.13
307	-5.83	-11.56

Arrhenius Plot.

Slope = -11684 +/- 591

Int. = 32.20 +/- .05

Corr. coeff. = .996

Eyring Plot.

Slope = -11400 +/- 587

Int. = 25.6 +/- 10

Corr. coeff. = .996

=> $E_a = 97.1 \pm 5.0 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 94.8 \pm 5.0 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = 15.4 \pm 20 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 3.2.2.4:cont'd.

(b) In the presence of excess ligand.

Temperature (K)	Ln(R)	Ln(R _t)
292.5	-6.92	-12.60
298.5	-6.38	-12.08
301.7	-5.93	-11.64
305	-5.72	-11.44
309	-5.25	-10.98

Arrhenius Plot.

Slope = -9,110 +/- 470

Int. = 24.17 +/- .06

Corr. coeff. = .996

Eyring Plot.

Slope = -8,800 +/- 472

Int. = 17.5 +/- .06

Corr. coeff. = .996

=> E_a = 75.7 +/- 4.0 KJmol⁻¹, ΔH[‡] = 73.2 +/- 4.0
KJmol⁻¹ and ΔS[‡] = -52 +/- 20 Jmol⁻¹K⁻¹

Figure 3.2.2.10: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ in the absence of excess ligand.

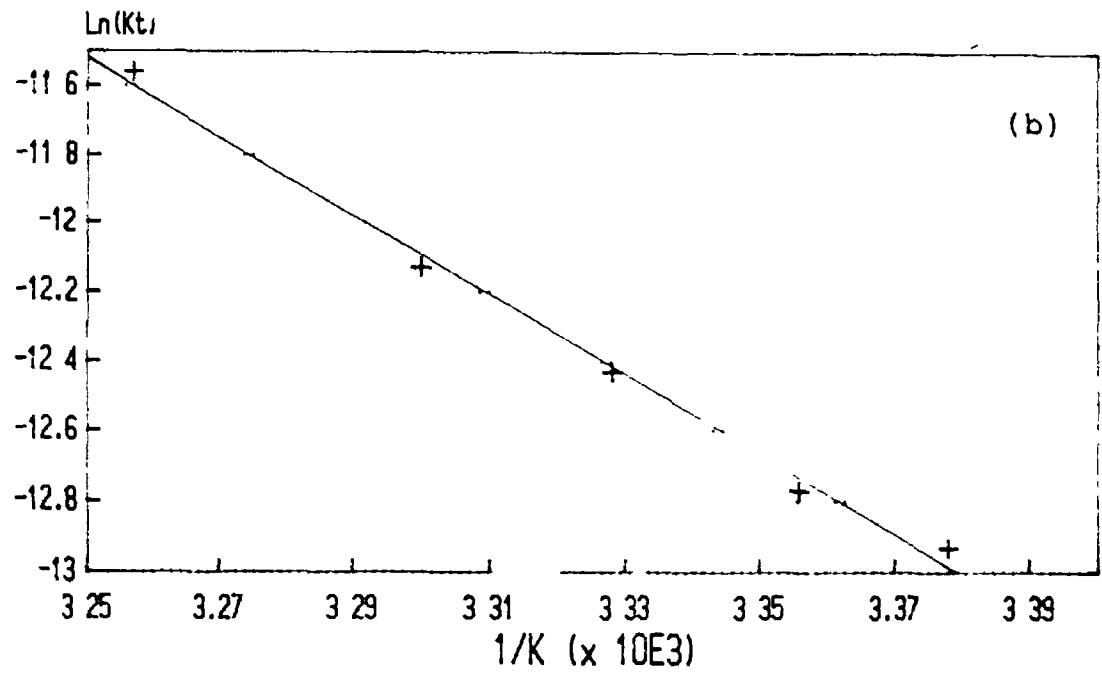
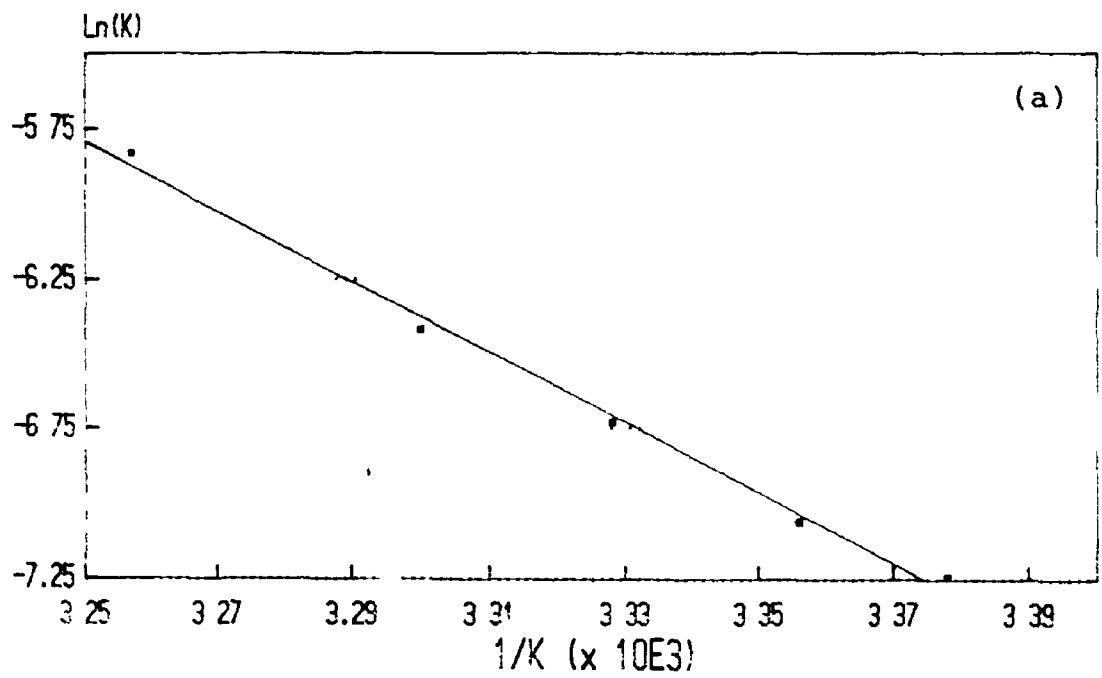
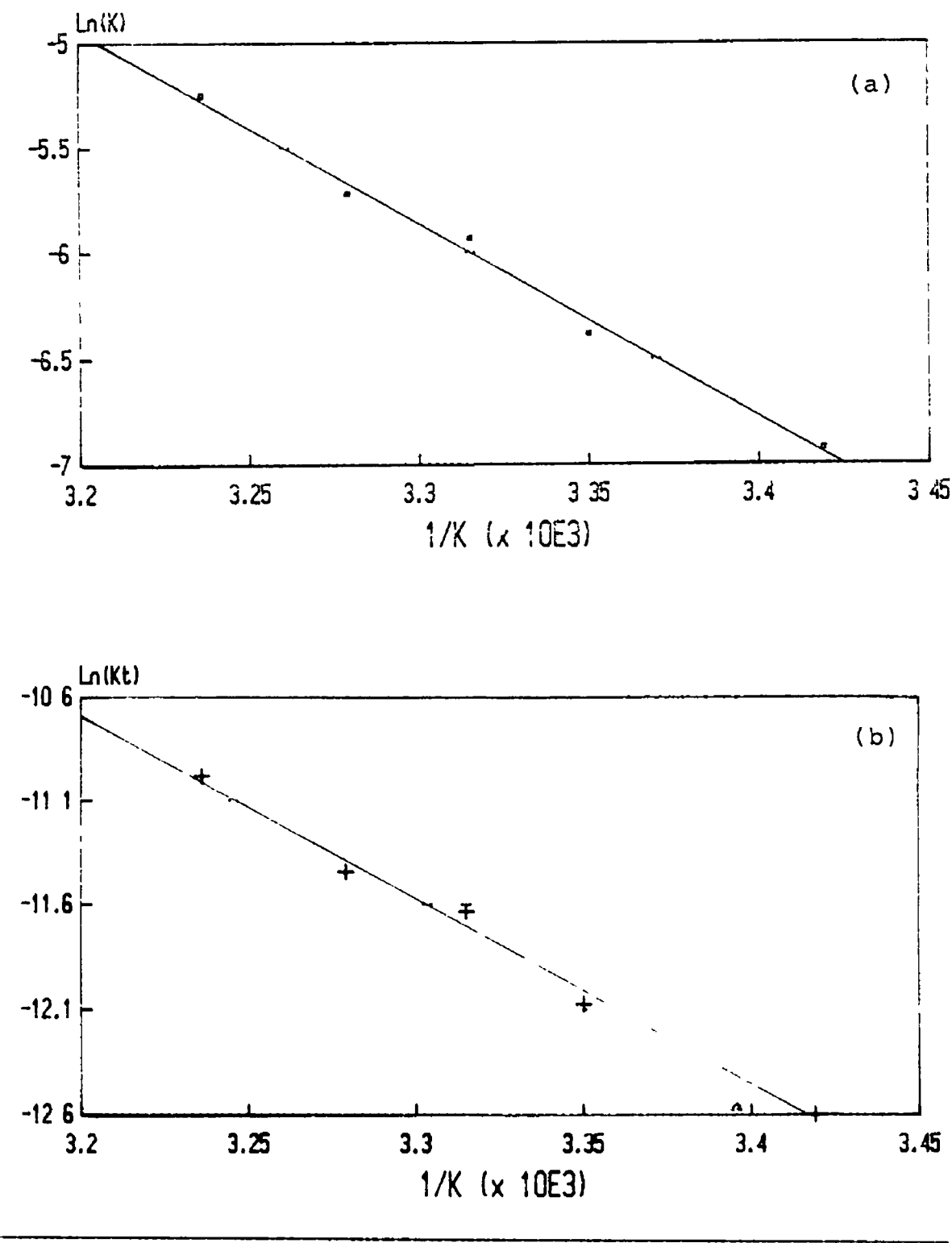


Figure 3.2.2.11: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ in the presence of excess bipy ligand.



Our studies on the $(\text{Cr}(\text{CO})_5)_2(\text{L})$ complexes ($\text{L} = \text{dmbipy}, \text{bipy}$) in toluene solution had indicated the complex nature of chelation reactions of molecules containing multidentate ligands. Previously these chelation reactions had been assumed to be quite simplistic (see Introduction). We had not fully understood why these bridging species were formed preferentially over a monodentate species (though we thought their formation was as a result of their insolubility in pentane). We were interested in discovering if all σ -donor/ π -acceptor multidentate ligand complexes would form bridging complexes, or what factors would favour monodentate co-ordination.

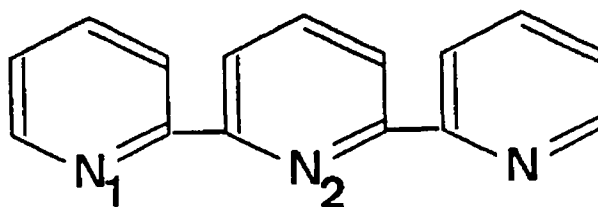
The successful isolation of monodentate $\text{Cr}(\text{CO})_5(\text{en})$ ($\text{en} = \text{ethylenediamine}$) has been attributed to poor overlap between the orbital of unco-ordinated nitrogen atom and the metal d orbital. We were interested in studying multidentate ligands which were more sterically hindered than en . The reaction of $\text{Cr}(\text{CO})_6$ with trpy ($\text{trpy} = \text{terpyridine}$) is the subject of the next section. The trpy ligand has potentially 3 binding sites, as there is free rotation about the $\text{C}-\text{C}'$ and $\text{C}'-\text{C}''$ bonds (see Figure 3.2.3.1).

3.2.3 The Synthesis and Characterisation of $\text{Cr}(\text{CO})_5(\text{trpy})$ and its Reactions in Toluene Solution

3.2.3.1 Isolation of $\text{Cr}(\text{CO})_5(\text{trpy})$

The reaction of $\text{Cr}(\text{CO})_6$ and trpy (1:3 molar ratio) in argon purged pentane solution at 268K, resulted in the formation of a yellow/orange compound whose composition was determined by elemental analysis to be $\text{Cr}(\text{CO})_5(\text{trpy})$. This is the first example of a monodentately co-ordinated trpy complex. It has been suggested by previous workers that the reason monodentate co-ordinated bidentate ligand complexes have not been isolated was that co-ordination of one pyridyl ring activates the second pyridyl ring towards co-ordination. This would explain why the reaction of $\text{Cr}(\text{CO})_5(\text{pyr})$ with pyr (pyr = pyridine) to form $\text{Cr}(\text{CO})_4(\text{pyr})_2$ was considerable slower than the formation of the chelate $\text{Cr}(\text{CO})_4(\text{diimine})$. It is thought likely in this synthesis that the isolation of $\text{Cr}(\text{CO})_5(\text{trpy})$ is purely as a result of its low solubility in pentane.

Figure 3.2.3.1: trpy Ligand.



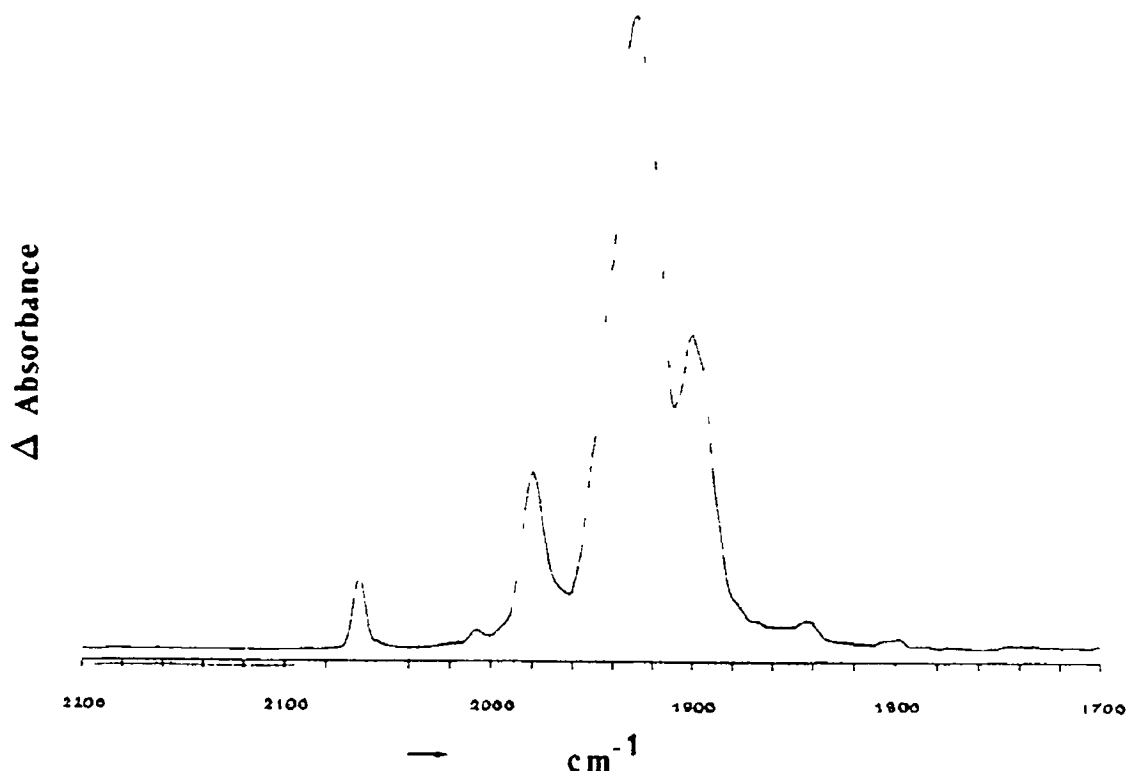
It is not known how the trpy ligand is co-ordinated to the $\text{Cr}(\text{CO})_5$ moiety, i.e. if it is co-ordinated via the N_1 or N_2 (see Figure 3.2 3.1) It would be difficult to

determine this point without structural information. However the extreme reactivity of the trpy complex (it is very air and thermally sensitive) prevented the successful isolation of crystals of $\text{Cr}(\text{CO})_5(\text{trpy})$. It was thought that the uv/vis and ir spectra of the complex may indicate something about its structure.

3.2.3.2 Ir Spectrum of $\text{Cr}(\text{CO})_5(\text{trpy})$ in Toluene Solution

The ir spectrum recorded ca. 2 minutes after dissolution of a sample of $\text{Cr}(\text{CO})_5(\text{trpy})$ in nitrogen purged toluene solution shows three bands 2062(w), 1928(s) and 1902(s) cm^{-1} (Figure 3.2.3.2). These bands can be assigned to the A_1 , E_1 and A_1^2 modes of a molecule of pseudo C_{4v} symmetry.

Figure 3.2.3.2: ir Spectrum (ν_{CO} region) of $\text{Cr}(\text{CO})_5(\text{trpy})$ in deoxygenated toluene solution.



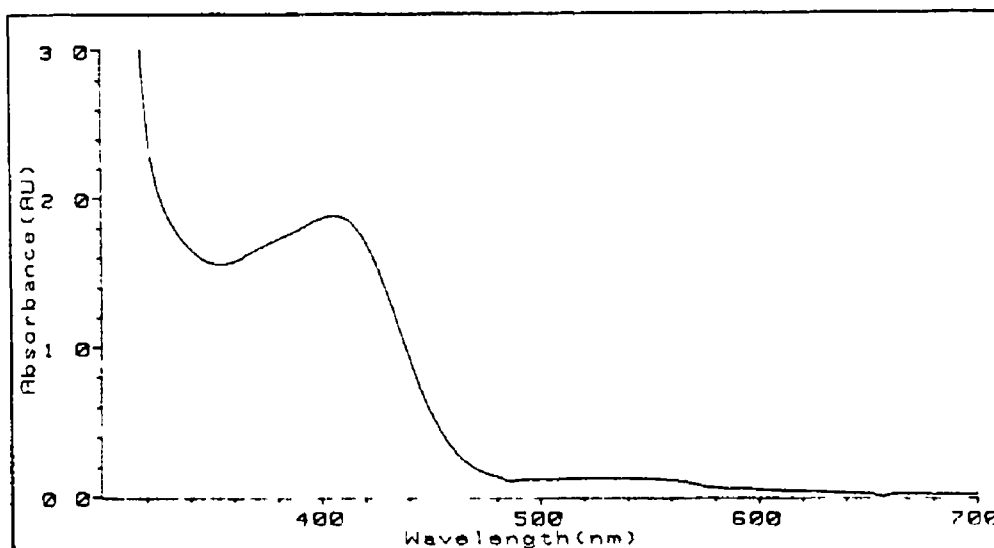
A band at 1980cm^{-1} (in KBr, as a corresponding band in toluene solution would overlap with the band at 1978cm^{-1} of $\text{Cr}(\text{CO})_6$), was assigned to the normally forbidden B_1 mode, as in the bipy and dmbipy complexes. However a comparison between Figure 3.2.3.2 and the spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ (Figure 3.2.2.2) shows that the degeneracy of the E mode is maintained in the trpy complex. The removal of the E mode degeneracy in $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ indicates that in these complexes the ligand is bridging. As in the $\text{Cr}(\text{CO})_5(\text{trpy})$ molecule, the ligand co-ordinates in a monodentate fashion its spectrum should be similar to $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in which the E mode degeneracy is maintained.

3.2.3.3 Uv/vis Spectrum of $\text{Cr}(\text{CO})_5(\text{trpy})$ in Toluene Solution

Figure 3.2.3.3 gives the uv/vis spectrum of a sample of $\text{Cr}(\text{CO})_5(\text{trpy})$ in degassed toluene solution. The spectrum exhibits a low energy band in the visible region, centred at 410nm and further strong bands in the uv region. Indeed the spectrum was almost identical to those of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ and was assumed to be as a result of similar transitions. Zulu and Lees in studying $\text{W}(\text{CO})_5\text{-L-W}(\text{CO})_5$ and $\text{W}(\text{CO})_5\text{L}$ complexes (L = bpy, bpe, or pyz) found that the $1A_1 \rightarrow 1E_1$ LF transitions (corresponding to the band at 410nm in $\text{Cr}(\text{CO})_5(\text{trpy})$) of the binuclear complexes are relatively unmoved from the corresponding mononuclear derivatives. This result is not surprising considering the transition is metal centred. Because the MLCT absorptions of $\text{Cr}(\text{CO})_5(\text{trpy})$, $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ are very strong in the uv region and because these bands overlap with LF bands, it is difficult to see the effect on the position of the

π^* -acceptor orbitals, on varying the diimine ligand. Measuring the effects of different diimine ligands on the MLCT absorption would be a good indication of the degree of π -co-ordination between the pyridyl moieties of the ligand.

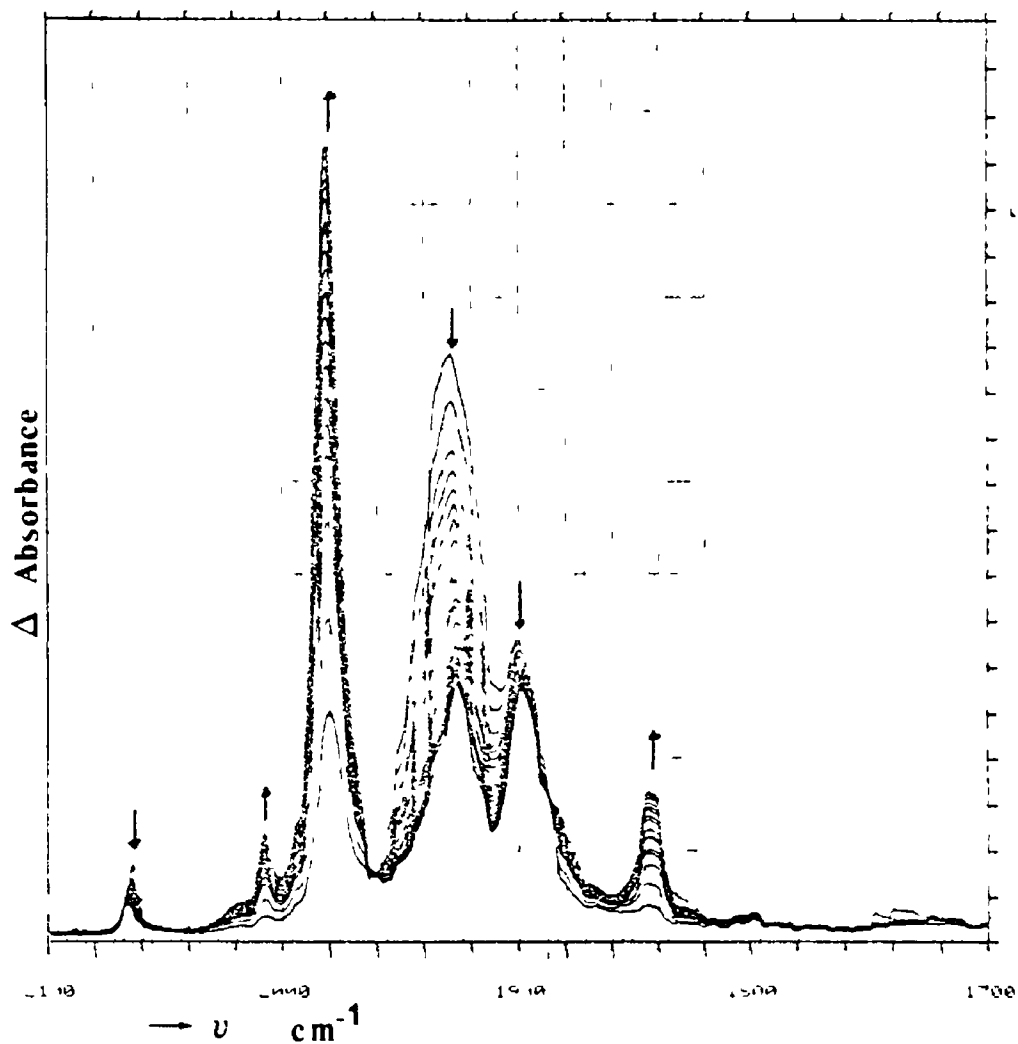
Figure 3.2.3.3: The uv/vis spectrum of $\text{Cr}(\text{CO})_5(\text{trpy})$ in degassed toluene solution at 297K.



3.2.3.4. Monitoring, by ir Spectroscopy, of the Reactions of $\text{Cr}(\text{CO})_5(\text{trpy})$ in Toluene Solution, at Ambient Temperature

The ir spectral changes recorded upon dissolution of $\text{Cr}(\text{CO})_5(\text{trpy})$ in nitrogen purged toluene solution are given in Figure 3.2.3.4. The bands assigned to $\text{Cr}(\text{CO})_5(\text{trpy})$ at 2062, 1928, and 1902 cm^{-1} are shown to diminish with the concomitant formation of bands at 2008, 1895, 1884 and 1842 cm^{-1} . These bands were assigned to the A_2 , B_1 , A_1 and B_2 vibrational modes of a pseudo- C_{2v} $\text{Cr}(\text{CO})_4(\text{trpy})$ tetracarbonyl species.

Figure 3.2.3.4: The ir spectral changes recorded upon standing of a solution of $\text{Cr}(\text{CO})_5(\text{trpy})$ ($7.4 \times 10^{-3} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 120s, and at 120s intervals thereafter, at ambient temperature.

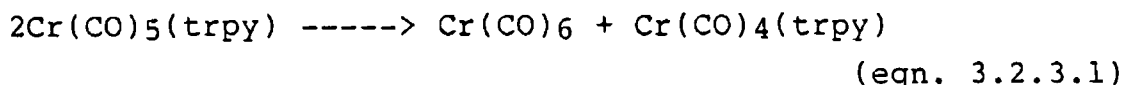


A strong band at 1980cm^{-1} , characteristic of $\text{Cr}(\text{CO})_6$, was also seen to form. The initial maintenance of an isosbestic point indicated that the reaction was at first uncomplicated by side or subsequent reactions. However as the reaction proceeded this isosbestic point was no longer maintained and the bands assigned to the tetracarbonyl complex diminished. Determination of the extinction coefficient of $\text{Cr}(\text{CO})_5(\text{trpy})$ ($\epsilon = 652 \pm 30 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ at 2062cm^{-1}) allowed the determination of the stoichiometry of the reaction in the initial stages. Unfortunately the synthesis of the presumed tetracarbonyl product $\text{Cr}(\text{CO})_4(\text{trpy})$, yielded a mixture of $\text{Cr}(\text{CO})_4(\text{trpy})$ and $\text{Cr}(\text{CO})_6$. Attempts to purify the tetracarbonyl complex, (by heating the solid sample under vacuum), only increased the amount of $\text{Cr}(\text{CO})_6$ present. It would thus appear that $\text{Cr}(\text{CO})_4(\text{trpy})$ is far less stable than the analogous bipy and dmbipy complexes. For this reason we have as yet been unable to obtain an extinction coefficient of the tetracarbonyl species. Table 3.2.3.1 summarises the results of a number of experiments:

Table 3.2.3.1: Absorbance changes and corresponding molar equivalents for $\text{Cr}(\text{CO})_5(\text{trpy})$, $\text{Cr}(\text{CO})_6$, and $\text{Cr}(\text{CO})_4(\text{trpy})$ during the chelation reaction.

Expt. number	Absorbance values (molar equivalents $\times 10^5$)				
	$\text{Cr}(\text{CO})_5(\text{trpy})$		$\text{Cr}(\text{CO})_4(\text{trpy})$		$\text{Cr}(\text{CO})_6$
1	.048	(7.36)	.125	---	.617 (4.26)
2	.015	(2.25)	.032	---	.224 (1.54)

The stoichiometry of the reaction would therefore appear to be as given in equation 3.2.3.1;



However this equation does not take account of all the reactions which are occurring in solution, it only applies to the initial reactions i.e. the formation of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\text{trpy})$ from $\text{Cr}(\text{CO})_5(\text{trpy})$. The chelation reaction was studied by uv/vis diode array spectroscopy in order to characterise this reaction and the subsequent reactions of $\text{Cr}(\text{CO})_4\text{trpy}$.

3.2.3.5 Monitoring, by uv/vis Spectroscopy, of the Reactions of $\text{Cr}(\text{CO})_5(\text{trpy})$ in Toluene Solution, at 295K

Figure 3.2.3.5 shows the uv/vis spectral changes recorded upon dissolution of $\text{Cr}(\text{CO})_5\text{trpy}$ in toluene solution. $\text{Cr}(\text{CO})_5(\text{trpy})$ is seen to initially form a complex whose absorption bands at 400nm and 515nm closely resemble those of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ or $\text{Cr}(\text{CO})_4(\text{bipy})$. This reaction occurs with good maintenance of an isosbestic point at 465nm. However within ca. 2000s a shoulder peak appeared at ca. 620nm. The sample was left for 16 hours and Figure 3.2.3 6 shows the recorded spectrum after this time. This relatively stable complex was fully formed within 18000s. Thus the ir results were corroborated by the uv/vis data, indicating that the $\text{Cr}(\text{CO})_4(\text{trpy})$ complex is itself very unstable in solution.

The rate constant for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ was determined over the initial grow-in period and showed the reaction followed good first order kinetics. The rate constant for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ was found to be $1.05 (+/- .01) \times 10^{-3} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297K.

Figure 3.2.3.5: (a) The uv/vis spectrum of $\text{Cr}(\text{CO})_5(\text{trpy})$ in degassed toluene solution at 296K, and the spectral changes occurring upon standing of this solution for 600, 3600, 5250, 7650 and 23250s.

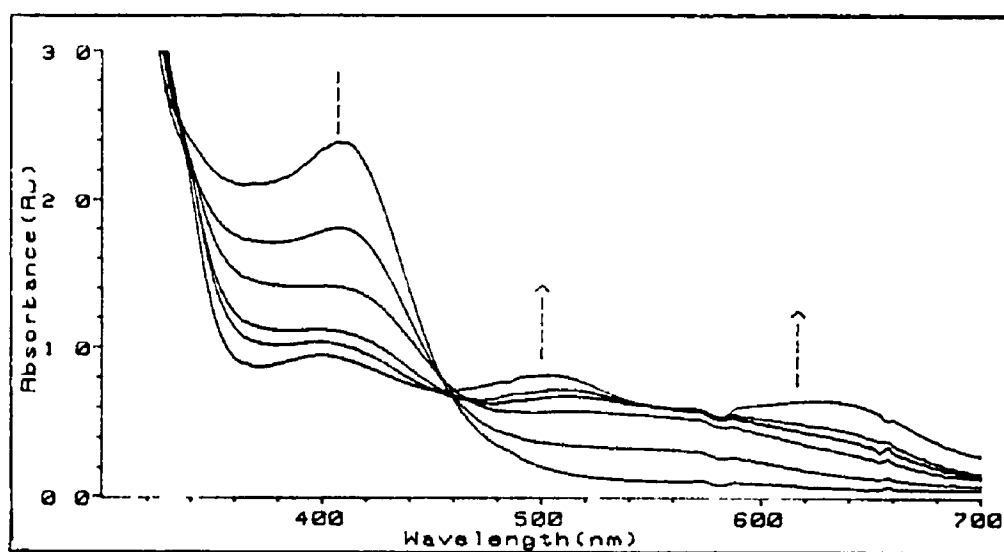
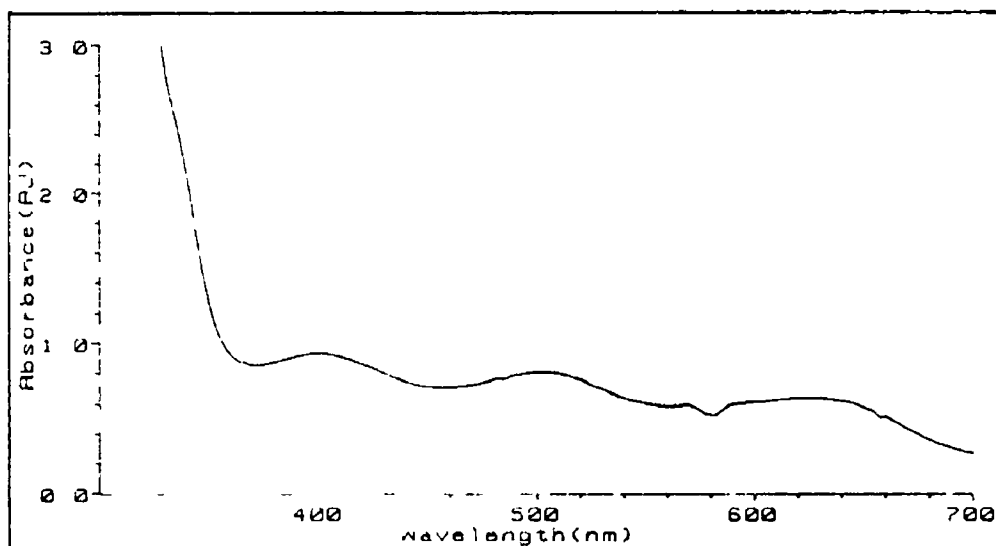
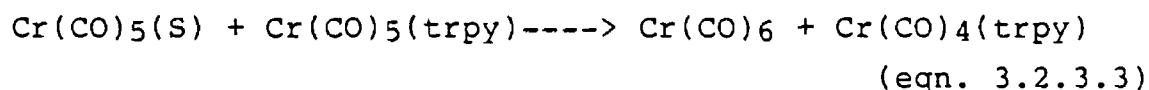
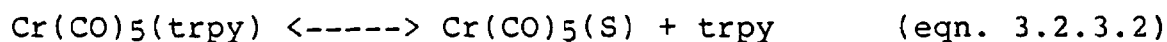


Figure 3.2.3.6: uv/vis Spectrum recorded upon completion of the chelation reaction.



Based on the ir and uv/vis results the following mechanism for the chelation reaction was initially proposed;

the initial reaction could be dissociation of the $\text{Cr}(\text{CO})_5(\text{trpy})$ molecule to form $\text{Cr}(\text{CO})_5$, which would then extract a CO ligand from another $\text{Cr}(\text{CO})_5(\text{trpy})$ molecule forming the chelate product. Either equation 3.2.3.2 or 3.2.3.3 could be the rate determining step in the reaction.



However a study of the chelation reaction in the presence of excess trpy, and a further study of the activation parameters for the formation of the chelate product in the presence and absence of ligand showed that this reaction scheme was not fully correct.

3.2.3.6 Monitoring, by ir Spectroscopy, of the Reactions of $\text{Cr}(\text{CO})_5(\text{trpy})$ in Toluene Solution, Containing Excess trpy Ligand, at Ambient Temperature

The spectral changes recorded upon dissolution of $\text{Cr}(\text{CO})_5(\text{trpy})$ in nitrogen purged toluene solution (containing an excess of trpy ligand) are given in Figure 3.2.3.7. In contrast to the chelation reaction of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in the presence and absence of excess ligand, there is apparently little change in the yield of $\text{Cr}(\text{CO})_6$ or $\text{Cr}(\text{CO})_4(\text{trpy})$ (as the extinction coefficient of $\text{Cr}(\text{CO})_4(\text{trpy})$ is not available, a comparison of the variation in absorbance value changes is given) Table 3.2.3.2 gives the results of two separate experiments;

Figure 3.2.3.7. The ir spectral changes occurring upon standing of a solution of $\text{Cr}(\text{CO})_5(\text{trpy})$ ($6.7 \times 10^{-4} \text{ mol dm}^{-3}$) and trpy ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) in deoxygenated toluene solution for 120, 620, 1,020, 2,620, and 4020s, at ambient temperature.

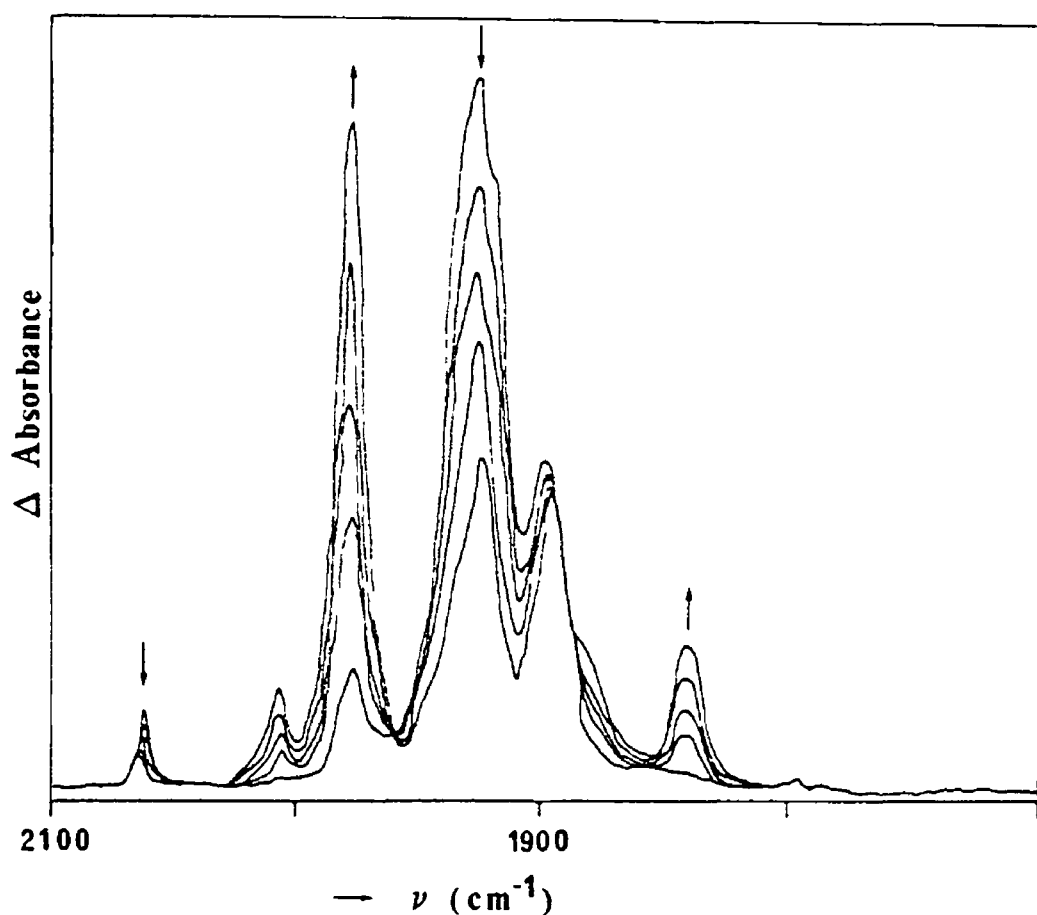


Table 3.2.3.2: Absorbance changes and corresponding molar equivalents for $\text{Cr}(\text{CO})_5(\text{trpy})$, $\text{Cr}(\text{CO})_4(\text{trpy})$ and $\text{Cr}(\text{CO})_6$ during the chelation reaction.

Expt. no.	Absorbance(A.U.) (molar equivalents) ($\times 10^5$)			
	$\text{Cr}(\text{CO})_5(\text{trpy})$	$\text{Cr}(\text{CO})_4(\text{trpy})$	$\text{Cr}(\text{CO})_6$	
1	.0434 (6.61)	.1480	---	.6300 (4.27)
2	.0200 (3.04)	.0660	---	.2850 (1.96)

The presence of excess trpy in solution inhibited the rate of formation of $\text{Cr}(\text{CO})_4(\text{trpy})$. These results are consistent with the reactions given in equations 3.2.3.2 and 3.2.3.3. Monitoring the chelation reactions under controlled conditions by uv/vis diode array spectroscopy allowed the determination of the exact effects of the ligand on k_{obs} .

3.2.3.7 The Dependence of k_{obs} , for the Formation of $\text{Cr}(\text{CO})_4(\text{trpy})$, on the Concentration of trpy and $\text{Cr}(\text{CO})_5(\text{trpy})$

Figure 3.2.3.8 shows the uv/vis spectral changes recorded for the chelation reaction in the presence of excess trpy. This reaction was found to follow first order kinetics, giving a value of $3.75 \times 10^{-4} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ (at a concentration of $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ of trpy) for k_{obs} . The presence of trpy on solution did not effect the yield of the tetracarbonyl species (see Figure 3.2.3.4 and Figure 3 2.3.8) but it is evident from Table 3.2.3.3 (and

Figure 3.2.3.9) that as the concentration of trpy was increased, k_{obs} decreases to a limiting value of ca. $3.71 \times 10^{-4} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. The spectral changes recorded in the presence of excess ligand are identical to those in the recorded in the absence of excess ligand. These observations agree well with the reaction scheme proposed in equations 3.2.3.2 and 3.2.3.3.

Figure 3.2.3.8: uv/vis Spectral changes occurring upon standing a solution of $\text{Cr}(\text{CO})_5(\text{trpy})$ and trpy ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) in degassed toluene solution at 296K, for 0, 2400, 4000, 7000, 19000, and 21600s.

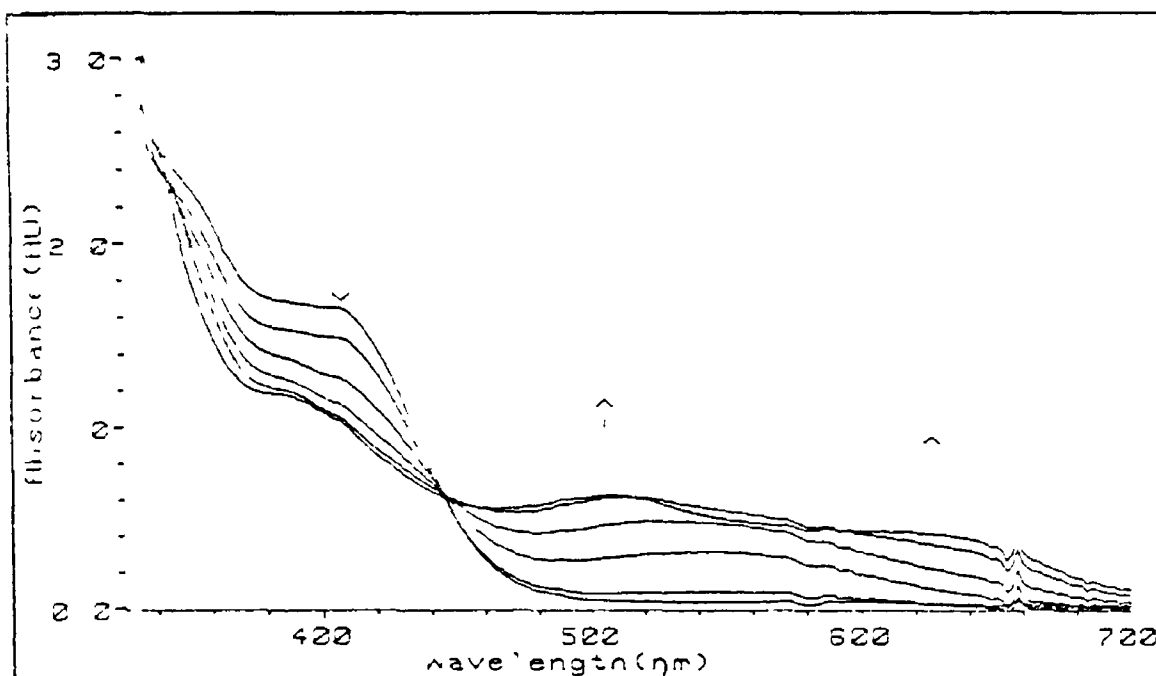
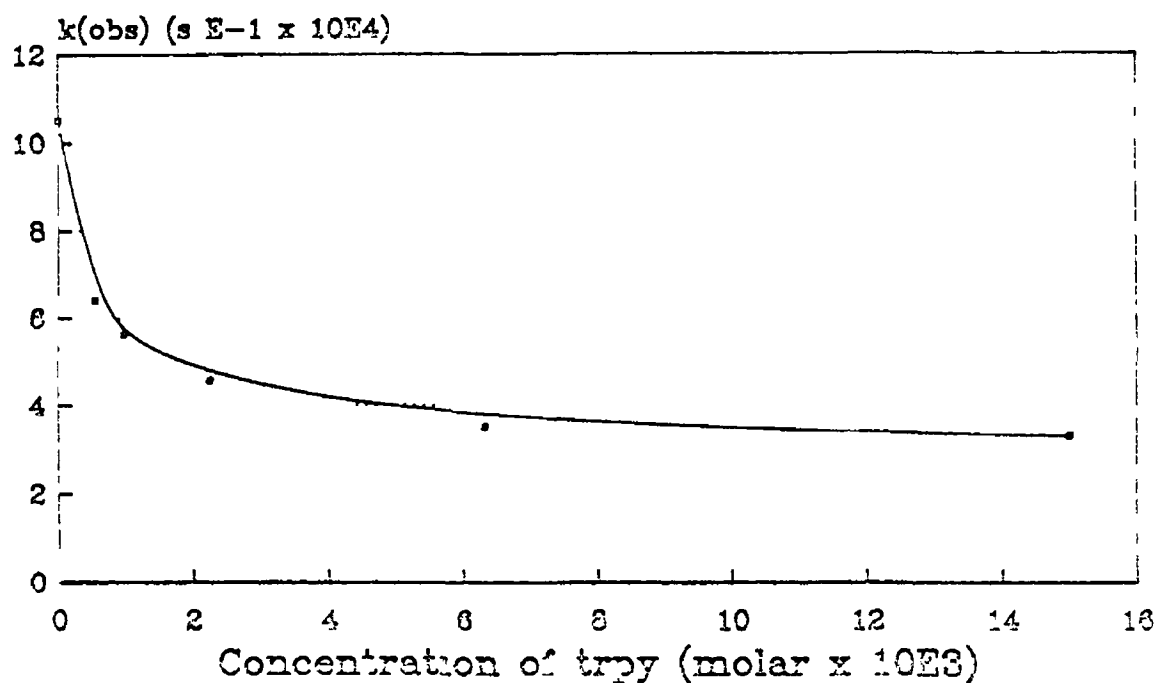


Table 3.2.3.3: k_{obs} for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ at varying concentrations of trpy.

Concentration of trpy $\text{mol dm}^{-3} \times 10^2$	k_{obs} $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \times 10^4$
0.00	10.50
1.61	4.68
2.00	3.74
2.50	3.71

Figure 3.2.3.9: The dependence of k_{obs} (s^{-1}), for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$, on the concentration of added trpy (mol dm^{-3}).



If the rate determining step in the chelation reaction is that given in equation 3.2.3.2, then the following should apply;

- increasing the concentration of trpy in solution would decrease the observed rate constant due to back reaction of equation 3.2.3.2. However it would have no effect on the yield of the final products of the reaction.

- k_{obs} should be independent of the concentration of $Cr(CO)_5(trpy)$ in solution.

- the entropy of activation would be expected to be positive (or perhaps a very small value), indicating the dissociation of trpy ligand from the $Cr(CO)_5$ fragment.

If the rate determining step is that given by equation 3.2.3.3 then;

- reaction kinetics would follow pseudo first order kinetics as the concentration of $Cr(CO)_5(S)$ in solution is much less than that of $Cr(CO)_5(trpy)$. k_{obs} would depend on the concentration of $Cr(CO)_5(S)$ in solution.

- the yield of final product would not be affected by the presence of excess trpy. However trpy in solution would effect the rate of reaction as it considerably affects the concentration of $Cr(CO)_5(S)$ in solution.

- the entropy of activation would be expected to be negative, indicating the associative nature of the transition state.

Therefore we studied the chelation reaction at varying concentrations of $Cr(CO)_5(trpy)$. Table 3.2.3.4 details

the values of k_{obs} measured for varying concentrations of $\text{Cr}(\text{CO})_5(\text{trpy})$ (given as initial absorbance values), clearly demonstrating that k_{obs} is independent of $\text{Cr}(\text{CO})_5(\text{trpy})$ concentration.

Table 3.2.3.4: k_{obs} for the formation of the chelate product at various starting concentrations of $\text{Cr}(\text{CO})_5(\text{trpy})$

Initial absorbance (A.U.), $k_{obs} (\text{s}^{-1}) \times 10^4$
at 410nm, of $\text{Cr}(\text{CO})_5(\text{trpy})$

0.71	10.47
0.53	11.43
0.74	11.50
0.21	10.04
0.44	10.60

3.2.3.8 Determination of the Activation Parameters for the Formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ in the Presence and Absence of Excess Ligand

Tables 3.2.3.5 and 3.2.3.6 give the experimental data used to determine the activation parameters for the formation of the chelate product (see also Figures 3.2.3.10 and 3.2.3.11). These results indicate that the nature of the rate determining step changes little on addition of excess ligand.

Table 3.2.3.5: Experimental data for the determination of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ in the absence of any excess ligand).

Temperature (K)	$\text{Ln}(R)$	$\text{Ln}(R_t)$
297	-6.89	-12.58
299	-6.69	-12.39
303	-6.38	-12.58
307	-6.08	-11.81
309	-5.95	-11.68
312	-5.85	-11.59

Arrhenius Plot.

Slope = -6560 ± 344

Int. = $15.24 \pm .49$

Corr. coeff. = .995

Eyring Plot.

Slope = -6262 ± 327

Int. = $8.54 \pm .046$

Corr. coeff. = .995

=> $E_a = 54.5 \pm 3 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 52.1 \pm 3 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -126 \pm 30 \text{ Jmol}^{-1}\text{K}^{-1}$

Table 3.2.3.6: Experimental data for the determination of the activation parameters for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ in the presence of excess ligand.

(a) Experiment 1

Temperature (K)	$\text{Ln}(R)$	$\text{Ln}(R_t)$
297	-7.81	-13.51
303.5	-7.55	-13.27
307	-7.32	-13.05
311	-6.88	-12.62

Arrhenius Plot.

Slope = -6053 ± 1240

Int. = $12.49 \pm .13$

Corr. coeff. = .962

Eyring Plot.

Slope = -5803 ± 1240

Int. = $6.00 \pm .13$

Corr. coeff. = .957

$\Rightarrow E_a = 50.3 \pm 4 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 48.2 \pm 4 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -148 \pm 30 \text{ Jmol}^{-1}\text{K}^{-1}$

(b) Experiment 2

Temperature (K)	$\text{Ln}(R)$	$\text{Ln}(R_t)$
296	-7.21	-12.89
309	-6.40	-12.13
320	-5.34	-11.11

Table 3.2.3.6:cont'd

<u>Arrhenius Plot.</u>	<u>Eyring Plot.</u>
Slope = -6992 +/- 508	Slope = -6691 +/- 555
Int. = 16.38 +/- .09	Int. = 9.67 +/- .10
Corr. coeff. = .994	Corr. coeff. = .993

=> $E_a = 58.1 \pm 4 \text{ KJmol}^{-1}$, $\Delta H^\ddagger = 55.6 \pm 4 \text{ KJmol}^{-1}$ and $\Delta S^\ddagger = -117 \pm 30 \text{ Jmol}^{-1}\text{K}^{-1}$

These results indicate that the nature of the chelation reaction changes little on addition of excess ligand. The differences in activation parameters are well within experimental error. $\Delta S^\ddagger$ being largely negative, the rate determining step involves an associative step. In Section 3.2.3.7, k_{obs} was shown to be independent of $\text{Cr}(\text{CO})_5(\text{trpy})$ concentration, indicating that the rate determining step is as given in equation 3.2.3.2. This reaction should have a positive entropy value, because of dissociation of the ligand from the $\text{Cr}(\text{CO})_5$ fragment. The small value of $\Delta H^\ddagger$, which is considerably less than the enthalpy of activation for the breaking of a $\text{Cr}(\text{CO})_5\text{-N}$ bond is a further indication that the reaction is associative. Thus it would appear that the equation scheme given by equations 3.2.3.2 and 3.2.3.3 is incomplete. Scheme 3.2.3.1 shows the proposed reaction scheme for the chelation reaction.

The rate determining step in the chelation reaction is the rearrangement of the bridging species into a conformation of greater order (hence the negative $\Delta S^\ddagger$ value).

Figure 3.2.3.10: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ in the absence of excess ligand.

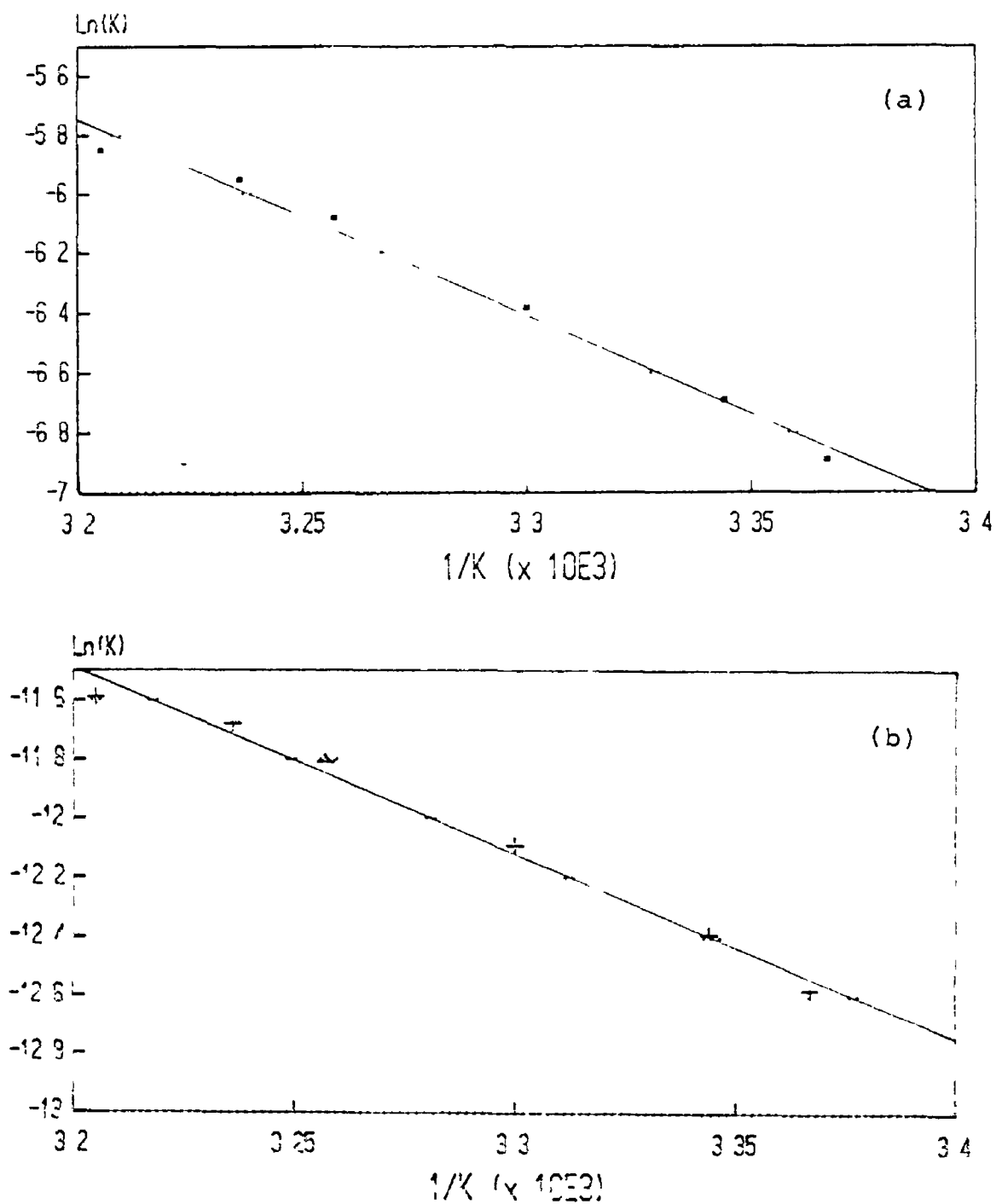
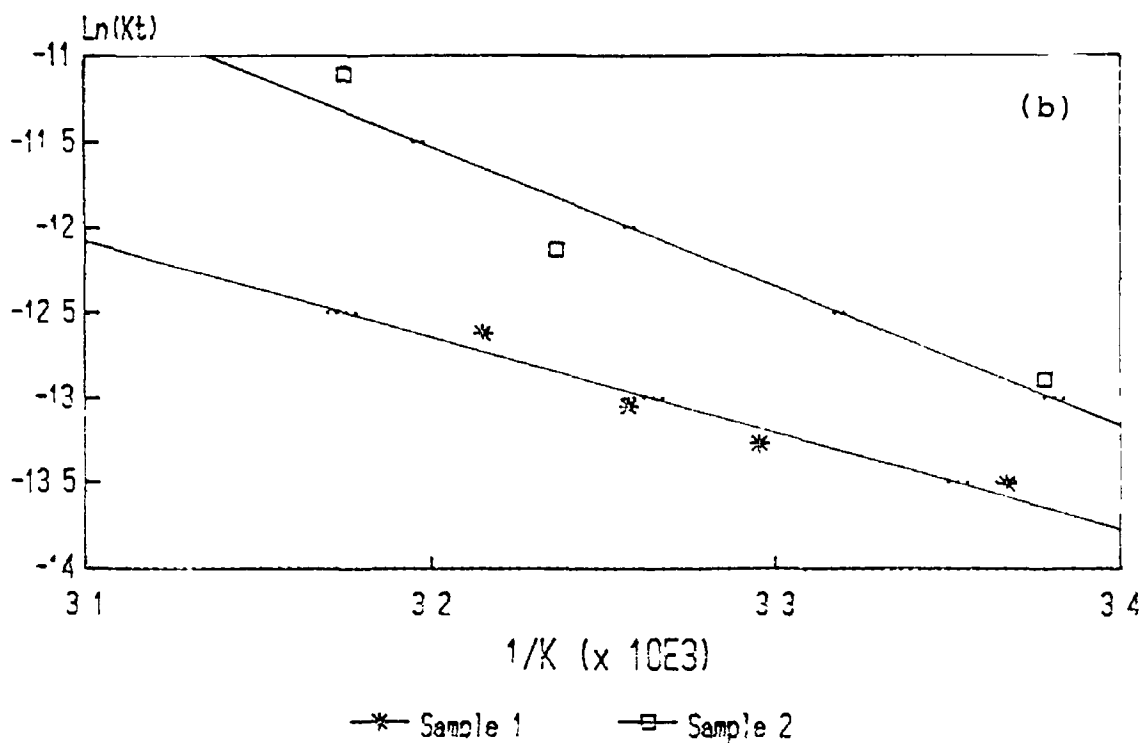
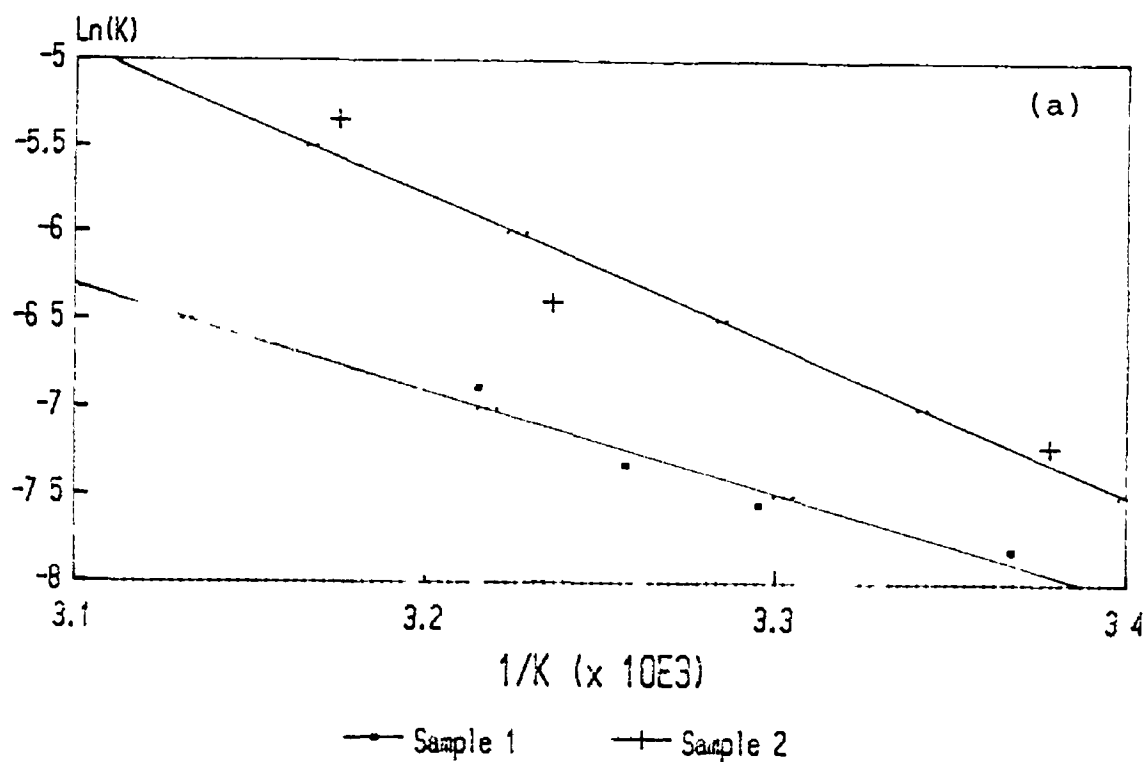
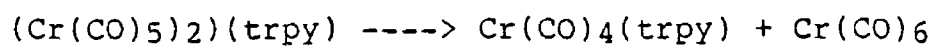
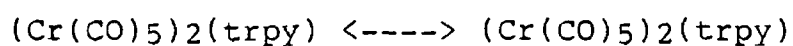
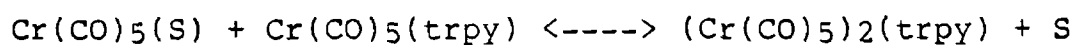
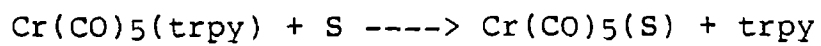


Figure 3.2.3.11: Arrhenius (a) and Eyring (b) plots for the formation of $\text{Cr}(\text{CO})_4(\text{trpy})$ in the presence of excess trpy ligand.



Proposed Reaction Scheme:



Scheme 3.2.3.1

3.2.4 Flash Photolysis Studies of $\text{Cr}(\text{CO})_6$ in Toluene and Cyclohexane Solution Containing Diimine Ligands

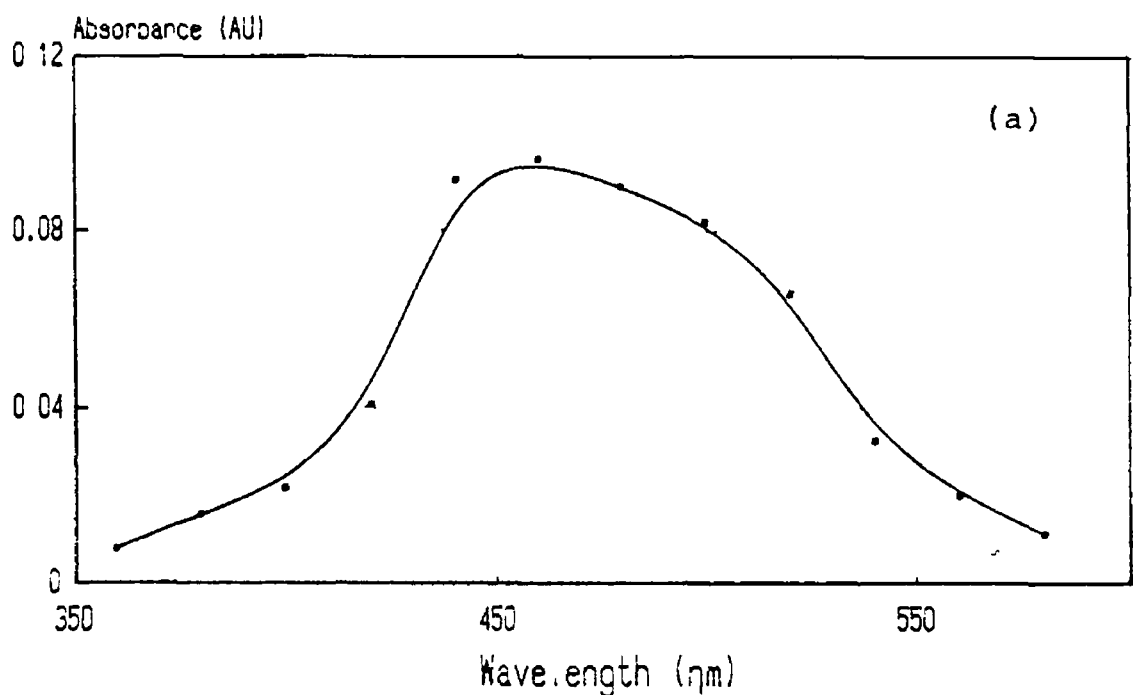
The isolation of the bridging complexes $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ and their reactions in toluene solution have been detailed in Sections 3.2.1 and 3.2.2. These complexes are formed from the reaction of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ with the appropriate ligand, the $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ molecule acting as a source of $\text{Cr}(\text{CO})_5$. However photolysis of the parent hexacarbonyl compound is also a source of $\text{Cr}(\text{CO})_5$, (as has been described in Section 2.1)

We therefore thought a study on the flash photolysis of $\text{Cr}(\text{CO})_6$ in toluene solution, in which the diimine ligand was also present may yield valuable insight into the formation of $(\text{Cr}(\text{CO})_5)_2(\text{diimine})$. Our studies on the chelation reactions of $\text{Cr}(\text{CO})_5(\text{trpy})$ had indicated that the formation of a intermediate bridging complex was central to the reaction. Thus a study of the reactions of photogenerated $\text{Cr}(\text{CO})_5(\text{S})$ (S = solvent) with diimine ligand may indicate if a bridging or mononuclear ligand complex was the direct precursor of the chelate product.

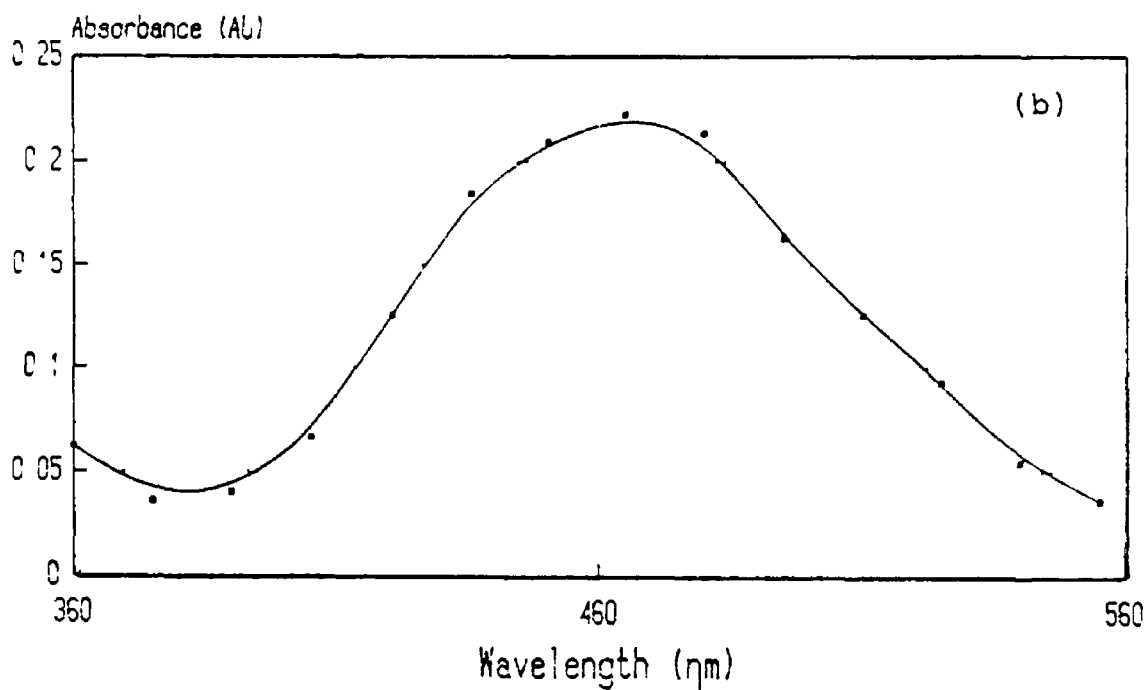
3.2.4.1 The Spectra of $\text{Cr}(\text{CO})_5(\text{S})$ (S = Toluene or Cyclohexane)

The spectra of the initially observed species upon flash photolysis of $\text{Cr}(\text{CO})_6$ in carbon monoxide saturated toluene solution containing bipy and dmbipy are given in Figure 3.2.4.1 (a and b). The spectrum of the initially observed species upon flash photolysis of $\text{Cr}(\text{CO})_6$ in carbon monoxide saturated cyclohexane solution containing bipy ligand is given in Figure 3.2.4.2.

Figure 3.2.4.1: uv/vis Difference spectra observed following flash photolysis of $\text{Cr}(\text{CO})_6$ in degassed toluene solution containing excess dmbipy (a) and bipy (b) ligands

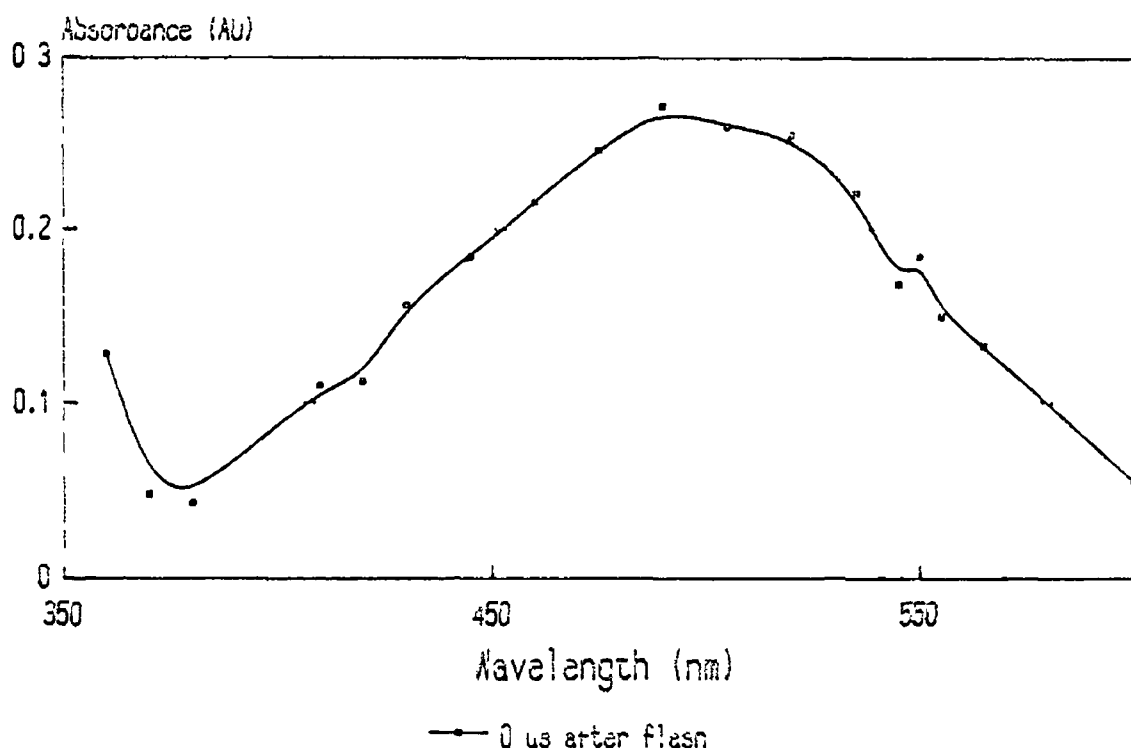


—•— 0 μs after flash



—•— 100 μs after flash

Figure 3.2.4.2: uv/vis Difference spectrum observed following flash photolysis of $\text{Cr}(\text{CO})_6$ in degassed cyclohexane solution, containing excess bipy ligand.



Spectra a and b are very similar, there are absorption maxima in the visible region at about 465nm and further strong absorption bands in the uv region. These spectra are identical to those obtained upon flash photolysis of $\text{Cr}(\text{CO})_6$ alone in benzene (Earlier studies by Peters *et al.*¹ have shown that the $\text{Cr}(\text{CO})_5$ fragment is very reactive and rapidly solvates in less than a nanosecond in neat benzene). Thus the initially observed transience is assigned to the $\text{Cr}(\text{CO})_5(\text{toluene})$ species.

The spectrum of the initially observed species in cyclohexane exhibits an absorption maximum in the uv region at ca. 500nm. The absorption maximum of $\text{Cr}(\text{CO})_5(\text{S})$ in room temperature cyclohexane has been previously reported at 503nm.² The difference in absorption maxima of the

solvated species in toluene and cyclohexane solution can be attributed to the varying strength in metal-solvent interactions. A consequence of increased metal-solvent interaction in the $\text{Cr}(\text{CO})_5(\text{S})$ molecule is the reduced reactivity of the molecule in solution. Such effects have been reported by numerous workers and was found to be the case here also (vide infra).

3.2.4.2 The Reactions of $\text{Cr}(\text{CO})_5(\text{S})$ (S = Toluene or Cyclohexane) with bipy and dmbipy

In the presence of diimine ligand the $\text{Cr}(\text{CO})_5(\text{S})$ transient was seen to decay with a concomitant grow-in of a product band (which was stable for greater than 2s). The spectrum of this second transient is given in Figure 3.2.4.3 and exhibits an absorption maximum at 440nm. Figure 3.2.4.4 shows the time resolved spectrum recorded at various time intervals after the flash photolysis of $\text{Cr}(\text{CO})_6$ in carbon monoxide saturated toluene solution, containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ bipy ligand, showing an isosbestic point at 475nm. Thus the conversion of $\text{Cr}(\text{CO})_5(\text{S})$ to the second observed transience appeared to be uncomplicated by side or subsequent reactions.

Oishi³ and Kalyanasundaram⁴ had conducted two independent flash photolysis studies on the photochemical carbonyl substitution in $\text{M}(\text{CO})_6$ (M= Cr, Mo, or W) with 1,10-phenanthroline and with 2,2'-bipy, dmbipy, and 5-chloro-1,10-phenanthroline. The spectral data for the initial and second transience observed species are given in Table 3.2.4.1. Both workers had assigned the transience at 410nm, (in their studies of $\text{Cr}(\text{CO})_6$ with bipy and dmbipy), to a $\text{Cr}(\text{CO})_5(\text{LL})$ complex (LL = dmbipy or bipy) with the diimine ligand co-ordinated in a monodentate fashion, based on their spectral similarity to $\text{Cr}(\text{CO})_5(\text{pyridine})$.

Figure 3.2.4.3: uv/vis Difference spectra observed following flash photolysis of $\text{Cr}(\text{CO})_6$ in degassed toluene solution containing excess dmbipy (a) and bipy (b) ligands.

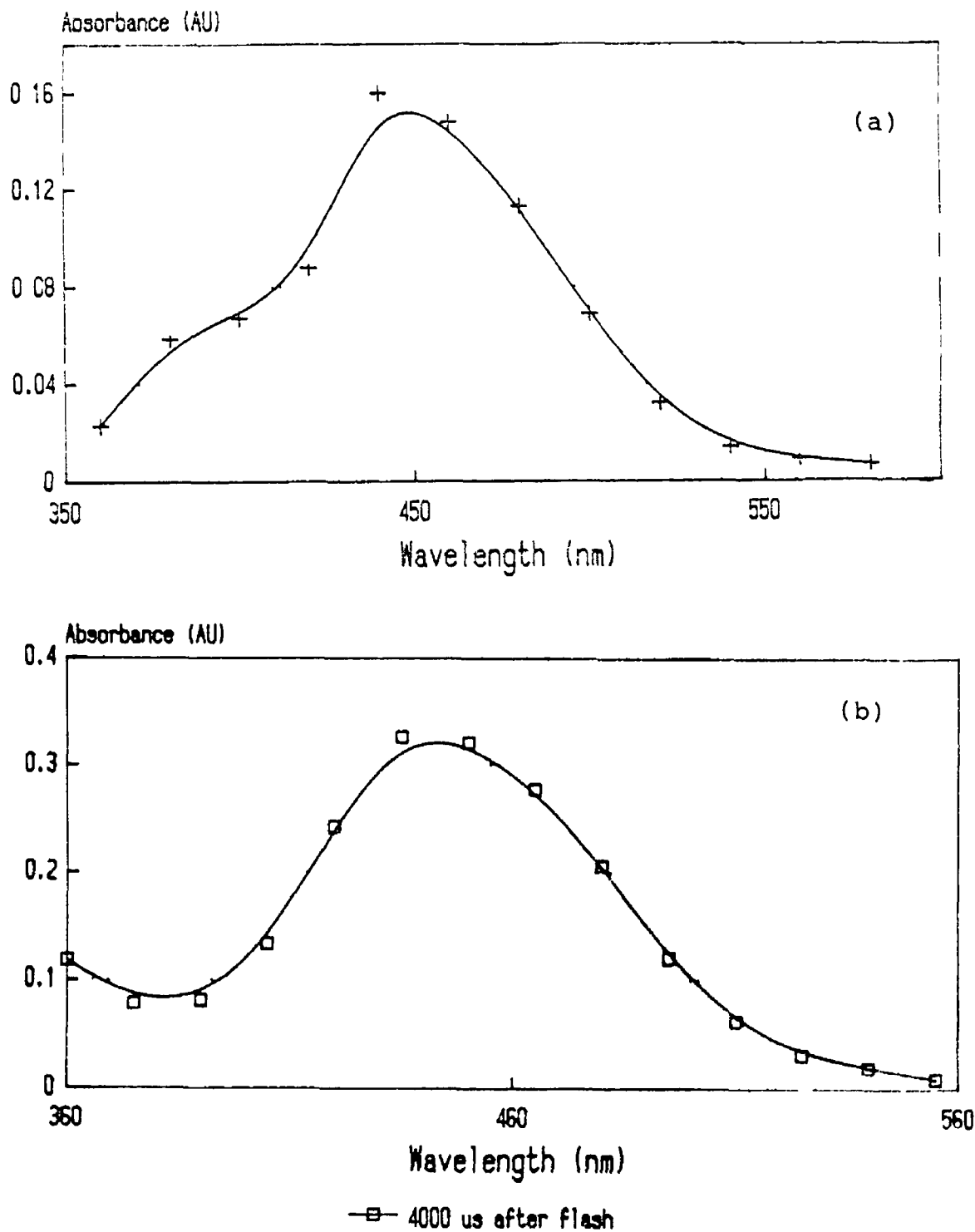
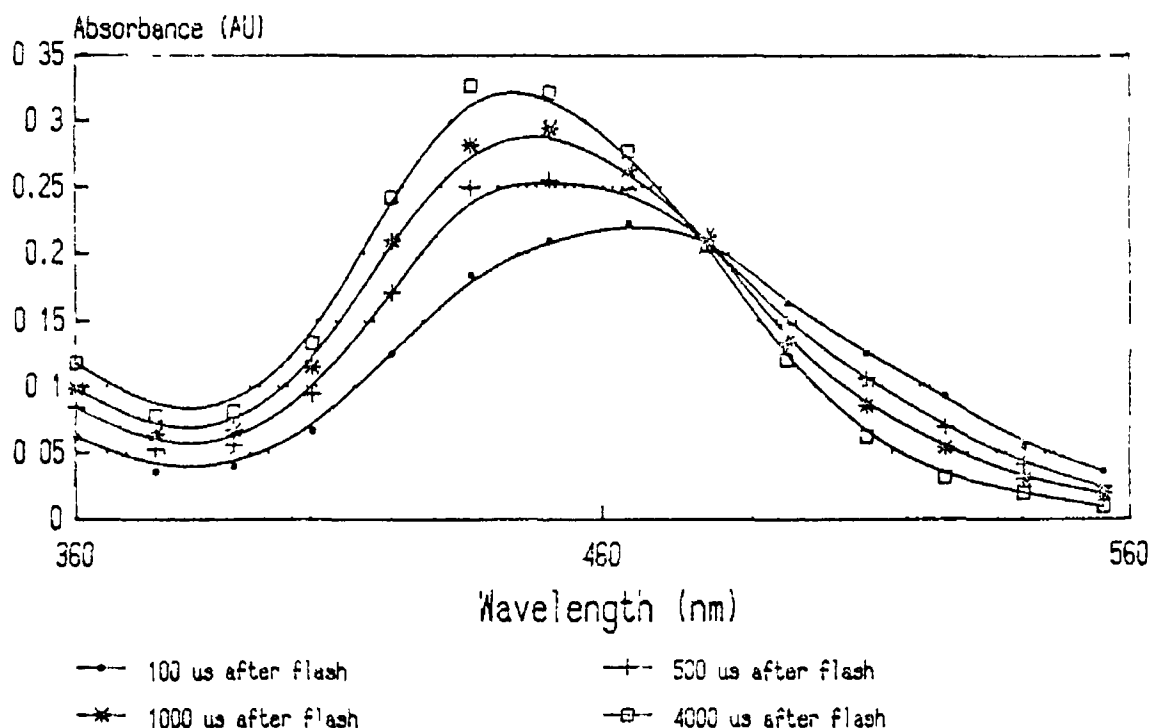
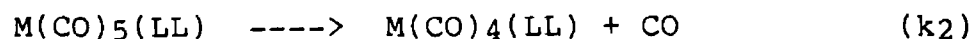
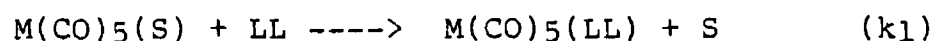
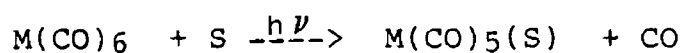


Figure 3.2.4.4: uv/vis Difference spectra recorded at various time intervals following the flash photolysis of $\text{Cr}(\text{CO})_6$ in toluene solution, containing an excess of bipy ligand.



The second observed transient had an absorption maximum at 440nm, which was 30nm greater than the absorption maximum of either $\text{Cr}(\text{CO})_5(\text{pyridine})$ or $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$. Kalyanasundaram had verified that his second transient was formed as a result of the reaction of $\text{Cr}(\text{CO})_5(\text{S})$ with diimine ligand by showing that the growth rate for the formation of the second species increased linearly with increasing ligand concentration. These results are consistent with the following reaction scheme;



Scheme 3.2.4.1

Table 3.2.4.2 gives the rate constant for the formation of this second species at varying concentrations of dmbipy and bipy in toluene and cyclohexane. What is immediately obvious from this table is that while the lifetime of $\text{Cr}(\text{CO})_5(\text{S})$ decreases as ligand concentration increases this is by no means a linear relationship. In all cases the rate constant is greater than that observed by previous workers. These differences in reaction rate cannot be explained by the different solvents.

Table 3.2.4.2: The variation in k_{obs} for the formation of $\text{Cr}(\text{CO})_5(\text{L})$ ($\text{L} = \text{dmbipy}$ or bipy), with solvent and concentration of L .

Solvent	L	Conc. (mol dm^{-3}) $\times 10^3$	k_{obs} (s^{-1})
Toluene	dmbipy	2.46	411
Toluene	dmbipy	0.40	328
Toluene	bipy	1.00	1141
Cyclohexane	bipy	1.00	363636

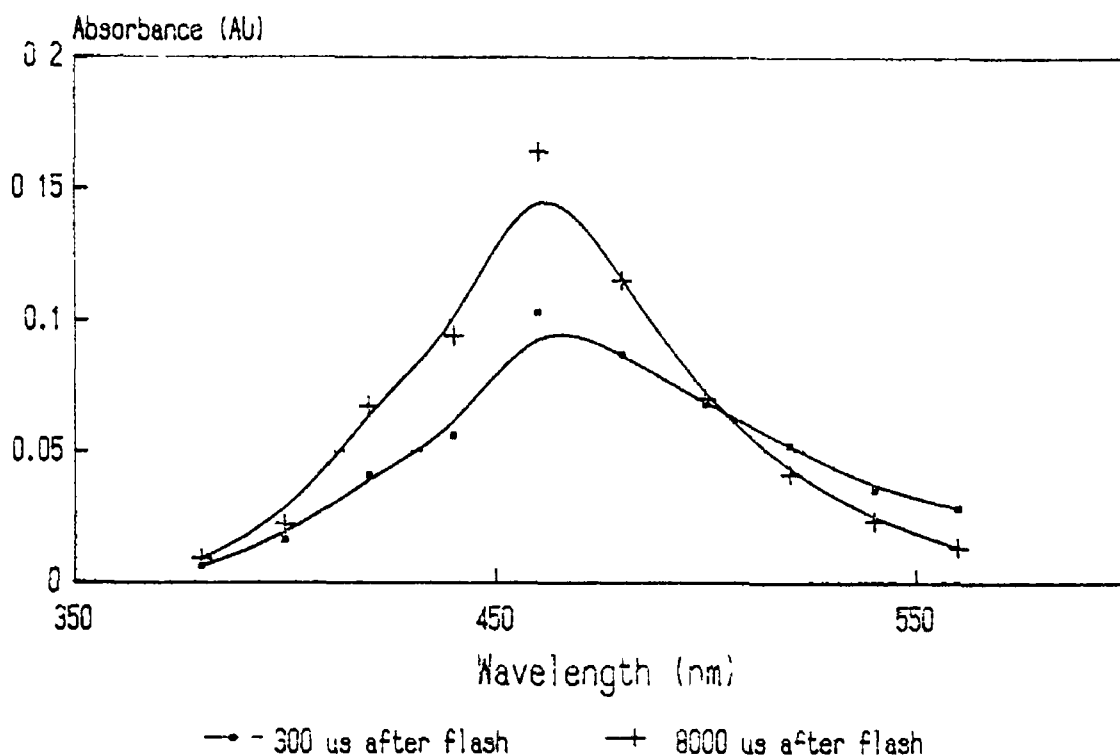
The reaction of $\text{Cr}(\text{CO})_5(\text{S})$ with diimine ligand can lead to the formation of two possible products, the $\text{Cr}(\text{CO})_5(\text{diimine})$ in which the diimine ligand is co-ordinated in a monodentate fashion, or the bridging $(\text{Cr}(\text{CO})_5)_2(\text{diimine})$ complex. This latter complex however would be expected to form in two sequential steps, one of which may be substantially faster than the other. Both of these compounds however would be expected to have similar LF absorption bands at ca. 410nm (the LF absorption maximum of $\text{Cr}(\text{CO})_5(\text{pyridine})$). The formation of a bridging species and indeed the formation of monodentate $\text{Cr}(\text{CO})_5(\text{diimine})$ would not be expected to significantly perturb the metal centred LF transitions.

Oishi,³ in his work on the flash photolysis of $\text{Cr}(\text{CO})_6$ in the presence of 1,10-phen, found that the absorption maximum of $\text{Cr}(\text{CO})_5(\text{phen})$ occurred at 440nm. He attributed this shift in the LF transition from those of typical LF bands of $\text{Cr}(\text{CO})_5(\text{py})$ (py= pyridine, 2,2'-bipy) to an electronic interaction between the non-co-ordinated nitrogen and Cr, which may give rise to distortion from a typical octahedral co-ordination.

While a similar phenomena could explain our results, it would not explain why Oishi himself did not see this transient in his study on the flash photolysis of $\text{Cr}(\text{CO})_6$ in the presence of bipy. Neither would it explain the non-linearity of k_{obs} for reaction 3 in Scheme 3.2.4.1 with ligand concentration. Thus it was thought that the second observed species may be as a result of the reaction of $\text{Cr}(\text{CO})_5(\text{S})$ with an impurity in the solvent. In addition spectra recorded at the end of flash photolysis experiments using 'dry' and H_2O saturated toluene solutions are very similar (vide infra).

Figure 3.2.4.5 shows the spectra recorded upon flash photolysis of $\text{Cr}(\text{CO})_6$ in H_2O saturated toluene solution containing dmbipy

Figure 3.2.4.5: uv/vis Difference spectrum observed following the flash photolysis of $\text{Cr}(\text{CO})_6$ in H_2O saturated toluene solution, containing an excess of dmbipy ligand.



The second observed species has an absorption maximum at ca. 460nm and the pseudo first order rate constant for the reaction is an order of magnitude faster than those previously recorded (i.e. $2.3 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$) in 'dry' toluene. Thus it is possible that the transient spectrum shown in Figure 3.2.4.2 is really a resultant spectrum of $\text{Cr}(\text{CO})_5(\text{diimine})$ and $\text{Cr}(\text{CO})_5(\text{H}_2\text{O})$. The presence of water in solution would account for the non-linear variation in observed lifetimes of $\text{Cr}(\text{CO})_5(\text{S})$ with ligand concentration. For this reason it is difficult

to determine the differing effects of bipy and dmbipy on the lifetime of $\text{Cr}(\text{CO})_5(\text{S})$. Obviously purer solvents are a necessary prerequisite before further investigations can be carried out on these systems.

It should be stated that in work carried out by a number of other groups using benzene, as a solvent these problems were not encountered.⁴ These workers found that the rate of formation of $\text{M}(\text{CO})_4(\text{LL})$ ($\text{M} = \text{Mo}, \text{Cr}, \text{or W}$; $\text{LL} = 5\text{-chloro-1,10-phen}, 1,10\text{-phen}, \text{dmbipy}, \text{or bipy}$) followed the order $\text{Mo} > \text{Cr} > \text{W}$, which is consistent with the calculated force constant of $\text{M}(\text{CO})_6$ in solution. For a given metal carbonyl, the reactivity of various ligands followed the order $5\text{-chloro-1,10-phen} \geq 1,10\text{-phen} > \text{bipy} > \text{dmbipy}$. The ordering of the rate data can be interpreted in terms of steric constraints for the co-ordination of the diimine ligand, and perhaps to differences in basicity of the ligands.

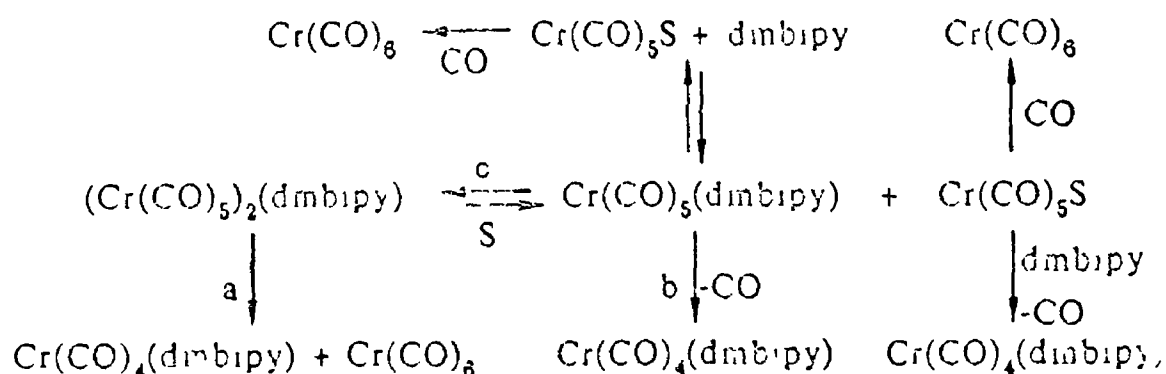
3.2.5 Summary

Section 3 has described the isolation and characterisation of $(\text{Cr}(\text{CO})_5)_2(\text{X})$ ($\text{X} = \text{dmbipy}$ or bipy) and $\text{Cr}(\text{CO})_5(\text{trpy})$ and their reactions in toluene solution. Such monodentately co-ordinated diimine and triimine ligands have not been previously isolated, mainly because of the reactive nature of these complexes in solution. The isolation of these complexes was thought to be as a result of their low solubility in pentane.

The uv/vis and ir spectroscopic features of these complexes have been studied and correlated well with the structural properties of the complexes. In the ir spectra of all three complexes, the enhanced intensity of the normally forbidden B_1 mode indicated that the local C_{4v} symmetry about the metal carbonyl centre was reduced upon co-ordination of the ligands. The ir spectra of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ showed the removal of the degeneracy of the E_1 mode. This E_1 mode was present however in the spectrum of $\text{Cr}(\text{CO})_5(\text{trpy})$. The removal of the E mode degeneracy in the dmbipy and bipy complexes was thought to be as a result of the diimine ligands acting as bridging ligands in these complexes.

The uv spectra of these complexes were typical of $\text{Cr}(\text{CO})_5(\text{pyr})$ ($\text{pyr} = \text{pyridine, picoline etc.}$) type complexes. The absence of a MLCT band at high wavelengths (i.e. $\lambda > 420\text{nm}$) indicated that there was little π^* conjugation present in the molecules. In addition the absence of an absorption band at 290nm, normally assigned to a $\pi - \pi^*$ transition in bipy complexes, suggests that the energy of the bipy based π^* energy level in these complexes is higher in the free ligand. This implies that the pyridyl ring systems are not coplanar.

The reactions of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ and $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ in toluene solution were very similar and followed the reaction scheme given below (Scheme 3.2.5.1).



S = TOLUENE

Scheme 3.2.5.1

kobs for the formation of the chelate product in the presence and absence of excess ligand are given in Table 3.2.5.1. In both cases the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ is considerably faster than the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$. This could be an indication that the rate determining step is the breaking of the Cr-N bond as the strength of the Cr-N interaction would vary with the pKa of the ligand. If this is the case the enthalpy of activation should be similar to that for the breaking of the Cr-N bond in pyridine, and this was found to be the case. The slightly lower enthalpy values for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ could also be an indication that there is associative character in the formation of the transition

state. The thermodynamic parametrs are given in Table 3.2.5.2

Table 3.2.5.1: k_{obs} (s^{-1}) for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ and $\text{Cr}(\text{CO})_4(\text{bipy})$ in the presence and absence of excess ligand.

Excess Ligand	k_{obs} (s^{-1}) for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ ($\times 10^3$)	k_{obs} (s^{-1}) for the formation of $\text{Cr}(\text{CO})_4(\text{bipy})$ ($\times 10^3$)
----	0.33	
dmbipy	1.14	
----		.83
bipy		1.70

Table 3.2.5.2: Thermodynamic parameters for the formation of $\text{Cr}(\text{CO})_4(\text{dmbipy})$ and $\text{Cr}(\text{CO})_4(\text{bipy})$, in the presence and absence of excess ligand.

	$\text{Cr}(\text{CO})_4(\text{dmbipy})$ $\Delta H^\ddagger$ a $\Delta S^\ddagger$ b		$\text{Cr}(\text{CO})_4(\text{bipy})$ $\Delta H^\ddagger$ a $\Delta S^\ddagger$ b	
- ligand	110	51	97	15
+ ligand	94	5.2	76	-52

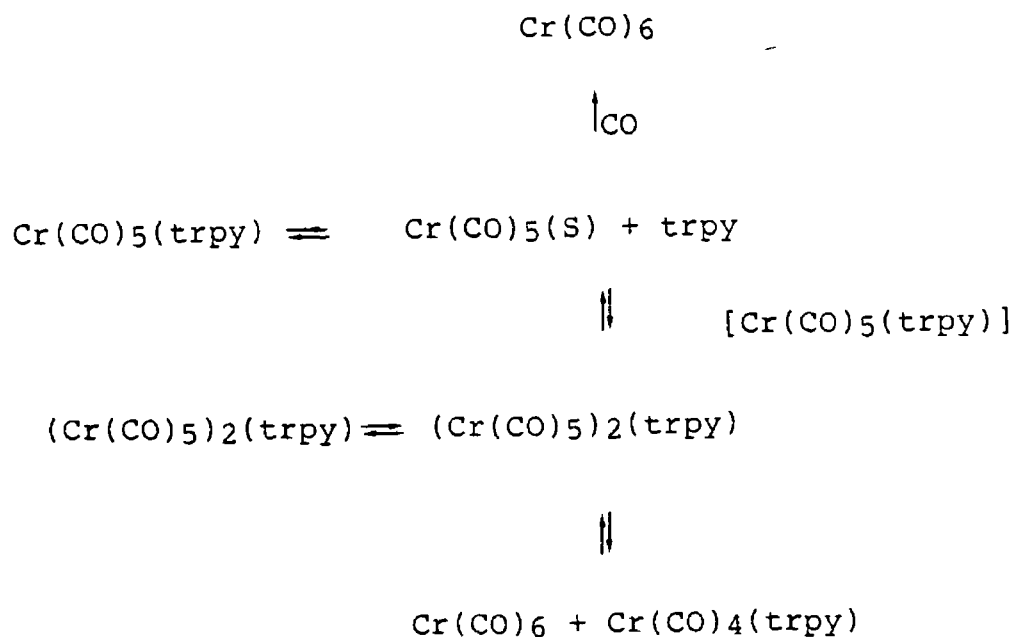
a $\Delta H^\ddagger$ is given in KJmol^{-1} ; b $\Delta S^\ddagger$ is given in $\text{Jmol}^{-1}\text{K}^{-1}$

In the absence of excess ligand the rate determining step is dissociative in nature, though less so in the case of the bipy complex. However as has been already stated these differences could be as a result of the differences in pK_a 's of the ligands. The differences in activation entropy between the two ligands indicate that in the bipy complex there is considerably more associative character in the formation of the transition state. This correlates with the steric hindrance of the chelation reaction by the presence of a methyl group to the co-ordinating nitrogen. Steric hindrance has previously been an indication of associative behaviour.

In the presence of excess ligand the enthalpies of activation are again similar (within experimental error) and would indicate that the rate determining step is again perhaps the breaking of the Cr-N bond in the formation of the transition state. However in the bipy complex the large negative value of $\Delta S^\ddagger$ indicates the associative character of this state. The presence of a methyl group on the α -C may prevent the formation of a similar transition state in the dmbipy complex.

The behaviour of $\text{Cr}(\text{CO})_5(\text{trpy})$ complex in solution was markedly different from that of the dmbipy and bipy complexes (See Scheme 3.2.5.2). Although a monodentately co-ordinated $\text{Cr}(\text{CO})_5(\text{trpy})$ complex was initially isolated, the formation of the chelate product $\text{Cr}(\text{CO})_4(\text{trpy})$ complex was seen to proceed via the intermediate formation of a bridging $(\text{Cr}(\text{CO})_5)_2(\text{trpy})$ complex. The full characterisation of these reactions has not been completed as yet and a great deal more work is needed before one could fully understand the reactions occurring in solution. Nevertheless, it would appear as if the formation of bridging complexes is an integral part of chelate formation in multidentate ligand complexes of the type described here. We attempted the monitoring by flash photolysis techniques of the initial reactions of

Cr(CO)₅(S) (S = toluene and cyclohexane) with diimine ligands, with a view to monitoring the formation of the bridging species in solution. However problems with the 'dryness' of the solvent have precluded the generation of reasonable results to date.



S = Toluene

Scheme 3.2.5.2:

3.3 EXPERIMENTAL SECTION

3.3.1 Materials

Cis-cyclooctene, bipy, dmbipy and trpy were supplied by Aldrich Chemical Co. and used without further purification. $\text{Cr}(\text{CO})_6$ was obtained from Strem Chemicals Inc., hexane from BDH (Spectrosol grade) and cyclohexane from BDH, (Spectrosol grade) were used as received. Toluene (Riedel de Haen, analar grade) was distilled from CaH_2 or LiAlH_4 before use. Carbon monoxide and argon gases were used as supplied by Cyrogas Ltd.

3.3.2 Equipment

3.3.2.1 Ir Spectral Studies

Samples for ir spectral studies were prepared under an nitrogen atmosphere. The toluene solution was initially deoxygenated by purging with nitrogen, before being added to an arbitrary amount of sample. Upon complete dissolution of the sample, it was transferred to an NaCl solution cell of .1mm pathlength (the concentration of the sample could be determined from its extinction coefficient; ϵ of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ at 2065cm^{-1} was $1,250 \pm 200 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$, ϵ of $(\text{Cr}(\text{CO})_5)_2(\text{bipy})$ at 2065cm^{-1} was $1,200 \pm 200 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$). The sample was then transferred as quickly as possible to a Perkin-Elmer 983G spectrophotometr, where the ensuing spectral changes of the sample were recorded (time elapse of 2 minutes was the usual delay between making up the sample and the recording of the first spectrum). Wavenumbers were accurate to $\pm 3\text{cm}^{-1}$.

3.3.2.2 Uv/vis Spectral Studies

Uv/vis spectra were obtained using a Hewlett-Packard 8452A diode-array spectrophotometer fitted with a ChemStation data Station. Peak positions are accurate to ± 2 nm. To obtain an uv/vis spectrum, the $(\text{Cr}(\text{CO})_5)_2(\text{L})$ ($\text{L} = \text{dmbipy}$ or bipy) or $\text{Cr}(\text{CO})_5(\text{trpy})$ compound was placed in the sample cuvette (10 mm path length). The solvent was then placed in a bulb attached to the cuvette, degassed by three freeze-pump-thaw cycles before being transferred in vacuo to the cuvette. The initial spectrum was obtained as soon as the solid had dissolved, usually within one minute of adding the solvent. Each spectrum, which took 0.1 s to acquire, was measured five times. This allowed the absorbance to be determined to ± 0.0001 absorbance units. Kinetic parameters were calculated using Hewlett-Packard kinetics software, which utilises a curve fitting routine for first order kinetics. The observed rate data were fitted to the following expression

$$A = A_1 + A_2 e^{-kt}$$

where A is the absorbance at time t , A_1 and A_2 are constants related to the initial and final absorbances at the monitoring wavelengths, and k is the observed first order rate constant (k_{obs}).

3.3.3 Flash Photolysis of $\text{Cr}(\text{CO})_6$ solutions containing diimine ligands.

Samples for flash photolysis were made up so that the absorbance of the sample at wavelength of excitation (355 nm) was between 1.0 to 1.6 (A.U.). Samples were degassed by three freeze-pump-thaw cycles, followed by a liquid pumping phase, and then placed under an atmosphere

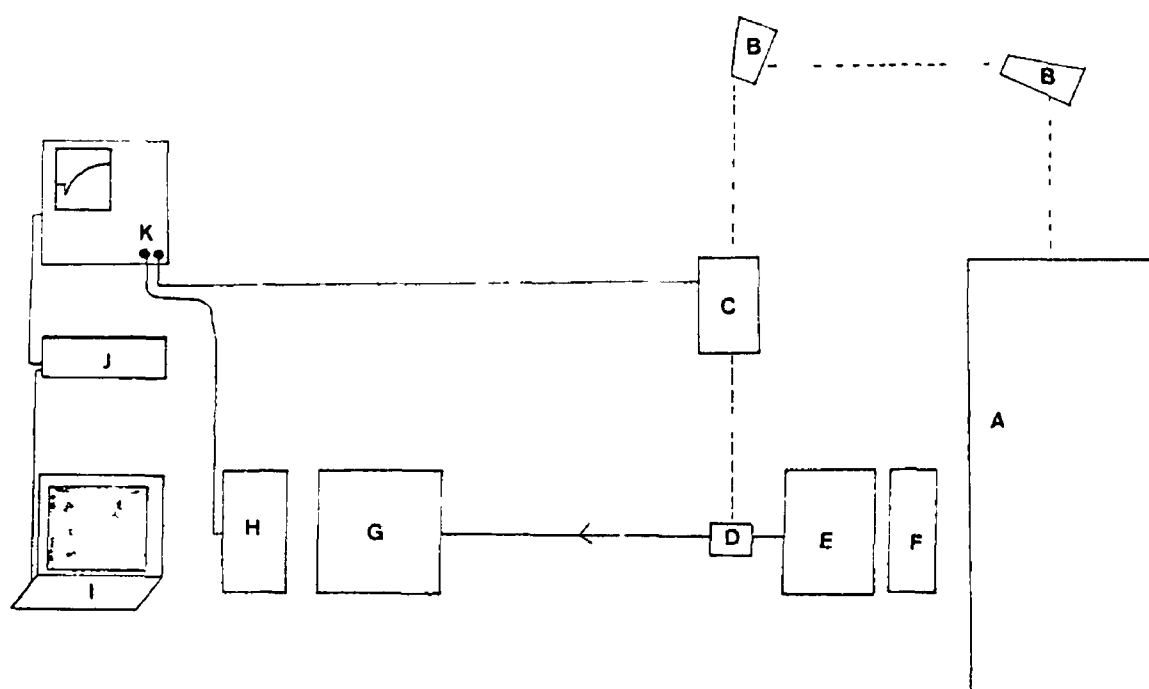
of carbon monoxide. The uv/vis absorbance value of the samples at the laser wavelength, before, during and after the experiments, showed decomposition of the sample to be minimal. Spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer.

A schematic diagram of the flash photolysis instrumentation is given in Figure 3.3.3.1. The excitation source is a Q-switched Nd-YAG (neodymium doped yttrium aluminium garnet) laser, which operates at 1064nm but can be frequency doubled or tripled to generate a second third or fourth harmonic frequency at 532, 355 and 266nm respectively. The power of the pulse can be varied by applying different voltages across the amplifier flash tube (the power at 355nm can vary between 20mj to ca. 60mj. The pulse time varies from 5 to 10 ns.

The circular laser pulse (ca. 4mm in diameter) is directed via two Pellin-Broca prisms onto the sample cuvette. A power meter, placed between the second Pellin-Broca prism and the sample, can be used to trigger the oscilloscope and also to measure pulse to pulse variation (this was estimated to be +/- 5% at most in these experiments and no correction was made for power variations).

The monitoring light source was an air cooled 250 watt xenon arc lamp (Applied Photophysics 40804) used at right angles to the laser beam. A uv filter (cut-off at 380nm or at 345nm) was placed between the xenon arc lamp and the sample holder to prevent photolysis of the sample by the monitoring beam. The lamp output is focussed on the front surface of the cell and the emerging beam focussed via a circular lens onto the slit of a f/3.4 monochromator (Applied Photophysics). The light detector was a Hamamatsu 5 stage photomultiplier which was operated at 850 volts. The signal output was connected via a variable load resistor to the transient analyser.

Figure 3.3.3.1: D.C.U. Laser flash photolysis system.



A	laser	F	power supply	K	oscilloscope
B	prism	G	monochromator		
C	power meter	H	photomultiplier		
D	sample	I	computer		
E	xenon arc lamp	J	IEEE		

The digital transient analyser was a Philips PM3311 oscilloscope. This oscilloscope works on a CCP principle with a sampling speed of 125MHz (maximum of 8ns per sample point in a single shot). The apparatus had an IEC/IEEE computer interface and is via this interface coupled and partially controlled by a BBC microcomputer (master series). Transient data are obtained and analysed as outlined in section 2.3.2.

3.3.3 Synthesis of $(\text{Cr}(\text{CO})_5)_x(\text{L})$ Complexes ($x = 1$ or 2 ; $\text{L} = \text{bipy}$, dmbipy , or trpy)

3.3.3.1 Preparation of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

$(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was prepared by treating the solid $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ (0.18gm; $0.6 \times 10^{-3}\text{M}$) with a solution containing 0.22gm ($1.2 \times 10^{-3}\text{M}$) of dmbipy in 10cm^3 of pentane. The reaction was carried out under a dry nitrogen atmosphere at ambient temperature. Upon dissolving the $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$, the colour of the solution changed from light yellow to orange, and the product precipitated from solution in high yield ($>85\%$). $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was collected by vacuum filtration and washed repeatedly with cold pentane to remove the excess dmbipy and cis-cyclooctene . Although $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was considerably stable at room temperature in air, it was stored at 253K under a N_2 atmosphere. Elemental analysis proved satisfactory for the proposed composition (calculated % (experimental%) C: 46.49 (46.19); H: 2.13 (2.17); N: 4.93 (4.64)).

3.3.3.2 Preparation of $\text{Cr(CO)}_5)_2(\text{bipy})$

$\text{Cr(CO)}_5)_2(\text{bipy})$ was prepared in an analogous way to $\text{Cr(CO)}_5)_2(\text{dmbipy})$. 0.6gm (2×10^{-3} mol) $\text{Cr(CO)}_5(\text{cis-cyclooctene})$ was added to a solution of 0.25gm (1.6×10^{-3} mol) bipy in deoxygenated pentane solution. The reaction was carried out at 273K as the bipy species proved to be a little less stable than the dmbipy analogue in air at room temperature. The yellow/orange $\text{Cr(CO)}_5)_2(\text{bipy})$ complex precipitated out of solution and was collected by vacuum filtration and placed immediately under an argon atmosphere. The sample was stored at 253K under argon, and under these conditions the sample showed little degradation over long timescales. Elemental analysis proved satisfactory for the proposed composition (calculated% (experimental %) C: 44.64 (45.84); H: 1.51 (1.52); 5.19 (5.52)).

3.3.3.3 Preparation of $\text{Cr(CO)}_4(\text{L})$ (L = bipy or dmbipy)

A solution containing 1.0gm ($4.5 \times 10^{-3}\text{M}$) of Cr(CO)_6 and 1.2gm ($6.5 \times 10^{-3}\text{M}$) of dmbipy (or 1gm of bipy) in spectroscopic grade n-hexane (200cm^3) was exposed to broad band radiation from a medium pressure mercury discharge lamp for 6 hours at room temperature. During the photolysis the solution was continuously purged with a stream of oxygen free nitrogen gas. The $\text{Cr(CO)}_4(\text{L})$ complex precipitated from solution and was collected by filtration after the photolysis was complete. The solid product was washed repeatedly with n-hexane to remove any unreacted L or Cr(CO)_6 . Any residual Cr(CO)_6 was removed by sublimation at room temperature. Elemental analysis of the products proved satisfactory for the dmbipy complex. A purer sample of $\text{Cr(CO)}_4(\text{bipy})$ has yet to be

prepared.: for $\text{Cr}(\text{CO})_4(\text{dmbipy})$ (calculated%
(experimental%) C: 55.17 (54.70); H: 3.45 (3.38); N: 8.05
(7.93)); for $\text{Cr}(\text{CO})_4(\text{bipy})$ (calculated% (experimental%)
C: 52.51 (48.28); H: 2.52 (2.50); N: 8.75 (8.15))

3.3.3.4 Preparation of $\text{Cr}(\text{CO})_5(\text{trpy})$

0.0152gm of trpy in 25cm³ of pentane was degassed by continuous purging with argon gas. 0.0142gm of $\text{Cr}(\text{CO})_5(\text{cis-cyclooctene})$ was then added to the degassed solution and the solution stirred under an argon atmosphere. Upon dissolution of the cyclooctene complex, orange-yellow crystals were seen to form and these crystals were isolated using an on-line filter to ensure maintenance of an argon atmosphere. No further purification steps were taken as the compound was highly air and thermally sensitive. The compound was stored under argon at 253K. Elemental analysis proved satisfactory for the proposed composition (calculated% (experimental%) C. 56.47 (56.02); H: 2.60 (2.59); N: 9.88 (9.47)).

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Section 4

STRUCTURAL AND SPECTROSCOPIC STUDIES OF
 $\text{Cr}(\text{CO})_5(2\text{-phpy})$, $\text{W}(\text{CO})_5(4\text{-phpy})$
AND $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

4.1 INTRODUCTION

4.1.1 Crystal Structures

Many chemists consider a crystal structure as definitive proof of the stereochemistry of a molecule. This may well be the greatest value of crystal structure determinations but it is not their only one. Structural determination can yield valuable insight into the chemical behaviour of a complex. For example 'strain' in a molecule which is evident from its crystal structure may explain the reactivity of the complex in solution.

Initial steps in the determination of a crystal structure consist of taking single-crystal photographs to find the unit cell dimensions and space group (as will be described in the experimental section). It is then necessary to determine the relative intensities of several thousand individual reflections, which is usually achieved by use of a computer controlled single-crystal diffractometer.

The presence of systematic absences in the reflection data can be used to determine the space group of the crystal. The type of symmetry present in the crystal determines the observed reflections. For example, suppose that a crystal contains a two-fold screw axis parallel to the z-axis, then an atom at x, y, z will be moved by the operation of the screw to a related position $x', y', z + 1/2$. Thus every atom in the structure that has a co-ordinate z is paired with another atom at different x - and y - co-ordinates but at $z + 1/2$. Thus the structure factor for the hkl reflections will be

$$F_{hkl} = \sum_i f_i \{ \cos 2\pi(hx_i + ky_i + lz_i) + \cos 2\pi(hx'_i + ky'_i + l(z_i + \frac{1}{2})) \}$$

For reflections of the type 00l this becomes

$$\begin{aligned}
 F_{00l} &= \sum_i f_i \{ \cos 2\pi l z_i + \cos 2\pi l (z_i + \frac{1}{2}) \} \\
 &= 2 \sum_i f_i \cos 2\pi l z_i \text{ for } l \text{ even} \\
 &\text{and zero for } l \text{ odd}
 \end{aligned}$$

The effects of glide and mirror planes are similar.

One then has to find an approximation to the structure. This usually involves consideration of the chemistry, the number of atoms of each element in the unit cell, and the way these can be fitted into a structure consistent with the space group. Physical properties, model building and analogies with known structures may help, as also may considerations of the magnitude of some of the largest structure factors. A trial structure is eventually formatted which assigns co-ordinates to each atom in the unit cell and so enables one to compute the structure factors for all the thousand or more reflections. The calculated structure factors (F_{calc}) are then compared with the observed ones (F_{obs}) by calculating a 'residual' (or discrepancy factor) such as

$$R = \frac{\sum_{hkl} ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum_{hkl} |F_{\text{obs}}|}$$

where the summations are taken over all reflections hkl. The agreement does not have to be very good at this stage. If R is less than about 0.4 it is probably sufficiently good to permit the structure to be refined. This involves very extensive computations to find changes in the atomic co-ordinates that minimise the discrepancies between the values of (F_{calc}) and (F_{obs}) and so reduce the value of R. Eventually it proves impractical to reduce R any further, which usually happens in the range 0.03 to 0.06

At this stage the atomic positions will probably be correct to within a few thousands of an Å. If the attempted refinement fails to reduce R substantially it is an indication that the trial structure was wrong and the initial moderate agreement between (F_{calc}) and (F_{obs}) was fortuitous.

An X-ray diffraction study, not only will confirm the number and types of atoms present in a molecule but will detail the orientation of each atom (or sets of atoms) relative to the other atoms in the molecule. Such details are of obvious importance in understanding the reactivity of the complex.

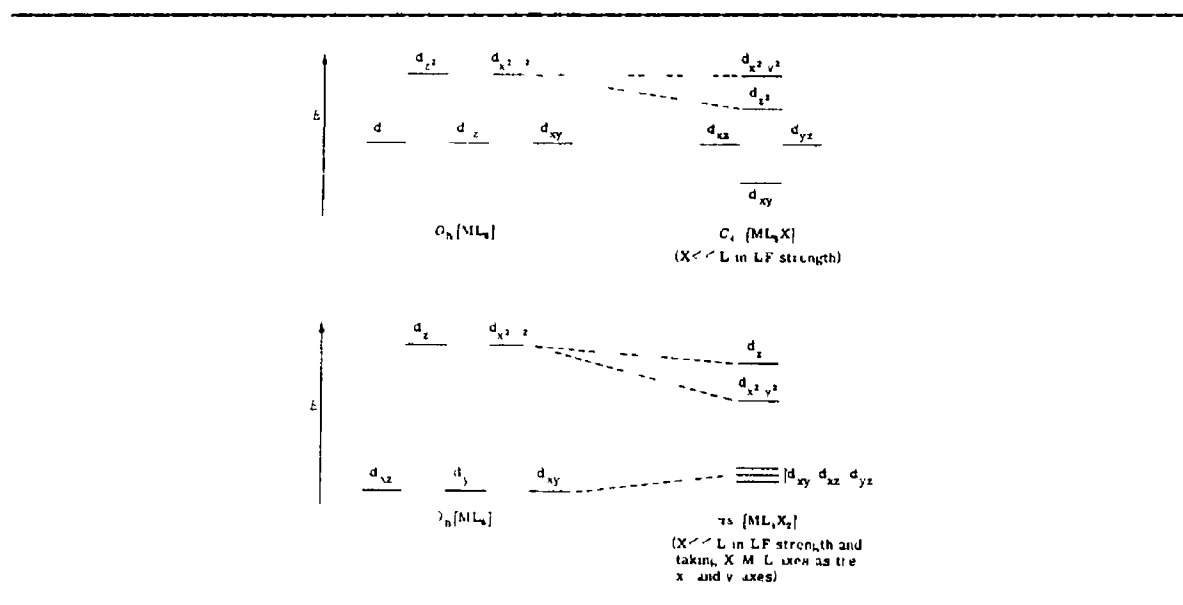
4.1.2 Uv/vis Spectra of $M(CO)_5(L)$ complexes

In section 1 it was shown how the symmetry of the carbonyl ligands affected the metallic orbitals of $M(CO)_6$ ($M = Mo, Cr, \text{ or } W$). The perturbation of the $M(CO)_6$ orbitals on replacing one of the carbonyl ligands allows the determination of the effect of varying ligands on the spectra of metal carbonyl complexes. This is because different ligands affect the energy levels within the molecule to varying degrees. The resulting spectra (which are after all only a reflection of the energy levels within the molecule) can therefore yield valuable information on the energy levels within the molecule. The magnitude of the extinction coefficient of transitions together with the position of these transitions can be used to determine the degree of overlap of the ligand orbitals with those of the metal (i.e. the orientation of ligand orbitals with respect to the metal).

Matrix isolation techniques have allowed the study of the (photogenerated) co-ordinatively unsaturated $M(CO)_5$ species by absorption spectroscopy. Vibrational spectra of

photogenerated $M(CO)_5$ in low-temperature matrices show it to have square pyramidal (C_{4v} structure).^{1,2} The removal of a carbonyl ligand from $M(CO)_6$ to generate the C_{4v} species should affect the d-orbital diagram as shown in Figure 4.1.2.1. The octahedral e_g orbitals will split such that the d_{z^2} orbital will have a lower energy than the $d_{x^2-y^2}$ orbital.

Figure 4.1.2.1: Orbital diagram showing the splitting of d-orbitals in an octahedral field



The lowest energy spectral feature of $M(CO)_5$ has been assigned as the $1A_1(e^4b_2^2) \rightarrow$

$1E(e^3b_2^2a_1^1)$ LF absorption,³ and the polarisation of the band is consistent with the interpretation.⁴ The electronic absorption spectrum of matrix isolated $M(CO)_5$ is very sensitive to the matrix, which correlates with the varying abilities of different matrices to 'split' the d orbitals of the metal. The lowest energy absorption band for $M(CO)_5$ is significantly red-shifted when compared to $M(CO)_6$, as expected from Figure 4.1 2.1.

Absorption spectra for $M(CO)_5(L)$ ($L \ll CO$ in LF strength) have been assigned in the low energy region.⁵⁻⁹ If L is lower in the spectrochemical series than CO, then the d

orbitals will be split in an analogous way to $M(CO)_5$. The principal antibonding M-L interaction will be localised along the z-axis. If L has low-lying π^* orbitals, MLCT may be the lowest energy transition in $M(CO)_5(L)$. Variation in the ligand L, results in variation in the CT band position. The more electron-releasing substituents give a higher energy CT absorption. MLCT bands are very solvent sensitive; more polar or polarisable solvents give blue-shifted CT band maxima, while LF bands are little affected. Consequently, when LF and MLCT bands are overlapping, it is possible to resolve them by varying the solvent.¹⁰

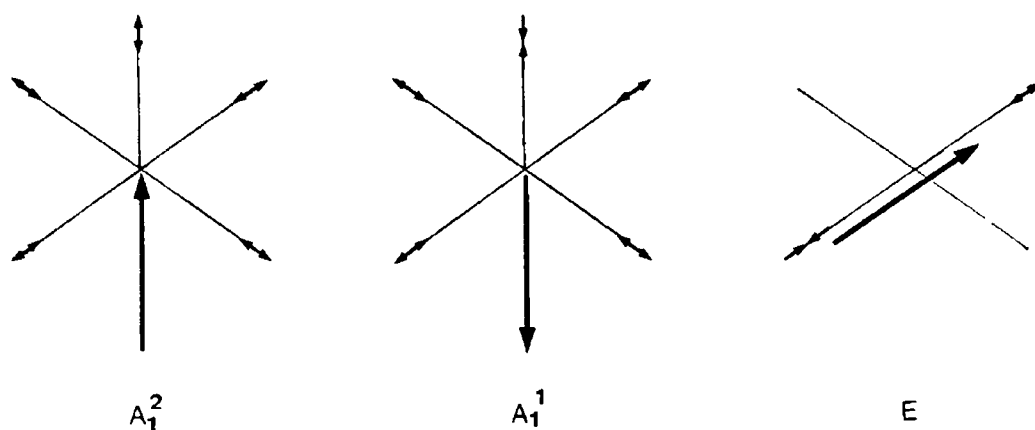
Complexes having ligands with low-lying excited states often exhibit intraligand (IL) transitions.¹¹ An example of such is the $\pi-\pi^*$ transition of pyridyl (and diimine), ligands. The ability of $M(CO)_5$ to interact with π orbitals of a ligand can be reflected in the position of this band. The presence or absence of such interactions can indicate the orientation of the ligand relative to the $M(CO)_5$ fragment. Electronic absorption spectra can not only tell one about the energy levels in the molecule but they can also indicate the type and relative strength of bonds within a molecule.

4.1.3 ir Spectra of $M(CO)_5(L)$ Complexes

Ir spectra of metal carbonyls have been a convenient source of information concerning the structure and bonding properties of these molecules. Section 2 has already indicated that ir spectroscopy is a useful tool in detecting bridging carbonyl groups. For neutral molecules, bridging molecules generally absorb in the range $1700-1860\text{cm}^{-1}$ while terminal ones generally absorb at higher frequencies ($1850-2125\text{cm}^{-1}$)

It is often possible to infer the symmetry of the arrangement of the carbonyl groups in a molecule from the number of carbonyl stretching bands. The carbonyl ligands of a monosubstituted carbonyl $M(CO)_5(L)$ have local C_{4v} symmetry. Formal symmetry rules show that the vibrations may be classed as in Figure 4.1.3.1. Elementary arguments have allowed more useful predictions to be made. First, the E vibration corresponds to the T_{1u} vibration of the parent hexacarbonyl and should account for very roughly 4/5 of the total intensity of absorption. The two A_1 vibrations are made up from the stretching mode of the unique carbonyl group and the symmetrical breathing mode of the other four. If these A_1 motions did not couple together the former would be allowed, accounting for the remaining 1/5 of the total intensity, while the latter would be almost forbidden (it could still have a small intensity due to non-coplanarity of the radial carbonyl groups and to electronic migration along the four-fold axis accompanying the symmetrical stretch of the radial carbonyl groups). In fact the two A_1 modes interact and some of the intensity of the strongly allowed one must be transferred to the other.

Figure 4.1.3.1: Vibrations of a molecule having local C_{4v} symmetry.



In $M(CO)_5(L)$ complexes in which the presence of an asymmetric ligand distorts the local symmetry of the carbonyl ligands from C_{4v} the formally forbidden B_1 mode gains intensity. This is because the molecule now possesses C_s symmetry.

Section 2 has also shown how bond angles may be determined from relative intensities. To make full use of vibrational spectra, Raman as well as infrared data should be obtained and mathematical analysis should be conducted to obtain force constants. The main use of force constants is in seeking a quantitative understanding of bonding relationships.

In this section a number of crystal structures of metal pentacarbonyl complexes will be described. Constraints upon the orientations of the molecules in a crystal, imposed by the 'packing' considerations of the crystal, have been suggested to distort molecules from their preferred conformation in solution. This chapter will show, by comparison of the structural and spectroscopic properties (in solution) of the complexes $Cr(CO)_5(2\text{-phpy})$, $W(CO)_5(4\text{-phpy})$ and $(Cr(CO)_5(dmbipy))$ (2-phpy = 2-phenylpyridine, 4-phpy = 4-phenylpyridine), that this variation is minimal if present at all.

4.2 RESULTS AND DISCUSSION

4.2.1 Structure and Spectroscopic Properties of $\text{Cr}(\text{CO})_5(2\text{-phpy})$

4 2.1 1 The Crystal Structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$

The crystal structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ was determined as outlined in the experimental section. Crystals of suitable quality were grown from ethanol solution, containing an excess of the 2-phpy ligand and were stored under a nitrogen atmosphere. The crystals were only moderately stable in air and decomposed slightly during data collection. The experimental section outlines the methodology used to obtain structural information. A diagram of the structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ is presented in Figure 4.2.1 1. A summary of the relative bond lengths and angles is given in Table 4 2 1.1.

Table 4 2 1.1: Selected bond distances (Å) and angles (deg) in the molecule $\text{Cr}(\text{CO})_5(2\text{-phpy})$.

Bond distances (Å)

Cr-N	2.223 (9)	C(5)-C(6)	1.477 (16)
Cr-C(12)	1.928 (12)	C(6)-C(7)	1 409 (19)
Cr-C(13)	1.890 (12)	C(7)-C(8)	1.393 (24)
Cr-C(14)	1.811 (13)	C(8)-C(9)	1.383 (22)
Cr-C(15)	1.883 (14)	C(9)-C(10)	1 411 (20)
Cr-C(16)	1.906 (14)	C(10)- C(11)	1 369 (18)
N-C(1)	1.356 (15)	C(11)-C(6)	1.384 (16)
N-C(5)	1.351 (14)	C(12)-O(1)	1.110 (16)

C(1)-C(2)	1.393 (18)	C(13)-O(2)	1.146 (16)
C(2)-C(3)	1.406 (20)	C(14)-O(3)	1.155 (16)
C(3)-C(4)	1.387 (21)	C(15)-O(4)	1.142 (18)
C(4)-C(5)	1.391 (17)	C(16)-O(5)	1.127 (14)

Bond Angles (degrees)

C(5)-N-C(1)	117.3 (10)	Cr-C(13)-O(2)	172.8 (11)
Cr-N-C(1)	114.5 (7)	Cr-C(14)-O(3)	177.5 (12)
Cr-N-C(5)	128.0 (7)	Cr-C(15)-O(4)	170.2 (12)
C(2)-C(1)-N	124.6 (11)	Cr-C(16)-O(5)	178.0 (12)
C(3)-C(2)-C(1)	116.9 (12)	C(12)-Cr-N	96.8 (4)
C(4)-C(3)-C(2)	119.1 (13)	C(13)-Cr-N	93.5 (4)
C(5)-C(4)-C(3)	120.1 (12)	C(13)-Cr-C(12)	92.5 (5)
C(4)-C(5)-N	122.0 (10)	C(14)-Cr-N	177.8 (5)
C(6)-C(5)-N	121.0 (10)	C(14)-Cr-C(12)	82.9 (5)
C(6)-C(5)-C(4)	117.0 (10)	C(14)-Cr-C(13)	88.7 (6)
C(7)-C(6)-C(5)	118.6 (31)	C(15)-Cr-N	94.3 (5)
C(11)-C(6)-C(5)	121.2 (10)	C(15)-Cr-C(12)	168.8 (5)
C(11)-C(6)-C(7)	121.1 (31)	C(15)-Cr-C(13)	86.1 (5)
C(8)-C(7)-C(6)	119.0 (53)	C(15)-Cr-C(14)	85.9 (6)
C(9)-C(8)-C(7)	120.3 (33)	C(16)-Cr-N	89.0 (4)
C(10)-C(9)-C(8)	120.1 (14)	C(16)-Cr-C(12)	91.5 (5)
C(11)-C(10)-C(9)	119.6 (12)	C(16)-Cr-C(13)	174.9 (5)
C(10)-C(11)-C(6)	120.8 (11)	C(16)-Cr-C(14)	88.8 (6)
Cr-C(12)-O(1)	170.1 (11)	C(16)-Cr-C(15)	89.4 (6)

Figure 4.2.1.1: X-ray crystal structure of
 $\text{Cr}(\text{CO})_5(2\text{-phpy})$

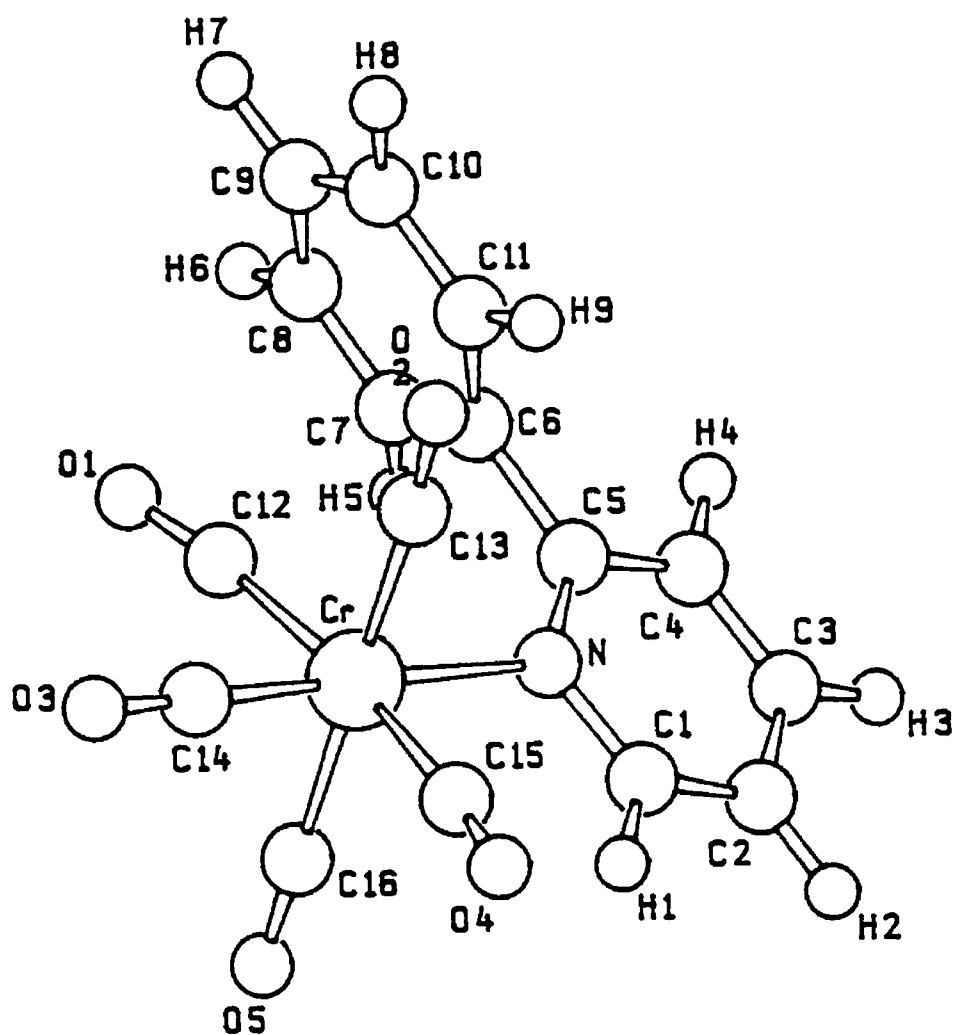
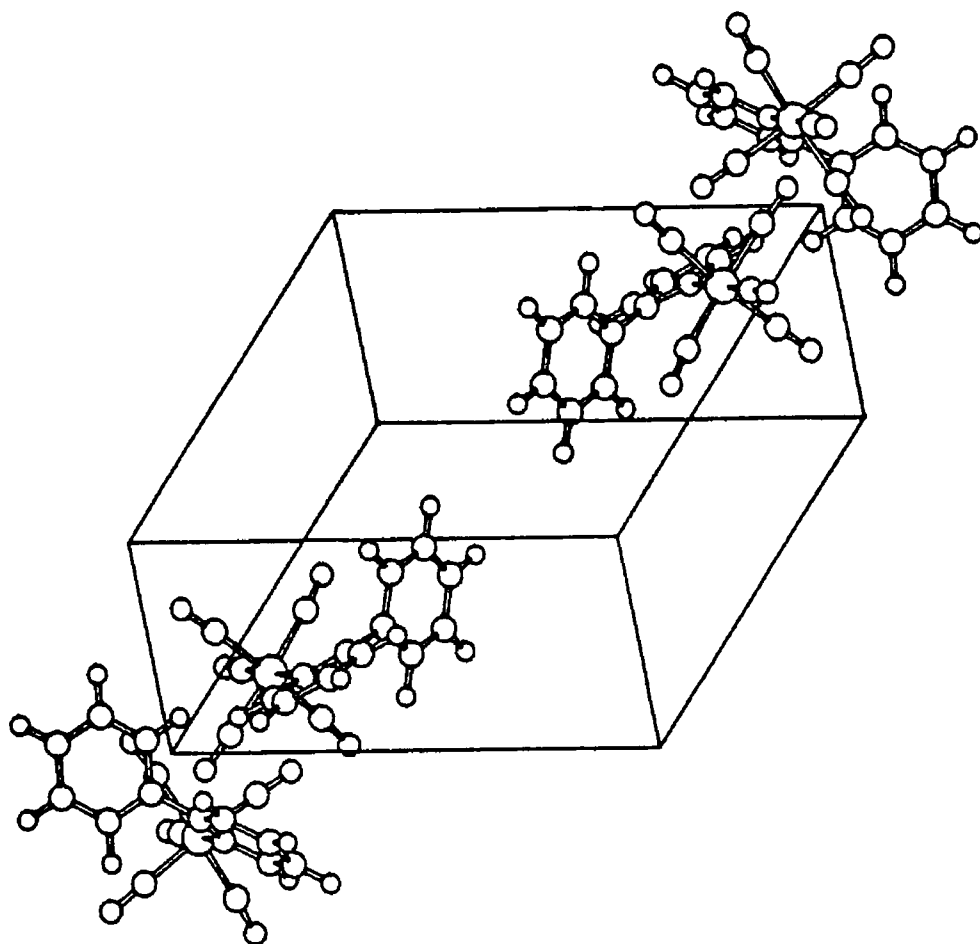


Figure 4 2.1.2: X-ray crystal structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ showing the unit cell.



The chromium atom is co-ordinated to five carbonyl ligands and a 2-phpy ligand in a distorted octahedral configuration. The Cr-C bonds are typically 1.90 (5) Å in length with the axial carbon being slightly shorter. The Cr-C bond length in Cr(CO)₆ was determined as 1.91 Å.¹² 2-phpy is a better σ donor but weaker

π -acceptor ligand than CO. Thus the increased electron density on the metal is donated to the carbonyl antibonding acceptor orbitals which lowers the C-CO bond order. The shorter Cr-C_{eq} bonds (C_{eq} indicates an equatorial carbon) relative to the C_{ax} bond (C_{ax} indicates an axial) may be a reflection of the increased σ donor ability of 2-phpy relative to CO.

The Cr-N bond of 2.176 Å is typical of Cr bonded to an amine. If there was backbonding between the metal atom and the π^* orbital of the pyridyl ring, there would be shortening of the Cr-N bond. There is no evidence for this in the molecule. The most interesting feature about the chromium atom is the value of the C_{eq}-Cr-C(14) bonds (C_{eq} are the equatorial carbons C(12), C(13), C(15), and C(16)). These angles are generally less than 90° while the C_{eq}-Cr-N angles are greater than 90°. Thus the presence of the 2-phpy ligand distorts the equatorial carbonyl ligands from pseudo C_{4v} symmetry, causing them to 'bend' away from the ligand. The C(14)-Cr-N angle is 177.5° indicating that the overall symmetry of the carbonyl ligands is retained to a large extent (if it were not, this angle would deviate greatly from 180°).

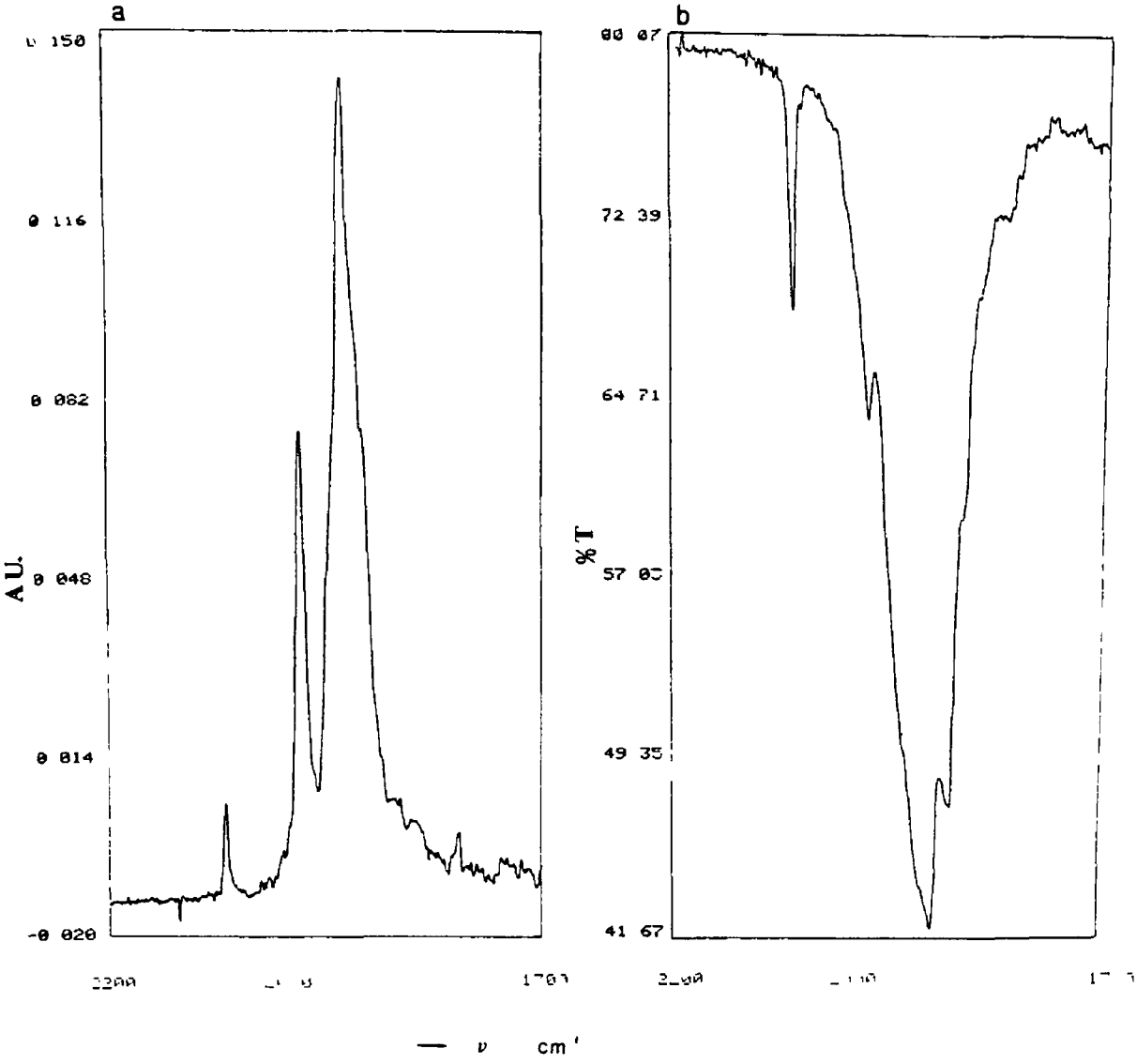
In the pyridyl ring, the C-C (1.394 Å) and C-N (1.353 Å) bond lengths are typical of pyridine complexes.¹³ The bond angles are only slightly distorted from the ideal hexagon values, particularly about the N atom. This could be an effect of the phenyl ring co-ordinated to C(5) distorting the symmetry about this atom. The C-C bond lengths of the phenyl ring vary considerably while the angles are all ca. 120°. The

variation in bond lengths may be because of the bonding of C(6)-C(5). However the two rings are found to be twisted by 110° relative to each other, preventing the interaction of the two systems. There are two possible explanations for this 'twisting'. It may be because of increased steric interactions between the phenyl and equatorial carbonyl ligands when the phenyl and pyridyl rings are coplanar. This 'twisting' may be a consequence of packing arrangements in the crystal. On studying the spectroscopic properties of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in solution it was thought likely that the former explanation is valid.

4.2.1.2 The ir Spectrum of $\text{Cr}(\text{CO})_5(2\text{-phpy})$

The $\text{Cr}(\text{CO})_5(2\text{-phpy})$ molecule was shown by x-ray crystallography to be of distorted square-planar geometry. Molecules of pseudo C_{4v} symmetry, as has been previously stated in Sections 2 and 3 are expected to have three ir-active transitions, the A_1 , E_1 and A_2 modes. Figure 4.2.1.2 gives the ir spectrum of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in nitrogen purged toluene solution and in a KBr disc. The bands at $2066(\text{w})$, $1930(\text{s})$ and $1912(\text{m,sh})\text{cm}^{-1}$ (in Figure 4.2.1.2(a)) can be assigned to these modes respectively. The band at ca 1980cm^{-1} is thought due to the formally forbidden B_1 mode, which has gained in intensity because the local C_{4v} symmetry of the carbonyl ligands has been perturbed by the 2-phpy ligand. Thus the perturbation of the carbonyl ligands which was evident from the X-ray crystal structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ manifests itself in the ir solution spectrum of the compound.

Figure 4.2.1.3: ir Spectrum of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in toluene solution (a) and in KBr disc (b).



4.2.1.3 The uv/vis Spectrum of $\text{Cr}(\text{CO})_5(2\text{-phpy})$

A great deal of studies have been carried out on the electronic absorption spectra of $\text{M}(\text{CO})_5(\text{L})$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$; $\text{L} = \text{pyridine (py)}, 4\text{-methylpyridine (4-Mepy)}, 4\text{-cyanopyridine (4-CNpy)}$ etc.). Table 4.2.1.2 shows the electronic absorption data for a series of $\text{Cr}(\text{CO})_5(\text{L})$ complexes in benzene solution. The assignation of the observed bands to the transitions shown were based on the behaviour of these bands in solvents of varying polarity and on varying the ligand L. MLCT bands are prone to blue shift as solvent polarity increases while LF bands are generally much less susceptible to change. This is because the solvent molecules can readily interact with the π^* orbitals (when populated) of the complexed ligand but they will not be able to interact directly with metal localised orbitals.

Table 4.2.1.2: Electronic absorption spectral data (nm) and assignments for $\text{Cr}(\text{CO})_5(\text{L})$ complexes in benzene solution.

Ligand (L)	$e4b22 \rightarrow e3b22b11$	$e4b22 \rightarrow e3b22a11$	MLCT
4-Mepyc	330(sh)	408	359(sh)
pyc	331(sh)	402	368(sh)
4-phpyc	345(sh)	396	a
4-CNpyc	350	b	436

a overlaps with $e4b22 \rightarrow e3b22a11$

b overlaps with MLCT transition

c Reference 14

Pyridine derivatives of metal carbonyls can be expected to possess low-energy M-py CT excited states as well as M-CO CT states due to the low oxidation state of the metal and accessibility of π^* orbitals. In addition electron withdrawing substituents on the pyridyl ring lower the energy of the MLCT band.

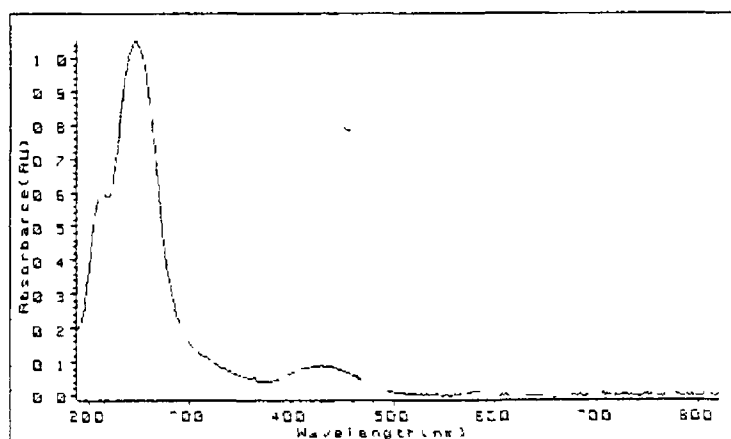
The uv/vis spectra of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ recorded in a number of different solvents are given in Figure 4.2.1.3. Table 4.2.1.3 summarises the spectroscopic data. Absorption spectra for $\text{M}(\text{CO})_5(\text{L})$ ($\text{L} \ll \text{CO}$ in LF strength) have been assigned by a number of workers. The absorption band at ca. 420nm in all these spectra has been assigned to the $1\text{A}(\text{e}^4\text{b}_2^2) \rightarrow 1\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ transition. LF bands are generally solvent insensitive, but this band position does vary with solvent. This could be due to mixing of the MLCT and LF absorption bands, examples of which have been reported by Lees et al.¹⁴

Table 4.2.1.3. Electronic absorption spectral data for $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in various solvents at 293K.

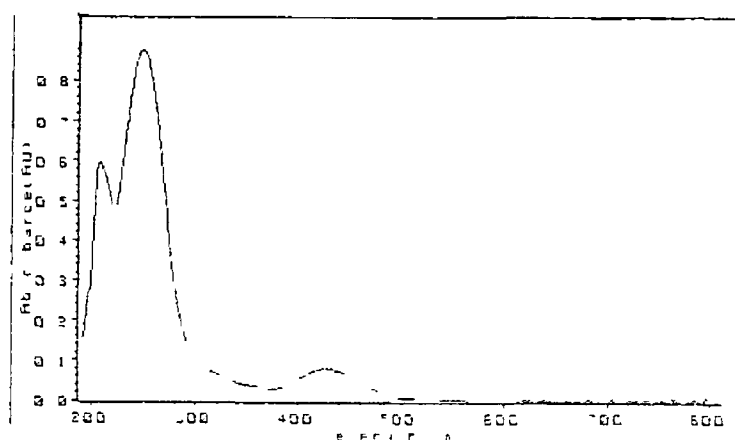
Solvent	Absorption bands (nm)
Methanol	430, 317(sh), 250,
Propan-2-ol	430, 310(sh), 250,
Hexane	415(sh), 310(sh), 247,
Pentane	415, 310(sh), 250,
Toluene	395, 320,
Ethanol	412, 317(sh), 250,

Figure 4.2.1.4: uv/vis Spectra of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in methanol(a), propan-2-ol(b), hexane(c)

a



b



c

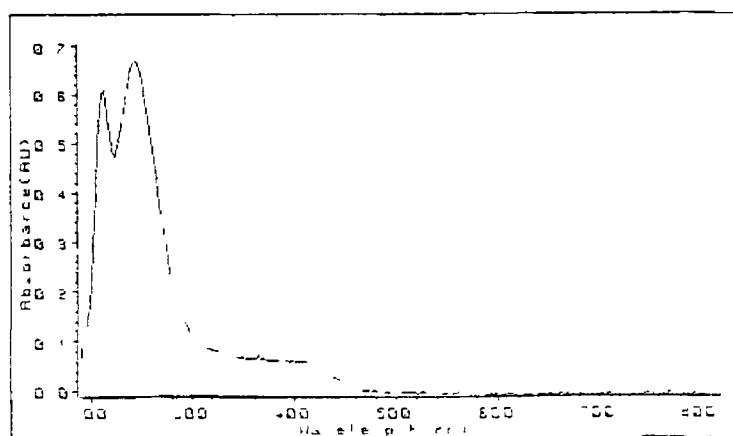
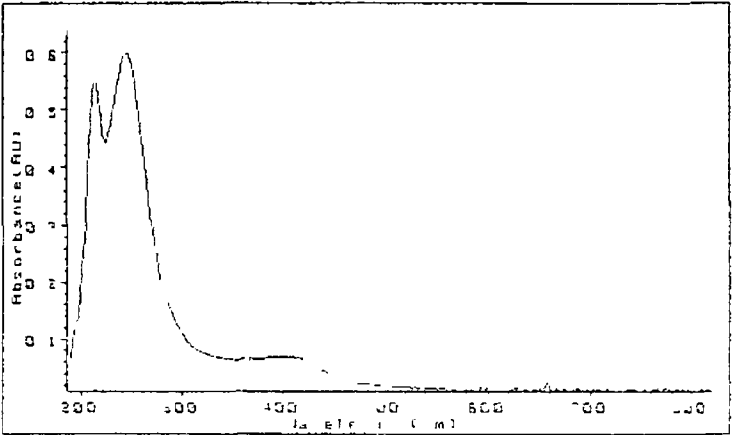


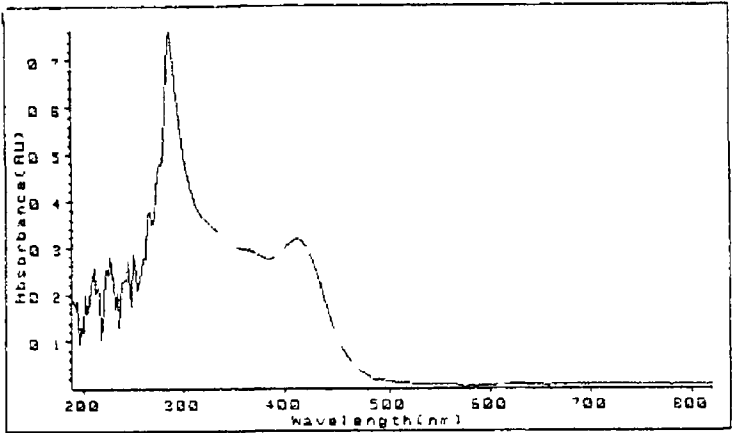
Figure 4.2.1.4:cont'd;

uv/vis Spectra of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ in
pentane(d), toluene(e) and ethanol(f).

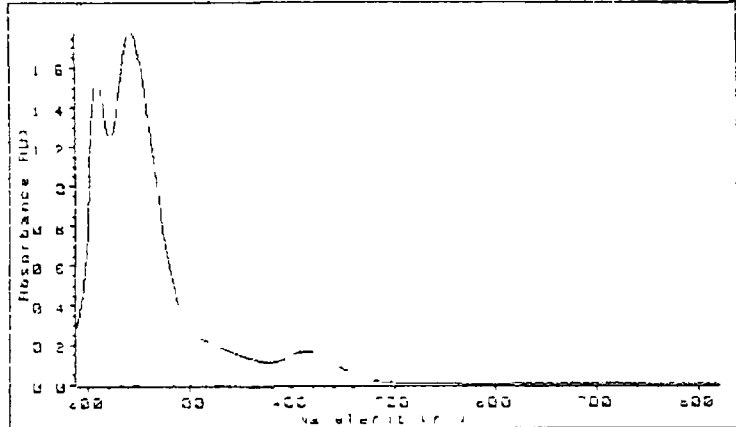
d



e



f



The overlapping bands in the uv/vis region are probably due to M-CO CT, M-(2-ppy) CT and LF bands. The bands in the above spectra at ca. 245nm are present also in the ligand and could therefore be due to an intraligand transition. This band does not vary with solvent and could therefore also be assigned to a LF transition. However the transition at ca. 275nm in the ligand is not present in the Cr(CO)₅(2-ppy) complex. This could be a $\pi - \pi^*$ transition; the energy of the π^* acceptor orbital would change upon complexing with the Cr(CO)₅ moiety thus changing the energy of the $\pi - \pi^*$ transition.

The spectral data for Cr(CO)₅(4-ppy) in varying solvents are given in Table 4.2.1 4. The absorption band at ca. 390nm varies greatly in profile and absorption maximum between solvents. This band is thought to be a mixture of MLCT and LF bands. However this band has considerably more MLCT character than the corresponding band in Cr(CO)₅(2-ppy). The band profile changes significantly on varying the solvent and this is consistent with a MLCT band. The pyridyl and phenyl rings of Cr(CO)₅(4-ppy) are coplanar(see crystal structure of W(CO)₅(4ppy) and thus interaction of the two pyridyl rings via the π systems of the two rings may allow delocalization of electron density. Thus the energy of the π^* orbital is lowered resulting in a lowering of the energy of the MLCT transition. The orientation of the pyridyl and phenyl rings in Cr(CO)₅(2-ppy) does not allow delocalization of the π^* electron density

The bands at 250nm are not solvent sensitive and the position of this band is at slightly lower energies than in the corresponding 2-ppy complex. If this band is as a result of a LF transition then, this would be an indication that 4-ppy was a more electron withdrawing molecule than 2-ppy. However as in the analogous Cr(CO)₅(2-ppy) this band is also present in the spectrum of 4-ppy alone.

4.2.2. The Structural and Spectroscopic Properties of $\text{W(CO)}_5(4\text{-phpy})$

4.2.2.1 The Crystal Structure of $\text{W(CO)}_5(4\text{-phpy})$

The crystal structure of $\text{Cr(CO)}_5(2\text{-phpy})$ had indicated that the presence of an asymmetric ligand on a Cr(CO)_5 moiety could distort the molecule from C_{4v} symmetry and this was reflected in the ir and uv spectra of the complex

We extended our study to a symmetric complex $\text{W(CO)}_5(4\text{-phpy})$ to see if similar effects were observed. Crystals of suitable quality were grown from nitrogen purged ethanol solution and the crystal structure determined as outlined in the experimental section. The crystals were air stable and showed no decomposition over the time scale of the data collection. Figure 4.2.2.1 shows this crystal structure and Table 4 2.2.1 gives the corresponding bond lengths and angles. Note that data for only half the molecule is given in this table. This is because the rest of the molecule is generated from this data by consideration of a mirror plane through C(1), C(4), C(5), N(8), W and C(9), and a rotation about this axes through 90° and 270° generated the remaining two Ceq. The crystallographic programs used to generate the crystal structure only determined the atoms given in the Table and the rest were generated from consideration of the symmetry elements

Table 4.2.2.1: Selected bond distances^a (Å) and angles^a (deg) in the molecule (W(CO)₅)(4-ppy).

Bond distances (Å)

C(1)-H(1)	1.080 (0)	C(6)-C(7)	1.358 (13)
C(1)-C(2)	1.332 (14)	C(7)-H(7)	1.080 (0)
C(2)-H(2)	1.080 (0)	C(7)-N(8)	1.330 (10)
C(2)-C(3)	1.388 (14)	N(8)-W	2.273 (9)
C(3)-H(3)	1.080 (0)	C(9)-O(9)	1.150 (15)
C(3)-C(4)	1.363 (12)	C(9)-W	1.963 (13)
C(4)-C(5)	1.483 (14)	C(10)-O(10)	1.127 (7)
C(5)-C(6)	1.356 (10)	C(10)-W	2.043 (6)
C(6)-H(6)	1.080 (0)		

a The C-H bond lengths and X-C-H bond angles were calculated

Bond Angles (degrees)

C(2)-C(1)-H(1)	165.7 (8)	C(7)-C(6)-H(6)	119.7 (6)
H(2)-C(2)-C(1)	118.4 (8)	H(7)-C(7)-C(6)	118.4 (6)
C(3)-C(2)-C(1)	122.6 (13)	N(8)-C(7)-C(6)	124.1 (9)
C(3)-C(2)-H(2)	119.0 (8)	N(8)-C(7)-H(7)	117.6 (5)
H(3)-C(3)-C(2)	120.0 (8)	W-C(9)-O(9)	180.0 (0)
C(4)-C(3)-C(2)	121.3 (11)	W-C(10)-O(10)	176.5 (6)
C(4)-C(3)-H(3)	118.7 (6)	W-N(8)-C(7)	122.9 (5)
C(5)-C(4)-C(3)	122.2 (6)	C(10)-W-C(9)	88.5 (2)
C(6)-C(5)-C(4)	122.5 (6)	N(8)-W-C(9)	180.0 (0)
H(6)-C(6)-C(5)	119.0 (6)	N(8)-W-C(10)	91.5 (2)
C(7)-C(6)-C(5)	121.3 (9)		

The R value for this structure was 0.035 and there were no significant peaks in the difference map. The average values of bond lengths of the ring C-C bonds (1.359Å) and bond angles (122°) are well within the ranges expected for this type of bond. The same can be said for the C-O bonds (average length = 1.139Å, angle at C 179°), the C(4)-C(5) bond (1.483Å) and the C-N bond (1.330Å). The W-C bonds are almost identical to those of W-C in W(CO)₆ (2.059Å).¹² This is possibly as a result of the increased π -acceptor ability of the 4-phpy ligand due to its ability to delocalise electron density throughout both ring systems.

The W-C_{eq} bonds are longer than the W-C_{ax} bond and this is likely a reflection of the greater sigma donor capacity of the 4-phpy ligand compared to the carbonyl ligands. However there is some distortion from ideal C_{4v} symmetry. The four equatorial carbons are distorted to a slight extent and this is reflected in the N-W-C bond angles (91.5°) and the W-C-O bond angles (176.5°), but this distortion is minimal compared to that observed in Cr(CO)₅(2-phpy). Considering the position of the phenyl rings relative to the equatorial carbons in the two compounds these differences are not surprising. Overall therefore this molecule is highly symmetrical and a study of the spectroscopic features of this complex should indicate this symmetry.

4.2.2.2 The IR and UV/VIS Spectra of W(CO)₅(4-phpy)

The IR carbonyl stretching frequencies of W(CO)₅(4-phpy) are given in Table 4.2.2.1 together with those of a number of similar W(CO)₅(L) complexes (L = pyrazine (pyz), 4,4'-bipy, bpe). The three moderate/strong band maxima are assigned to A₁¹, E and A₁² modes and are characteristic of C_{4v} arrangement of the carbonyl ligands.

at the metal centre. However even these symmetrical ligands cause distortion about this centre indicated by the presence of a very weak B₁ mode.

Figure 4.2.2.3: ir Spectrum of $W(CO)_5(4\text{-phpy})$ in toluene solution.

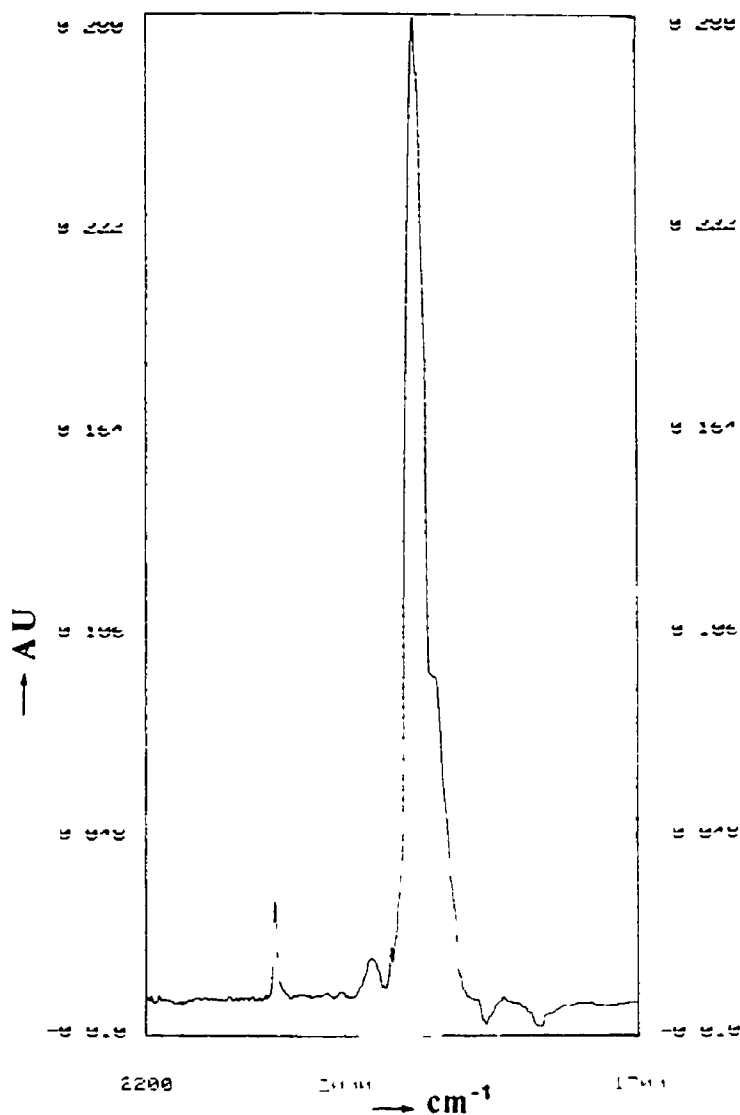


Table 4.2.2.2: Infrared carbonyl stretching frequencies and assignments for $W(CO)_5(L)$ complexes

Ligand	A_{11}	$\nu_{CO}, \text{ cm}^{-1}$		
		B_1	E	A_{12}
4-phpya	2067	1980	1950	1900
pyrazineb	2068	1985	1933	1880
4-4'-bipyb	2070	1988	1923	1885
bpeb	2070	1975	1925	1880

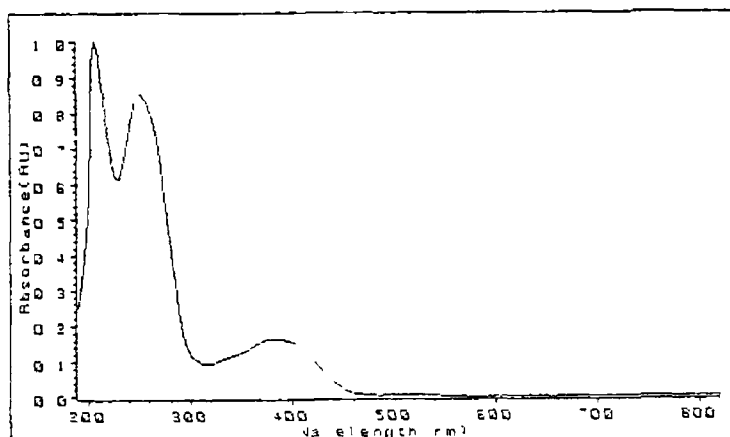
a in toluene

b in nujol mull (reference 15).

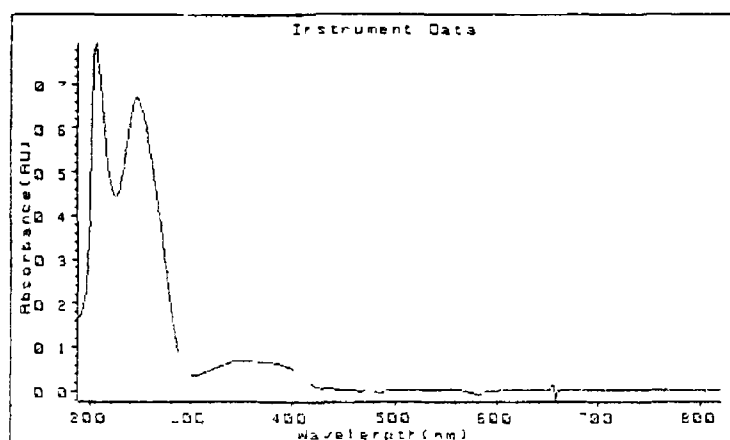
The uv/vis spectra of $W(CO)_5(4\text{-phpy})$ in a variety of solvents are given in Figure 4.2.2.3 (the spectral band positions are summarised in Table 4.2.2.3) The spectral bands vary considerably in profile and wavelength maximum between the different solvents. The absorption band at ca 250nm is invariant and is possibly because of an intraligand transition (this band is present in $Cr(CO)_5(2\text{-phpy})$ and $Cr(CO)_5(4\text{-phpy})$ also). The assignment of the remaining bands was based on comparison of these bands to those already characterised for similar compounds and on their behaviour in different solvents.

Figure 4.2.2.4: uv/vis Spectra of $W(CO)_5(4\text{-phpy})$ in methanol(a), propan-2-ol(b), hexane(c)

a



b



c

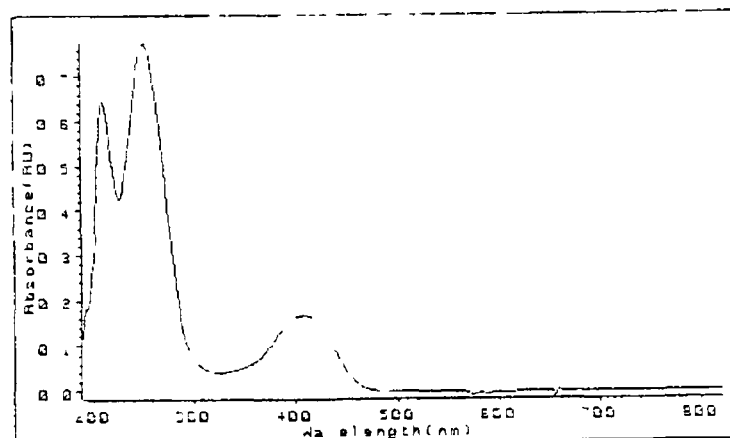
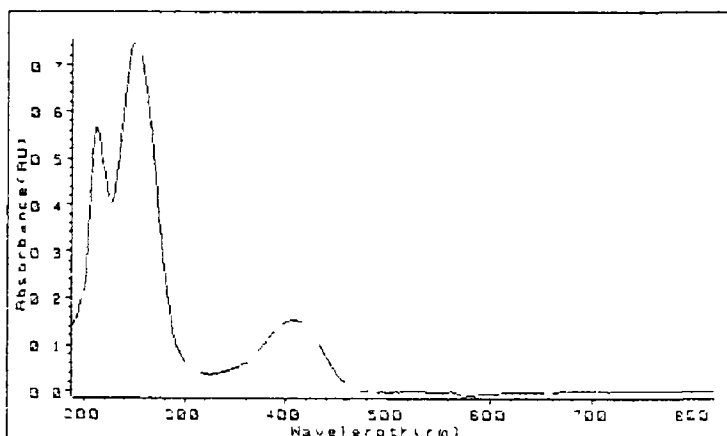


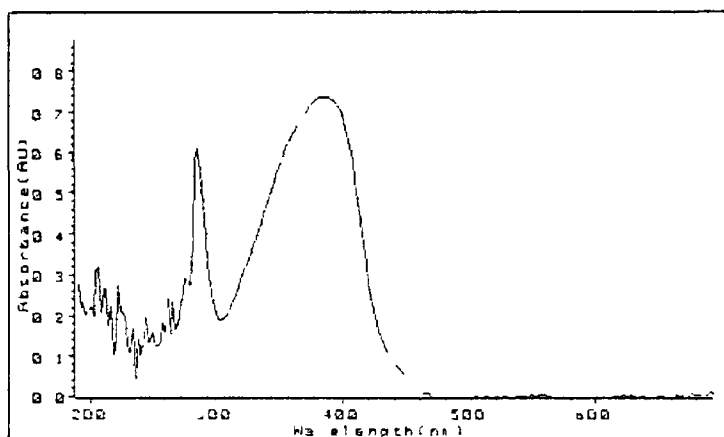
Figure 4.2.2.4:cont'd;

uv/vis Spectra of $W(CO)_5(4\text{-phpy})$ in
pentane(d), toluene(e) and ethanol(f)

d



e



f

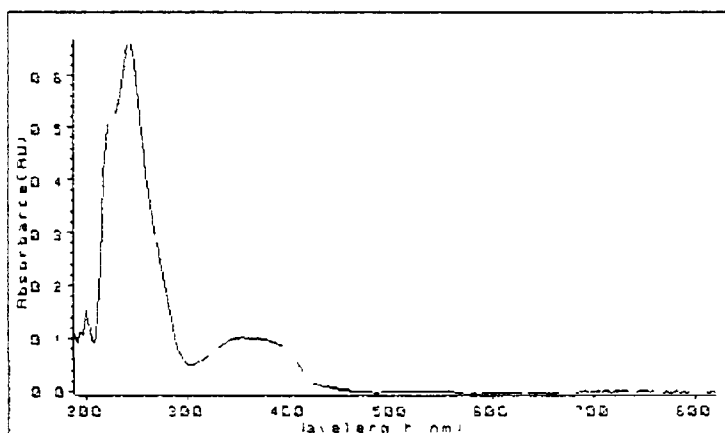


Table 4.2.2.3: Electronic absorption spectral data for
W(CO)₅(4-phpy) in various solvents at
293K.

Solvent	Absorption bands (nm)
Methanol	380(sh), 345, 250,
Propan-2-ol	375(sh), 350, 250,
Hexane	405, 360(sh), 250,
Pentane	405, 365(sh), 250,
Toluene	395, 375(sh),
Ethanol	380(sh), 350, 250,

The absorption maximum of the band at ca. 380nm varies with solvent and therefore can be assumed to have some MLCT character. However the $1A_1 \rightarrow 1E$ LF transition of W(CO)₅(pyr) has been determined to be at ca. 390nm (in benzene).¹⁶ The changing profile of this band at ca. 380nm could therefore be the result of overlapping absorption bands, one of which is solvent sensitive and one which is not. The formally spin-forbidden $1A_1 \rightarrow 3E$ LF transition occurs as a shoulder on the $1A_1 \rightarrow 1E$ absorption. In all the spectra shown the peak profiles at ca. 390nm are considerably 'distorted' compared to the chromium 2-phpy analogue. This may be a reflection that the MLCT band in W(CO)₅(4-phpy) is at longer wavelengths in the tungsten compound as a result of the efficient overlap

of the pyridyl and phenyl-ring systems interacting thus lowering the energy of the π^* orbital. The corresponding MLCT transition is likewise lowered in energy.

4.2.3. The Structural and Spectroscopic properties of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

4.2.3.1 The Crystal Structure of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

Section 3 of this thesis has dealt in detail in the chelation reactions of pentacarbonyl chromium compounds bonded to bridging and non-bridging multidentate ligands. The isolation of these complexes was surprising considering the reactivity of these complexes in solution. The crystal structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ had shown that the phenyl and pyridyl rings of the 2-phpy ligand were not coplanar in the solid phase although solution studies on the bipy ligand had shown that bipy exists normally in a S-trans configuration. The uv/vis and ir spectra of the bridging species have been discussed in Section 3 and they will be referred to again in this section. It will be shown that there is good correlation between the spectroscopic properties of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ in solution and the solid state structural properties

Table 4.2.1.1: Selected bond distances (Å) and angles
(deg) in the molecule
(Cr(CO)5)2(dmbipy).

Bond distances (Å)

Cr(1)-N(1)	2.322 (25)	C(5)-C(6)	1.512 (47)
Cr(1)-C(15)	1.984 (41)	C(6)-C(7)	1.530 (42)
Cr(1)-C(16)	1.822 (44)	C(7)-C(8)	1.366 (42)
Cr(1)-C(17)	1.753 (33)	C(7)-N(12)	1.377 (38)
Cr(1)-C(18)	1.720 (37)	C(8)-C(9)	1.371 (40)
Cr(1)-C(19)	1.790 (41)	C(9)-C(10)	1.371 (51)
Cr(2)-N(12)	2.171 (22)	C(9)-C(14)	1.582 (50)
Cr(2)-C(20)	1.904 (56)	C(10)-C(11)	1.427 (55)
Cr(2)-C(21)	1.869 (36)	C(11)-N(12)	1.455 (43)
Cr(2)-C(22)	1.886 (38)	C(15)-O(15)	1.100 (52)
Cr(2)-C(23)	1.780 (33)	C(16)-O(16)	1.175 (55)
Cr(2)-C(24)	1.805 (39)	C(17)-O(17)	1.309 (45)
N(1)-C(2)	1.415 (41)	C(18)-O(18)	1.237 (48)
N(1)-C(6)	1.276 (37)	C(19)-O(19)	1.246 (46)
C(2)-C(3)	1.376 (56)	C(20)-O(20)	1.150 (62)
C(3)-C(4)	1.472 (48)	C(21)-O(21)	1.108 (43)
C(4)-C(5)	1.257 (45)	C(22)-O(22)	1.104 (53)
C(4)-C(13)	1.500 (45)	C(23)-O(23)	1.228 (43)
		C(24)-O(24)	1.153 (45)

Bond angles

N(1)-Cr(1)-C(15)	94.2 (14)	C(2)-N(1)-C(6)	123.8 (26)
N(1)-Cr(1)-C(16)	92.5 (15)	N(1)-C(2)-C(3)	116.7 (31)
N(1)-Cr(1)-C(17)	100.3 (12)	C(2)-C(3)-C(4)	120.3 (33)
N(1)-Cr(1)-C(18)	89.5 (14)	C(3)-C(4)-C(5)	120.0 (30)
N(1)-Cr(1)-C(19)	176.2 (14)	C(3)-C(4)-C(13)	121.2 (27)
C(15)-Cr(1)-C(16)	91.5 (19)	C(5)-C(4)-C(13)	118.9 (29)
C(15)-Cr(1)-C(17)	164.6 (16)	C(4)-C(5)-C(6)	120.2 (31)
C(15)-Cr(1)-C(18)	91.5 (17)	N(1)-C(6)-C(5)	118.7 (26)
C(15)-Cr(1)-C(19)	82.1 (18)	N(1)-C(6)-C(7)	120.3 (26)
C(16)-Cr(1)-C(17)	82.6 (18)	C(5)-C(6)-C(7)	120.1 (26)
C(16)-Cr(1)-C(18)	176.3 (19)	C(6)-C(7)-C(8)	119.4 (29)
C(16)-Cr(1)-C(19)	87.6 (19)	C(6)-C(7)-N(12)	108.3 (26)
C(17)-Cr(1)-C(18)	93.9 (16)	C(8)-C(7)-N(12)	129.5 (30)
C(17)-Cr(1)-C(19)	83.5 (17)	C(7)-C(8)-C(9)	117.7 (29)
C(18)-Cr(1)-C(19)	90.6 (18)	C(8)-C(9)-C(10)	118.1 (30)
N(12)-Cr(2)-C(20)	88.5 (18)	C(8)-C(9)-C(14)	120.2 (29)
N(12)-Cr(2)-C(21)	90.0 (12)	C(10)-C(9)-C(14)	120.6 (31)
N(12)-Cr(2)-C(22)	85.7 (13)	C(9)-C(10)-C(11)	122.2 (36)
N(12)-Cr(2)-C(23)	97.9 (13)	C(10)-C(10)-N(12)	119.0 (32)
N(12)-Cr(2)-C(24)	178.3 (15)	Cr(2)-N(12)-C(7)	134.2 (20)
C(20)-Cr(2)-C(21)	82.3 (20)	Cr(2)-N(12)-C(11)	113.6 (19)
C(20)-Cr(2)-C(22)	98.4 (21)	C(7)-N(12)-C(11)	109.7 (25)
C(20)-Cr(2)-C(23)	163.6 (21)	Cr(1)-C(15)-O(15)	172.8 (38)
C(20)-Cr(2)-C(24)	89.9 (22)	Cr(1)-C(16)-O(16)	168.2 (39)
C(21)-Cr(2)-C(22)	175.7 (16)	Cr(1)-C(17)-O(17)	176.3 (28)
C(21)-Cr(2)-C(23)	82.6 (16)	Cr(1)-C(18)-O(18)	174.0 (32)
C(21)-Cr(2)-C(24)	89.2 (17)	Cr(1)-C(19)-O(19)	177.1 (33)
C(22)-Cr(2)-C(23)	97.2 (16)	Cr(2)-C(20)-O(20)	161.0 (46)
C(22)-Cr(2)-C(24)	95.0 (18)	Cr(2)-C(21)-O(21)	170.0 (31)
C(23)-Cr(2)-C(24)	83.5 (18)	Cr(2)-C(22)-O(22)	169.0 (35)
Cr(1)-N(1)-C(2)	108.6 (19)	Cr(2)-C(23)-O(23)	162.0 (30)
Cr(1)-N(1)-C(6)	127.5 (20)	Cr(2)-C(24)-O(24)	174.6 (36)

Figure 4.2.3.1: X-ray crystal structure of
(Cr(CO)₅)₂(dmbipy).

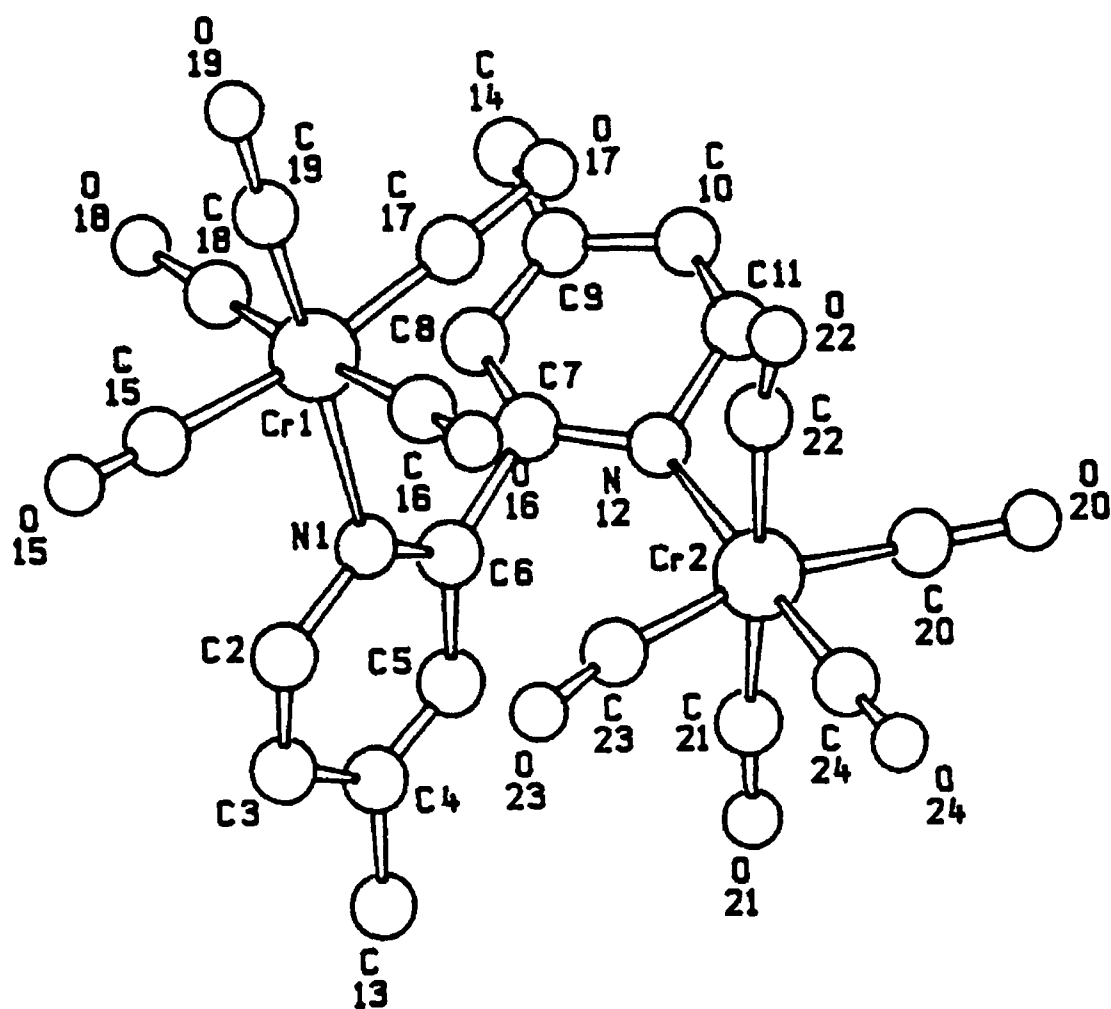


Figure 4.2.1.2: X-ray crystal structure of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ showing the unit cell.

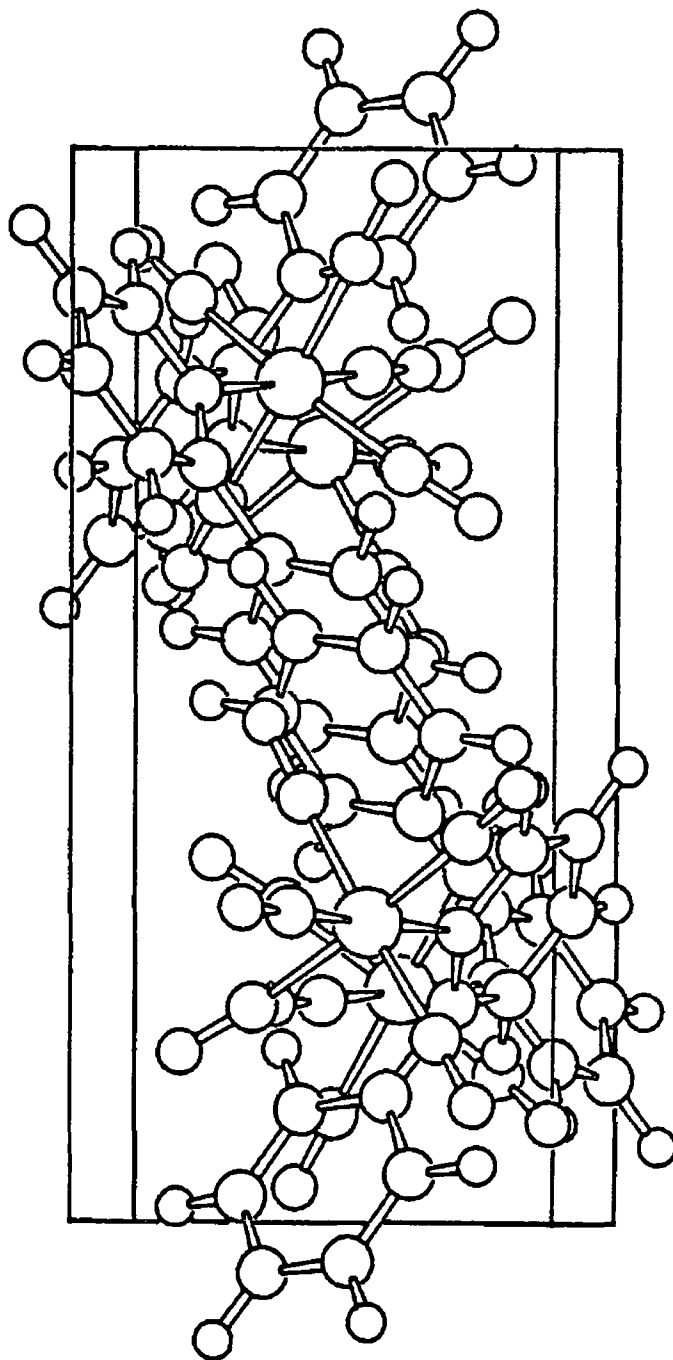
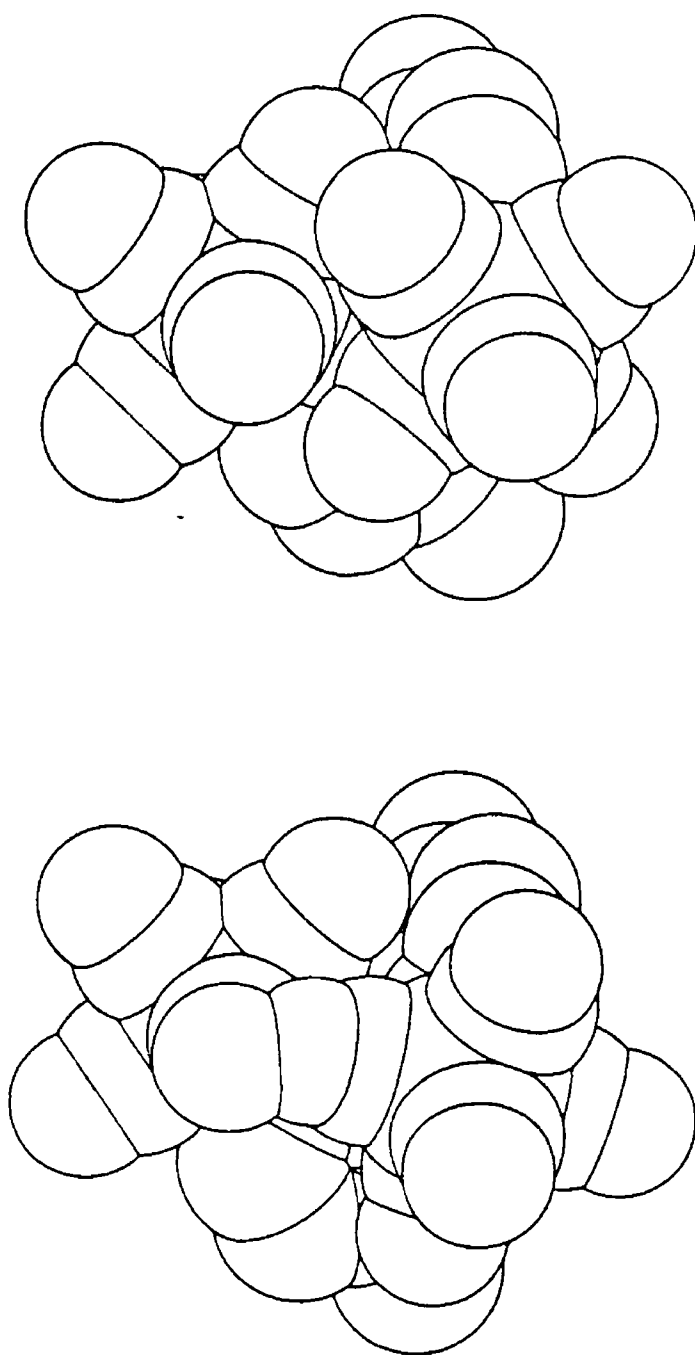


Figure 4.2.3.3: Space filling model of the crystal structure of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$, showing the effect of rotation about the Cr-N bond.



(Cr(CO)₅)₂(dmbipy) was obtained from the reaction of Cr(CO)₅(cis-cyclooctene) with dmbipy in argon purged pentane solution at room temperature. The reactivity of this complex had been outlined in Section 3 and only non-polar solvents could be used to grow crystals. Very small red-brown crystals of marginal quality for x-ray work were obtained from degassed toluene solution at -30°C. An X-ray structure determination and refinement to R = 0.10 confirmed the bipyridyl-bridged binuclear structure of the molecule (Figure 4.2.3.1). While the R value may not be satisfactory, a difference map showed no extraneous peaks and there was no reason to believe the structure was incorrect.

The bond lengths and angles of the molecule are given in Table 4.2.3.1. The mean values for Cr-N (2.25Å), C-O (1.18Å), C-N (1.3Å), ring C-C (1.38Å) and ligand bridged and terminal Me C-C (1.54Å) bond lengths are in good agreement with literature values.¹³ The Cr-C bonds (1.83Å) are considerably shorter than the Cr-C bonds in Cr(CO)₆.¹² This is probably a reflection of the decreased π -acceptor ability of dmbipy ligand relative to carbonyl ligands. Similarly mean values for the angles around the chromium atom (90° and 177°), for Cr-C-O (170°) and within the pyridyl rings (119°) are as expected. With regard to the orientations of Cr(1)-N(2) and Cr(2)-N(12) the longer C(1)-N(1) bond may be a reflection of steric strain within the molecule. This strain is reflected in the considerable distortion of bond angles about the co-ordinating nitrogen atoms e.g. Cr(2)-N(12)-C(7) was determined to be 134.2° while C(7)-N(2)-C(11) was found to be 109.7°.

As with Cr(CO)₅(2-pphy), the dmbipy ligand appears to distort the equatorial carbonyl ligands. This can be seen from the variation in Cr-C-O bond angles (less than 180°) and the C-Cr-N angles (generally greater than 90°). The most striking feature of the structure shown in Figure

4.2.3.1 is the mutually perpendicular orientation of the ligand pyridyl rings (the experimentally determined angle is 89°). Such a structure precludes efficient overlap of the two pyridyl π -systems.

4.2.3.2 Ir and uv/vis Spectra of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$

The ir and uv/vis spectra of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ have been discussed in Sections 3.2.1. and 3.2.1.3. There were two notable features of the ir spectrum (Figure 3.2.1.4) . These are;

(i) the enhanced intensity of the formally forbidden B₁ mode which indicated that the local symmetry at the metal centre was reduced from formal C_{4v};

(ii) the removal of the degeneracy of the E mode. This was not seen to occur in the spectrum of $\text{Cr}(\text{CO})_5(2\text{-phpy})$, also an asymmetric ligand, and was therefore thought to be a consequence of the dmbipy ligand acting as a bridge between $\text{Cr}(\text{CO})_5$ moieties. A molecular modelling programme (Schakel) showed that the Cr-N bond could not rotate freely because of the positions of the $\text{Cr}(\text{CO})_5$ moieties. Rotation must occur synchronously to avoid 'collisions' of the carbonyl groups (see Figure 3.2.1 5).

The determination of the crystal structure of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ has shown that there is considerable strain within the molecule which is reflected in the ir spectrum.

The uv/vis spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ was given in Figure 3.2.1.6. The band at 410nm was assigned to a LF transition with some MLCT character while those in the uv region were assigned to overlapping LF and MLCT transitions. If π conjugation between the pyridyl rings

could occur, one would expect the band at 410nm to vary from the analogous band in $\text{Cr(CO)}_5(\text{pyr})$ where only one Cr(CO)_5 moiety is present. Conjugation within the ligand would lower the energy of the π^* orbital. This was not found to be the case As was stated in section 3.2.1.3, the absence of a band at 290nm normally assigned to the $\pi - \pi^*$ transition in bipyridyl complexes, suggests that the energy of the dmbipy based π^* energy level in $(\text{Cr(CO)}_5)_2(\text{dmbipy})$ is higher than in either the free ligand or $\text{Cr(CO)}_4(\text{dmbipy})$. This is further evidence that the two pyridyl rings are not coplanar in solution.

4.3 EXPERIMENTAL

4.3.1 X-ray Data Collection

4.3.1.1 Apparatus

The Nicolet P3/R3 four circle diffractometer consisted of a stainless steel full circle and a base goniometer which incorporates the X-ray tube as an integral part. Each of the four axes was operated independently by a separate axis drive gear coupled to a non-contacting magnetic encoder and each has a full 360° range. 2θ ranges from -110° to 158° and ω from -72° to 72°. All potential collision points are protected by limit switches

The X-ray generator, located inside the main body of the diffractor module, supplied voltage and current to the X-ray tube filament. Both voltage and current are adjustable. A tube-cooling system using open-flow, filtered tap water is also included. The X-ray tube mount is an integral part of the base goniometer. Three dimensional alignment is easily accomplished by a set of worm gears that allow fine adjustment. The X-ray tube pivots horizontally about the focal spot for take-off angle changes. In addition, anode mounting ensures minimum alignment change due to temperature variations.

The monochromator contains a highly ordered graphite crystal with a dispersion of less than 0.6° and mounts directly on the tube shield without additional hardware. The detector unit is mounted on the 2θ arm of the goniometer and includes the photomultiplier tube, pre-amplifier, amplifier, detection crystal (a Tl-doped iodide scintillation counter) and pulse height analyser as a compact integrated unit.

4.3.1.2 Data Collection

The collection of data for the determination of a crystal structure occurs in five stages;

(a) Centring

This programme performs all the necessary functions for defining the reflection array, from preliminary set-up operations through refinement of angles for each reflection in the array. From co-ordinates on the rotation photograph, the centring programme searches for the reflections and refines the angles. The programme calculates 2θ for the reflection, assuming ω to be zero. After driving to these angles, it searches for the reflection by rotating ω at slow speed in 120° steps up to 360°, if necessary. A reflection is generally accepted if the intensity > 1000 counts/s.

The exact centring procedure used is defined by two major sets of parameters selected by the user, the first of which determines the method used to calculate the centre (half-height or centre of mass method). The second determines which axes to centre on and in what order.

(b) Autoindexing

Based on the set of refined angles from the centring programme, this programme produces a list of up to thirty possible axial vectors and the angles between these vectors. The user selects three solutions and identifies them by number as the a, b and c axes. These can be input into the programme which can index each reflection in the array and output a calculated cell volume. Left or right handedness is indicated by a negative or positive cell volume. Cell dimensions a, b and c in Å and the three angles in degrees are then calculated. Once the solutions

have been selected, axial photographs can be taken. These are used to obtain a quick survey of various regions of reciprocal space and to verify both axial lengths and crystal symmetry, calculated by the autoindexing routine.

(c) Axial Photographs

Three pieces of information can be obtained from axial photographs,

(i) Symmetry information: Autoindexing may indicate too high a symmetry. A partial rotation photograph about unique monoclinic axis should have symmetry about a central horizontal line. For orthorhombic crystals, there will be symmetry in all three rotation photographs.

(ii) Axial length: The distance between the layer lines on the photograph should correspond to axial length calculations.

(iii) Twinning: One or more spots lying off the layer line indicates twinning or presence of satellite crystals.

(d) Least Squares Orientation Matrix

From indices and refined angles, the programme calculates an orientation matrix, unit cell parameters and volume. Using the least squares orientation matrix, the programme also calculates two sets of angles for comparison with the observed value. The programme also calculates hkl values and angles from the orientation matrix for reflections in the array, especially for those reflections with hkl or angles unknown.

(e) Data Collection

This programme collects data automatically in either the bisecting mode (circle between the detector arm and the X-ray tube) or the parallel mode (detector arm between the circle and the X-ray tube). Data is always collected with a $2\theta:\theta$ scan with scanning at half the speed of 2θ . For a given hkl, data can be collected at one or more values. A profile of the peak is always measured. If the intensity is large, a coincidence correction is made from each step of the profile. Up to ten check reflections can be periodically measured.

Recentring extend the options available during data collection. It is triggered by check reflections intensities falling. Up to fifteen reflections in the reflection array will be centred automatically and a new least squares orientation matrix will be calculated.

4.3.1.3 Programmes Used in Solving the Crystal Structures

Two different programmes were used to determine the crystal structures of $\text{Cr}(\text{CO})_5\text{2(dmbipy)}$, $\text{Cr}(\text{CO})_5\text{2(phpy)}$ and $\text{W}(\text{CO})_5\text{4(phpy)}$. Multan 87¹⁶ was used to determine the positions of the atoms in the unit cell, and Shelx76¹⁷ was used to refine the structures. A summary of both programmes is given below.

Multan 87

Multan 87 consists of three separate programmes which, when run in series, will perform all the necessary calculations from the normalisation of structure factors to the output of a picture of the structure. The three programmes consist of five logical sections specified below.

(a) 'Normal' computes normalised structure amplitudes from $F(\text{obs})$ values using either a K-curve or a Debye curve. It outputs intensities statistics as a check on the scaling and an aid to space group determination.

(b) 'First' sets up the phase relationships. These are used in the convergence procedure to pick the best reflections for phase determination. Either a small number of reflections may be chosen to fix the origin and enantiomorph plus a small number of others to give a 'good' start or the majority of the strong reflections may form the starting set. The results are written in a disk file which forms the input to 'last'.

(c) 'Last' determines the phases for for all reflections from the starting set found by the convergence procedure, or independently from it. Initial values for unknown phases are assigned by magic integer phase permutation. Figures of merit are computed for each phase set produced. These results are written to disk and can be read by 'Exfft'.

(d) 'Exfft' computes an E-map from a set of normalised structure factors.

(e) 'Search' finds the co-ordinates of the highest peaks in the E-map and looks for groups of peaks which could form a molecule or a molecular fragment. It computes bond lengths and angles from each molecular fragment and outputs on the lineprinter a properly scaled view of the peaks plotted on the least squares plane. Each fragment is interpreted in terms of bonded atoms by applying simple stereochemical constraints and alternatives interpretations are output if found.

In order to run Multan 87, command and data files must be setup, telling Multan how to interpret the E-map (which will be generated from the F(obs) data file). Data cards give the cell contents, the symmetry, the cell dimensions and the format of the data. Initial runs of Multan 87 usually only locate the heavy atoms in the structure. The position of these atoms can be input to the programme in the data file, allowing the determination of the atoms surrounding these heavy atoms.

ShelX-76

Once the positions of the atoms in the unit cell have been determined, the atomic co-ordinates, together with the lattice and symmetry type are inputted to ShelX-76, the refinement programme. This programme essentially compares experimental F(obs) with calculated F(obs), (based on the inputted data cards). It can refine atoms by letting them some atoms behave anisotropically and fixing restraints to others (eg. those carbons in a benzene ring). Intensities which are weak or inconsistent with the symmetry of the molecule can also be omitted thus increasing the R value.

4.3.1.4 The Crystal Structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ (2-phpy = 2 phenylpyridine)

The Crystal Structure of $\text{Cr}(\text{CO})_5(2\text{-phpy})$ has been determined. Data were measured on the Nicolet P3 four-circle diffractometer, using a θ - 2θ scan technique. The intensity data were collected and cell parameters were determined as outlined in Sections 4.3.1.1 and 4.3.1.2. Table 4.3.1.1 outlines the parameters of the crystal and Table 4.3.1.2 details the experimental conditions used in the measurement of intensity data.

The crystal decomposed slightly, during the data collection time, as indicated by the changing of the crystal colour to yellow/grey from its original yellow/orange colour. The positions of the chromium atoms were found initially by Multan 87. A weighted Fourier transform was then performed using the chromium atom position to determine the positions of all the other non-hydrogen atoms in the molecule. These co-ordinates were then refined by ShelX and an initial R-value of 0.3363 was obtained.

The data was treated by three cycles of least squares refinement, reducing the R-value to 0.1269. Using the scale factor of this file and allowing first the chromium atom to go anisotropic and then all atoms to go anisotropic the R-value was reduced to 0.1043. In calculating the position of the H atoms and omitting those reflections where $(I) < (4 \times I)$ reduced the R-value to 0.0789 with 208 refined parameters and 1734 F values.

Table 4.3.1.1. Summary of crystal data of
Cr(CO)₅(2-phpy)

Cell Type	Monoclinic
Space Group	P2 ₁ /c
a, Å	6.323(4)
b, Å	13.636(12)
c, Å	18.170(9)
β	92.60(5)°
V, (Å) ³	1540(2)
D _{calc} , g/cm ³	1.497

Table 4.3.1.2. Summary of collection parameters and data intensities for Cr(CO)₅(2-phpyr).

(MoK),cm-1 0.71069 Å

Data Collection Range h, 0 to 9· k, 0 to 20: l,-26 to 26.

2 theta range, (°) 0 to 60

Scan Rate (2 th/min) 5.33 (I < 1,000), 58.6 (I > 2500)

Orientation Matrix 0.00227 -0.06804 0.02056
 0.02398 -0.02689 -0.05016
 0.15905 0.00502 0.00980

Orientation Stds. hkl, 1,1,-6; 2,0,-6; 2,3,2

Intensity Stds.a hkl, 1,1,-6; 0,3,8

F₀₀₀ 704

No. of reflections 3381

4.3.1 5 The Crystal Structure of (Cr(CO)₅)₂(dmbipy)

Data were measured as for Cr(CO)₅(2-phpy) to yield 939 observations with I > 3 (I). The crystal data is summarised in Table 4.3.1.3 and the parameters used in the collection of the X-ray intensity data given in Table 4.3.1.4.

Data were measured on the basis of a triclinic cell given above to yield 1190 observations of which 251 had $I < 3$ (I) and were not considered further. The positions of all non-H atoms were determined using ShelX76 on the Prime computer of the University of Dundee. All other calculations were done with the NRC suite of programmes on the Honeywell DPS8 computer of the University of Aberdeen. Structure factors for neutral atoms were taken from reference 18. 2θ was only taken to 40° because of the weak diffraction of the small crystal ($0.2 \times 0.2 \times 0.2 \text{ mm}^3$).

Table 4.3.1.3: Summary of crystal data of
(Cr(CO)₅)₂dmbipy

Cell Type	Monoclinic
Space Group	P2 ₁ /c
a, Å	9.321(20)
b, Å	12.361(13)
c, Å	10.564(2)
β	100.09(16)°
V, (Å) ³	1198(2)
D _{calc} , g/cm ³	1.575

Table 4.3.1.2: Summary of collection parameters and data intensities for $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$.

(MoK), cm⁻¹ 0.71069 Å

Data Collection Range h, 0 to 10; k, 0 to 13; l, -11 to 11.

2 theta range, (°) 0 to 60

Scan Rate (2 θ/min) 5.33 (I < 1,500), 58.6 (I > 2500)

Orientation Matrix 0.08418 -0.05044 0.00048
 0.00458 0.02023 -0.04543
 0.06904 0.05993 0.01572

Orientation Stds. hkl, 0,4,6; 2,0,2; 2,0,-2; 0,5,1

Intensity Stds.^a hkl, 0,4,0; 2,0,2

F₀₀₀ 572

No of reflections 816

After refinement R was 0.14 over all observed data, but excluding 120 weak observations with (F)/F in excess of 0.4 gave R and R' values of 0.10 and 0.13 respectively for 155 refined parameters and 816 F's refining Cr anisotropically and all other non-hydrogen atoms isotropically. Due to the limited quality of the data no attempt was made to determine the H atoms positions nor the absolute configuration of the molecule. At this stage the maximum feature in the difference map was 0.8 e Å⁻³ and the distribution of F against F₀ and $(\sin^2 \theta)^2$ was satisfactory. Therefore it was concluded that although the structure was determined with no great accuracy it is nevertheless correct.

4.3.1.6 The Crystal Structure of $\text{W}(\text{CO})_5(4\text{-phpy})$

The crystal structure of $\text{W}(\text{CO})_5(4\text{-phpy})$ was determined in an analogous way to that of $\text{Cr}(\text{CO})_5(2\text{-phpy})$. Data were measured on the basis of a monoclinic cell to yield 1601 observations with $I > 3(I)$. The crystal data is summarised in Table 4.3.1.5 and the parameters used in the collection of the X-ray intensity data are given in Table 4.3.1.6. This data was treated by an absorption correction was programme¹⁹ to correct for absorption by the tungsten atom.

Table 4.3.1.5. Summary of crystal data of $\text{W}(\text{CO})_5(4\text{-phpy})$

Cell Type	Monoclinic
Space Group	Cmcm
$a, \text{\AA}$	7 866(5)
$b, \text{\AA}$	12.538(4)
$c, \text{\AA}$	16.239(6)
$V, (\text{\AA})^3$	1602(2)
$D_{\text{calc}}, \text{g/cm}^3$	1 985

Table 4.3.1.2: Summary of collection parameters and data intensities for W(CO)5(4-phpyr).

(MoK),cm-1	0.71069 Å
Data Collection Range	h, 0 to 12; k, 0 to 18; l, 0 to 24.
2 theta range, (°)	0 to 60
Scan Rate (2 th/min)	5.33 (I < 1,000), 58.6 (I > 2500)
Orientation Matrix	0.00932 -0.07854 -0.00974 0.02148 0.01342 -0.05981 0.12495 0.00356 0.01099
Orientation Stds.	hkl, 2,5,7; 2,8,0; 0,0,10
Intensity Stds	hkl, 2,5,7; 2,8,0
F ₀₀₀	904
No. of reflections	1601

The W(CO)5(4-phpy) crystal belongs to the space group Amma. The structure was solved in the standard setting of this space group, which is Cmc₂m. For this latter space group the cell dimensions are rearranged from their original values a, b, c to a', b', c' in the following manner;

$$\begin{aligned}a' &= b \\b' &= c \\c' &= a\end{aligned}$$

As a result the original hkl values must also be reordered klh. The position of the W atom was determined by the use of the Multan87 programme. A weighted Fourier transform calculation, using the position of the tungsten atom, yielded the co-ordinates of half the molecule. The co-ordinates of the remaining non-hydrogen atoms in the molecule were generated by consideration of the symmetry of the molecule. The structure was refined using the ShelX76 programme. The initial co-ordinates had an R-value of .65 but this was reduced to 0.095 after three cycles of least squares refinement. Allowing the W atom to go anisotropic reduced the R-value to 0.09. Allowing all atoms to be anisotropic and by fixing the positions of the H atoms the R-value was reduced to 0.05. This value was decreased further (to 0.035) by omitting all intensity data in which $I < 3\sigma(I)$. A difference map showed no significant peaks and the distribution of F against (F_o) and $(\sin 2\theta)^2$ was satisfactory.

4.3.2 The Synthesis of $\text{Cr}(\text{CO})_5(2\text{-phpy})$

250 cm³ of a continuously purged solution of diethyl ether, containing 0.5 g (2.28 mmol) of $\text{Cr}(\text{CO})_6$, was photolysed for 3 hours with a medium pressure mercury lamp. After photolysis the $\text{Cr}(\text{CO})_5(\text{diethylether})$ complex was filtered under argon to remove any unreacted $\text{Cr}(\text{CO})_6$ and 0.35 cm³ (2.38 mmol) of 2-phpy added. The solvent was removed under reduced pressure and the residual solvent redissolved in toluene under an argon atmosphere. The resulting crystals were recrystallised from deaerated toluene solution containing an excess of 2-phpy.

$\text{W}(\text{CO})_5(4\text{-phpy})$ was supplied by Mr. Cormac Hegarty and was used without further purification. The synthesis of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ has been described in Section 3.5.

4.3.3 Ir and uv/vis Spectral Measurements

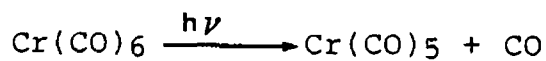
Ir spectra were measured on a Perkin-Elmer 983-9 spectrophotometer. Ir spectra of the carbonyl complexes were prepared under a nitrogen atmosphere in nitrogen purged toluene solution. Spectra were recorded in sodium chloride solution cells (pathlength 0.1mm) as soon as possible after the sample was made up (usually about 15 to 2 minutes). Uv/vis spectra were recorded on a Hewlett-Packard 8452a diode-array spectrophotometer, which has a .1s acquisition time. The $\text{Cr}(\text{CO})_5(2\text{-phpy})$ and $\text{W}(\text{CO})_5(4\text{-phpy})$ samples were dissolved in nitrogen purged solvents before spectral measurements were taken. The spectrum of $(\text{Cr}(\text{CO})_5)_2(\text{dmbipy})$ complex was measured in freeze-pump-thaw degassed toluene solution.

4.4 References

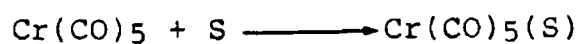
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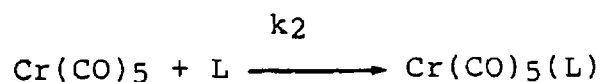
Appendix 1



k_1



k_{-1}



$$\frac{d[\text{Cr(CO)}_5]}{dt} = -k_1[\text{S}][\text{Cr(CO)}_5] + k_{-1}[\text{Cr(CO)}_5(\text{S})] - k_2[\text{Cr(CO)}_5][\text{L}]$$

$$\Rightarrow [\text{Cr(CO)}_5] = \frac{k_{-1}[\text{Cr(CO)}_5(\text{S})]}{k_1[\text{S}] + k_2[\text{L}]}$$

$$\frac{d[\text{Cr(CO)}_5(\text{S})]}{dt} = \frac{-k_2k_{-1}[\text{Cr(CO)}_5(\text{S})]}{k_1[\text{S}] + k_2[\text{L}]}$$

If $k_1[\text{S}] \gg k_2[\text{L}]$ then the above equation can be simplified

$$\frac{d[\text{Cr(CO)}_5(\text{S})]}{dt} = \frac{-k_{\text{app}}[\text{L}][\text{Cr(CO)}_5(\text{S})]}{k_1[\text{S}]}$$

where $k_{\text{app}} = k_{-1}k_2$

$$\frac{1}{k_1[\text{S}]}$$

Appendix 2

Intensity Calculations.

For CpMn(CO)_3

If the proportion of ^{12}C is $(1-x)$ and that of ^{13}C is x , then,

Concentration of $(^{12}\text{CO})_3 \propto (1-x)^3$

Concentration of $(^{13}\text{CO})_3 \propto x^3$

Intensity Ratio of $\frac{2029\text{cm}^{-1}}{1982\text{cm}^{-1}} = y$

$$\text{Then } \frac{(1-x)}{x} = 3\sqrt{y}$$

$$\Rightarrow x = \frac{1}{1 + 3\sqrt{y}}$$

From the spectrum of a ^{13}CO enriched CpMn(CO)_3 sample,

$$\text{Ratio of } \frac{2029\text{cm}^{-1}}{1982\text{cm}^{-1}} = 12.3$$

$$\Rightarrow x = 0.3 \quad \text{i.e. } 30\%$$

For a dicarbonyl species:

The intensities of the peaks will be related to the proportion of ^{12}CO and ^{13}CO present

Probability of $(^{12}\text{CO})_2 = (1-x)^2$

Probability of $(^{12}\text{CO})(^{13}\text{CO}) = 2x(1-x)$

Probability of $(^{13}\text{CO})_2 = (x)^2$

As $x = 0.3$

	<u>Calculated</u>	<u>Observed</u>
Intensity(^{12}CO)	0.49	1.95cm
Intensity($^{12}\text{CO})(^{13}\text{CO})^a$	0.42	1.60cm
Intensity(^{13}CO)	0.09	0.45cm

a There is a change in symmetry which might affect the intensity of this band slightly

Publications to Date:

"Structure and reactivity of $(\eta^5\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ in room temperature solution. Evidence for formation of a dinuclear intermediate detected by laser flash photolysis and time resolved infrared spectroscopy"

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