The Photochemically induced reactions
of *trans-bis* dinitrogen *bis* diphos tungsten(O).

by

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This Thesis contains no material previously submitted for a degree or diploma in any University, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where the due reference is made in the text.

R.J.W. Thomas

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My sincere thanks are due to Ms. P. Ashwood for extensive help in preparing diagrams.

Abstract

The photochemically induced reactions of $trans$-W(O)(N$_2$)$_2$(dppe)$_2$ with various small molecules has been studied using the techniques of preparative chemistry, quantum yield determinations and flash photolysis.

It was found that a general class of photochemically induced substitution reactions of $trans$-W(N$_2$)$_2$(dppe)$_2$ existed, leading to the production of $trans$-W(^{15}N$_2$)$_2$(dppe)$_2$, $trans$ and cis W(CO)$_2$(dppe)$_2$, W(H$_4$)(dppe)$_2$, and WH$_2$(PHBu$_2$)(dppe)$_2$. It was also determined that the previously reported reactions of $trans$-W(N$_2$)$_2$(dppe)$_2$ with alkyl and acyl halides required light activation.

Quantum yield measurements for the reaction of $trans$-W(N$_2$)$_2$(dppe)$_2$ with various species showed that there was a limiting quantum yield of 0.4, and, in the case of the reaction with 1-bromobutane, the quantum yield was dependent on substituent concentration in the range 0.01 to 0.05 molar.

Flash photolysis experiments demonstrated that two relaxation processes followed a perturbation from the photostationary state. Upon flash photolysis an immediate decrease in absorbance (in the range 290 - 400 nm) was observed, which was attributed to loss of both dinitrogen ligands. The absorbance (and presumably dinitrogen ligands) was then recovered in two consecutive first order processes, one process being effectively complete in 5 milliseconds, the second process being complete in 2 seconds.

Isotopic labelling experiments involving labelling with one labilisation by light, and the relative rates of isotopomer formation strongly suggested that two dinitrogen ligands were exchanged with dinitrogen in the solvent upon absorption of a photon of light. Some of the results discussed in this thesis have been published in Inorganica Chimica Acta. (Appendix D)

Preamble

In 1973 A.A. Diamantis[1] while working in the Sussex laboratories of the A.R.C. unit of nitrogen fixation under the guidance of Professor J. Chatt, found that a reaction occurred between $W(N_2)_2(dppe)_2$ and alkyl halides. (Specifically methyl bromide, ethyl bromide and tertiary butyl bromide.) This reaction produced complexes characterised as $BrW(NNR)(dppe)_2$ and $Br_2W(NNHR)(dppe)_2$. Diamantis noted that the reaction of the dinitrogen complex and the alkyl halides depended on the light intensity, in that the reaction proceeded more rapidly when irradiated by a 100 watt lamp than in the diffuse light in the laboratory. When reactive alkyl bromides such as MeBr and EtBr were used a green product was formed in addition to the alkyl azo and alkyl diazenido complexes. This was later shown to contain an azo butanol group, derived from the methyl or ethyl radical attack on thf[2].

In late 1973 Diamantis returned to the University of Adelaide where the opportunity to further investigate this reaction did not occur until 1975, when the research work described in this thesis was commenced.

Initially the aims of this project were:

(a) To investigate the reaction between $W(N_2)_2(dppe)_2$ and various alkyl halides to determine whether the reaction is photochemically induced.

(b) To determine the mechanism of this reaction.

(c) To investigate the possibility of the existence of other photochemically induced reactions of $W(N_2)_2(dppe)_2$ and $Mo(N_2)_2(dppe)_2$.

The research work commenced as an identification of the products of the photochemical reaction, during the investigation of the system it became obvious that the techniques of flash photolysis, quantum yield determination and emission lifetime determination would yield more information as to the mechanism of the reaction than would preparative techniques. The project was advised in this area by Dr. G.S. Laurence and co-workers, who made available equipment for flash photolysis, laser excited emission and kinetic studies.

Thus in retrospect the project became divided into a number of sections, which provided data at various levels.

(1) Flash photolysis and isotopic labelling: The use of flash photolysis allowed the chemical changes which occurred upon irradiating $W(N_2)_2(dppe)_2$ to be directly observed, while isotopic labelling showed that this change involved labilisation of both dinitrogen ligands. The reaction scheme proposed on the basis of these results is shown below:

$$W(N_2)_2(dppe)_2 \longrightarrow W(dppe)_2(solv)_2 + 2N_2$$
$$\downarrow$$
$$W(N_2)(dppe)_2(solv)$$
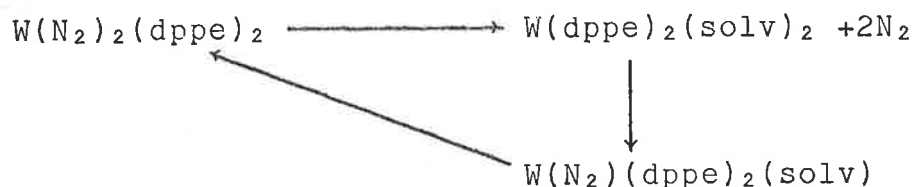
(2) Preparative techniques: It was attempted to react $W(N_2)_2(dppe)_2$ with various substrates in the dark and with visible light irradiation. This enabled the proposed reaction mechanism to be confirmed on the preparative scale, and also led to the production of some novel compounds.

The thesis has been presented in four chapters:

(1) An introduction to dinitrogen complex chemistry, a brief survey of the literature and a survey of some inorganic photochemistry reviews.

(2) Preparative scale photochemistry of $W(N_2)_2(dppe)_2$.

(3) Quantum yield determinations and flash photolysis results and a discussion on the mechanism involved. Some data on $Mo(N_2)_2(dppe)_2$ has also been included, this derives in part from this work and in part from work by Ashwood[3].

(4) Materials and methods.

CONTENTS

ABBREVIATIONS

In this work a number of abbreviations have been used. The intent of these abbreviations is explained below.

P	Any monodentate organophosphine ligand
dp	Any bidentate organophosphine ligand
dppe	The bidentate organophosphine ligand 1,2,bis(diphenylphosphino)ethane
thf	Tetrahydrofuran
dmso	Dimethylsulphoxide
dmf	Dimethylformamide
ox	Oxalate, $C_2O_4^{2-}$

CHAPTER 1

1.0 Introduction

The chemistry of metal dinitrogen complexes is a
relatively new field of study, the first such compound,
$[Ru(NH_3)_5N_2]Cl_2$ having been discovered in 1965.[4] Since
then many other dinitrogen complexes have been formed, or
postulated as existing in reaction mixtures.

Complexes formed between transition metals and
gaseous molecules, such as dinitrogen, carbon monoxide,
dioxygen, and dinitrogen oxide have been extensively
studied particularly during the last decade partly in an
effort to increase our understanding of enzyme systems,
and to generate models of enzymes mimicking systems such
as oxygen carriers and nitrogenases. An example of this
is the reversible oxygen carrier *bis*(salicylaldehyde)-
ethylenediaminecobalt(II) , which has been known for
quite some time, and has contributed greatly to our
knowledge of the dioxygen carrying capabilities of
haemoglobin.[5]

Dinitrogen complexes are compounds of transition
metals with the dinitrogen molecule attached directly to
the metal as a ligand. The formation reaction of the
dinitrogen complexes is the only definite reaction of
molecular dinitrogen known to occur at room temperature
and pressure, with reagents mild enough to exist in
water.[6]

Dinitrogen complexes are mostly diamagnetic
compounds obeying the effective atomic number rule,
although some paramagnetic complexes are known. Terminal
dinitrogen complexes are characterized by a sharp band,

or bands, in the infra red spectrum between 1900 cm^{-1} and 2220 cm^{-1}, due to the $\nu(N\equiv N)_{sy}$ mode. The difference in $\nu(N\equiv N)_{sy}$ for a dinitrogen complex and the Raman absorption of gaseous dinitrogen (2331 cm^{-1}) can be used as a crude measure of the lowering of the bond order of dinitrogen caused by coordination. The high intensity of the infra red absorption assigned to the $\nu(N\equiv N)_{sy}$ mode suggests that the nitrogen atoms have become electronically asymetric . This is supported by the observed negative correlation between frequency and intensity for $\nu(N\equiv N)_{asy}$[7] and X-ray photoelectron spectra for dinitrogen complexes of Ir(1), Co(1), Fe(II), Re[8] and Ir[8]

1.1 Bonding in dinitrogen complexes

Dinitrogen is the most inert of the common diatomic molecules, only reacting at room temperature with extremely reactive groups (excepting low valent metal centres to form dinitrogen complexes) such as CH_2, CF_3HC,[9] or Li.

Table 1.1 lists various properties of dinitrogen and some of its analogues. Points of interest are the extremely high bond energy of the N≡N triple bond compared to the N=N double bond, the short bond length of dinitrogen, high value of $\nu(N\equiv N)$, high value of the dissociation energy, and the extremely high ionization energy which is approximately as great as that of argon. There is considerable uncertainty as to the value of the electron affinity of dinitrogen.

TABLE 1.1

(From G.J. Leigh, 1971[6])

(a) Physical properties	N_2	O_2	C_2H_2	CO	NO	
Bond length (Å)	1.098	1.207	1.208	1.128	1.150	
Stretching frequency (cm^{-1})	2331	1555	1974	2143	1876	
Ionization energy (eV)	15.6	12.3	11.4	14.5	9.3	
Dissociation energy ($kJ\ mol^{-1}$)	942	494	837	984	628	
(b) Comparison of bond energies ($kJ\ mol^{-1}$)	N–N	N–O	O–O	C–C	C–N	C–O
Triple bond	942	1055		812	879	984
Ratio	2.25	∿3.0		1.32	1.43	1.38
Double bond	418	∿333	401	615	615	712
Ratio	2.62	2.0	2.91	1.77	2.10	2.02
Single bond	159	∿168	138	347	293	352

The great stability of dinitrogen is a consequence of its electronic structure, which is similar to that of carbon monoxide. Simple molecular orbital theory predicts that the sequence of molecular orbitals for a homonuclear diatomic molecule such as dinitrogen is $\sigma g2s$, $\sigma u2s$, $\sigma g2p$, $\Pi u2p$, $\Pi g2p$, $\sigma u2p$, such as occurs in the dioxygen molecule. However, for dinitrogen the sequence is altered by the interchange of $\Pi u2p$ and $\sigma g2p$.[10] This is due to the strong configurational interaction between $\sigma g2p$ and $\sigma g2s$ levels which raises the former above $\Pi u2p$. The sequence of molecular orbitals can be represented as in figure 1.1.

The essential features of the bonding of dinitrogen to a metal atom are the donation of a pair of electrons from the $\sigma g2p$ orbital into an unfilled metal d orbital to form a σ bond, and a back donation of metal non-bonding d orbital electrons into the strongly antibonding $\Pi g2p$ orbitals of the dinitrogen molecule (Fig. 1.2).

It would be expected that donation of the $\sigma g2p$ electrons to the metal would result in a decrease in the N-N bond energy. However, it strengthens the bond, due to decreased electronic repulsion in the volume between the nitrogen nuclei. The donation of metal $d\Pi$ electrons to the $\sigma g2p$ orbital does result in overall weakening of the bond.[6] This is therefore a very similar pattern to the bonding of CO in metal carbonyls.

Because of this bonding, the dinitrogen ligand is extremely sensitive to the nature of the other ligands attached to the metal centre. The co-ligands normally found are ammonia, chloride, hydride, and organic phosphines.
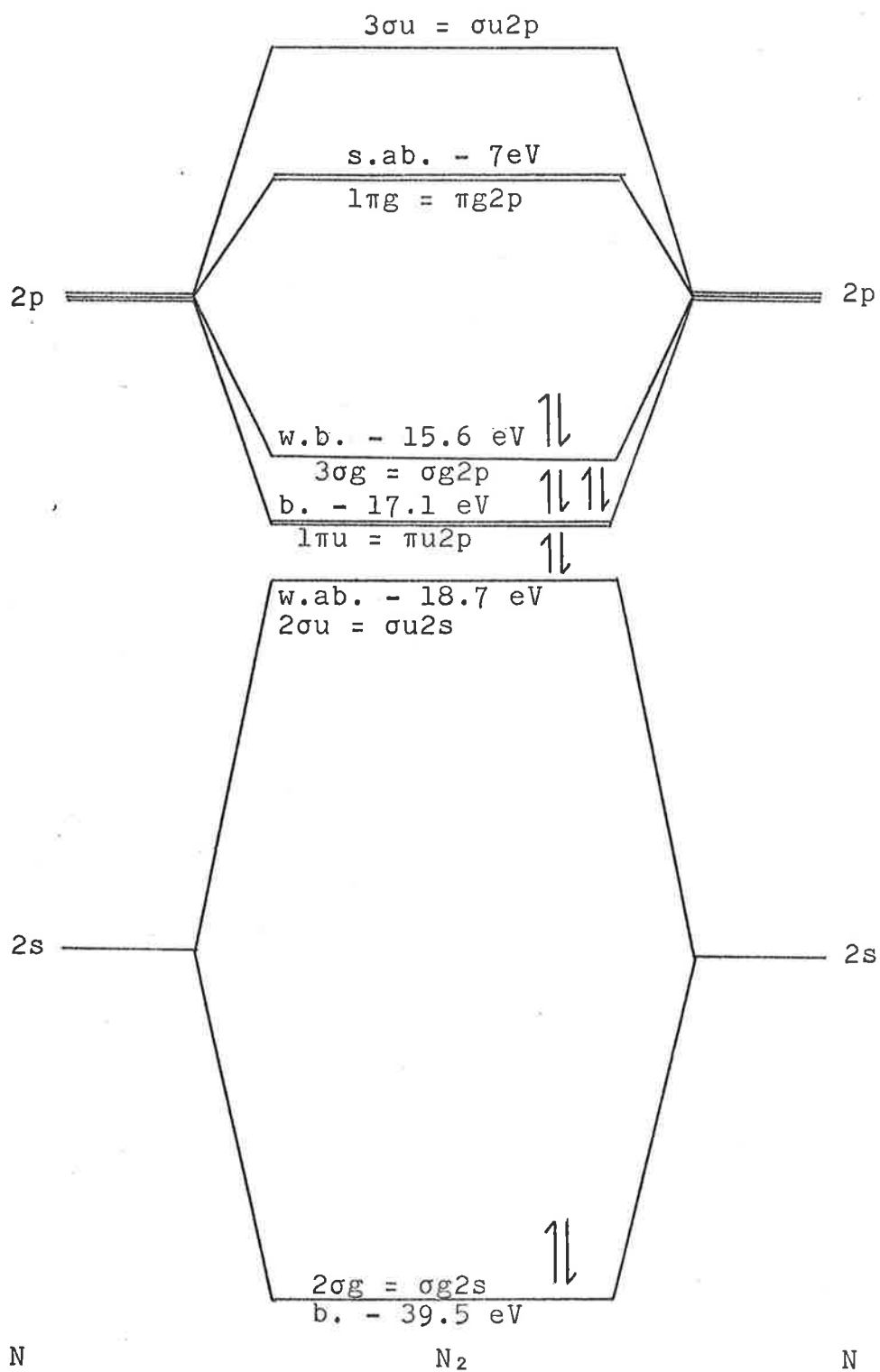
FIGURE 1.1 Correlation diagram for dinitrogen, from Hewitt and Cutting.[10]
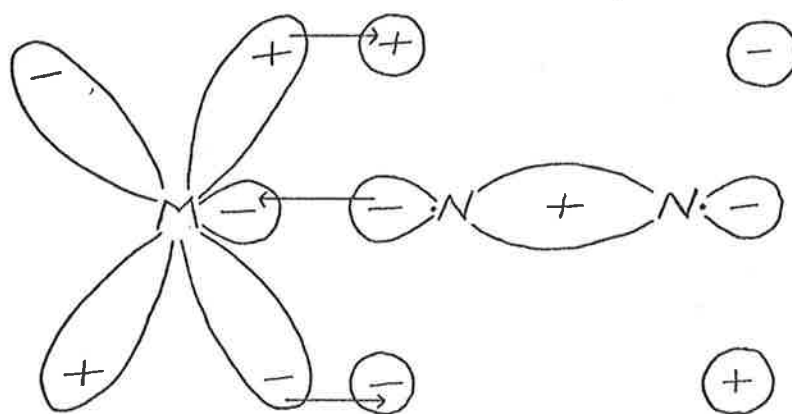
FIGURE 1.2   Representation of bonding
between dinitrogen and a
metal atom.

Dinitrogen has been observed to bind in a variety of ways:

(I) $M-N\equiv N$

(II) $M\overset{\displaystyle N}{\underset{\displaystyle N}{\big\langle\;\|}}$

(III)
$$\underset{\displaystyle M\qquad\quad M}{\overset{\displaystyle N}{\overset{\|}{\underset{\displaystyle N}{\diagup\quad\diagdown}}}}$$

(IV) $M-N=N-M$

(V) $N\equiv N-M-N\equiv N$ (*trans*)

(VI)
$$\begin{array}{c} N \\ \| \\ N \\ | \\ N\equiv N-M \end{array}$$
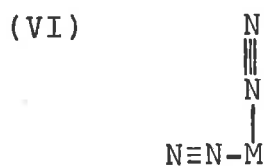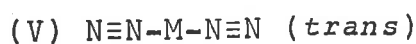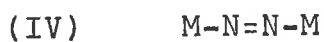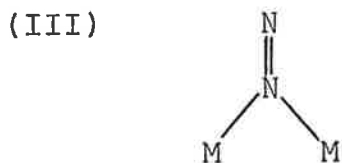
However, structures (I), (IV), (V), and (VI) are the only commonly observed species. A di-hapto structure, (II), is probably involved in the rotation of the dinitrogen ligand in $\left[(NH_3)_5Ru^{15}N-^{14}N\right]^{2+}$.[12] A crystal structure has been carried out on a dihapto RhN_2 complex, and although there are anomalous bond lengths reported it would seem that there is evidence for structure (II) existing as a stable entity.[13]

1.2 The nature of the dinitrogen coordination site

In 1966 Shilov et al reacted dinitrogen gas with a mixture containing $RuCl_3$ and zinc amalgam in thf solution.[15] This yielded a Ru(thf) complex containing coordinated dinitrogen, providing the first evidence that dinitrogen complexes could be formed directly from dinitrogen gas. Discovery of other such formation reactions rapidly followed.

Harrison and Taube[16] then showed that dinitrogen could displace water from $(NH_3)_5RuOH_2{}^{2+}$, to yield $[N_2(Ru(NH_3)_5)_2]^{4+}{}_{(aq)}$. This observation is important in that if dinitrogen complexes are to serve as models for nitrogenase there are a number of prerequisites for the coordination site: (a) N_2 must be able to compete (in an aqueous environment) for the active site, which is probably a metal centre. (b) Ammonia must not bond strongly to the active centre. (c) Dinitrogen analogues (such as $N_3{}^-$, C_2H_2, CO) should also react with the metal

The phrase "NH_3 can be displaced from a coordination site by dinitrogen" is a somewhat abbreviated description of the reaction which actually proceeds as

$$(NH_3)_6Ru{}^{2+}_{aq}$$

$$\downarrow$$

$$\left[(NH_3)_5RuOH_2\right]^{2+}_{aq} + NH_3$$

$$\tfrac{1}{2}\left[((NH_3)_5Ru)_2N_2\right]^{4+} \qquad \left[(NH_3)_6Ru\right]^{2+}$$
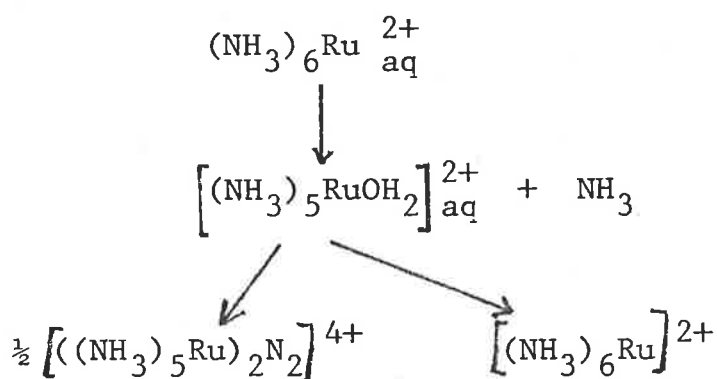
The ammonia has been displaced in the sense that water competes with ammonia quite successfully in the equilibrium steps.[16]

Overall, it would appear that metal dinitrogen complexes should provide a model system for the nitrogenase fixation reactions.

In nitrogenase the two metals iron and molybdenum appear to be necessary for ammonia production, with the active site probably at a molybdenum metal centre. This would seem to indicate that the study of the molybdenum complexes would perhaps yield the most information about the activation of dinitrogen at a metal centre. This is not to suggest that the dinitrogen complexes formed are necessarily at all like those involved in nitrogenases. However, the chemistry of transition metal dinitrogen complexes can obviously enhance our understanding of metal/dinitrogen bonding and reactivity.

Thus metal dinitrogen complexes are of some interest in two principal aspects: (1) their formation and bonding and (2) their reactivity (particularly towards reduction).

For some years after the first reports of $[(NH_3)_5RuN_2]Cl_2$ no reduction of coordinated dinitrogen to NH_3 or hydrazine could be achieved by using mild reagents. Indeed, coordinated dinitrogen seemed to be as inert as free N_2 toward reduction. It was found to be possible to produce NH_3 and N_2H_4 from reaction "brews" of ill defined constituents, and a report was published of a yield of 200 moles of reduced products per mole of metal. However, these systems used strong reducing conditions in exotic solvents.[18]

1.3 Dinitrogen complexes of Mo and W

The greatest degree of success in "fixing" ligated dinitrogen has been experienced with the system $M(N_2)_2(P_4)$ where M = Mo or W and P = ½dppe, ~~Me₃P~~, Me_2PhP or $MePh_2P$.

This has been achieved since 1970, when Bell, Chatt and Leigh[19] reported that reduction of $WCl_4(PR_3)_2$ by sodium amalgam in a thf solution of an appropriate phosphine under a dinitrogen atmosphere, yielded *cis*-$W(N_2)_2(P)_4$ and *trans*-$W(N_2)_2(dp)_2$. Improved syntheses were later developed.[20,21] Various syntheses were also reported for $Mo(N_2)_2(dp)_2$ and $Mo(N_2)_2(P)_4$.[22,23,24] A direct synthesis of $Mo(N_2)_2(dppe)_2$ has been reported from $MoCl_5$ and dppe by reduction using sodium amalgam in thf, under a dinitrogen atmosphere.[25] This technique was found by Ashwood[3] to be superior to the previous syntheses. A crystal structure of *trans*-$Mo(N_2)_2(dppe)_2$ has been published,[26] (figure 1.3) and it is normally presumed that $W(N_2)_2(dppe)_2$ is isostructural with the molybdenum analogue.

1.4 Reaction with RCOCl

The first report of a reaction involving the formation of a N_2-C bond in a metal dinitrogen complex was published in 1972, when it was reported that *trans*-$W(N_2)_2(dppe)_2$ reacted with RCOCl, to yield $WCl_2(N_2HCOR)(dppe)_2$.[27]

This reaction was believed to be thermal, but it has been found in this work that in fact the reaction is photochemically induced (section 2.2.5). The N_2H_2 and N_2H complexes (described below) can be acetylated in the
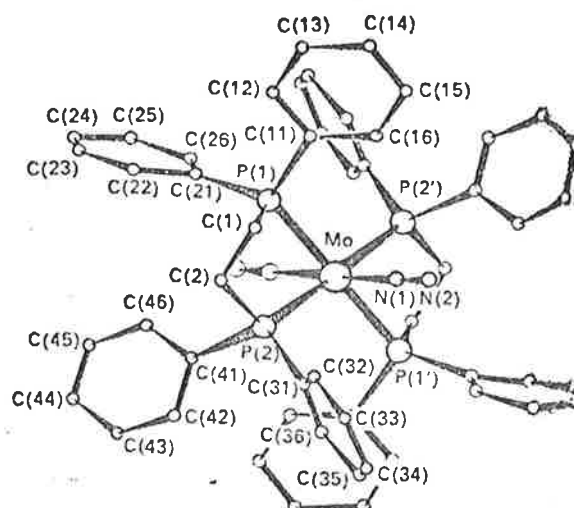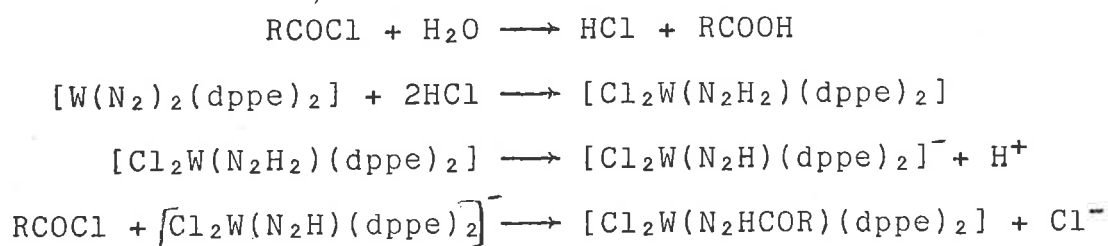
FIGURE 1.3 Structure of *trans*-[Mo(N₂)₂(dppe)₂] (from T. Uchida, Y. Uchida, M. Hidai and T. Kodama, *Acta Cryst.*, 1975, B31, 1197).

dark by acetyl halides to yield the previously synthesised [$X_2M(N_2HCOR)(dppe)_2$]. This explains why the reaction between $W(N_2)_2(dppe)_2$ and RCOCl can occur in the dark if moisture is present.

Under such conditions the following reaction scheme would be expected to occur.

$$RCOCl + H_2O \longrightarrow HCl + RCOOH$$
$$[W(N_2)_2(dppe)_2] + 2HCl \longrightarrow [Cl_2W(N_2H_2)(dppe)_2]$$
$$[Cl_2W(N_2H_2)(dppe)_2] \longrightarrow [Cl_2W(N_2H)(dppe)_2]^- + H^+$$
$$RCOCl + [Cl_2W(N_2H)(dppe)_2]^- \longrightarrow [Cl_2W(N_2HCOR)(dppe)_2] + Cl^-$$

1.5 Protonation reactions

In 1972 it was reported[20],[28] that $M(N_2)_2(dppe)_2$ (M = W, Mo) could be protonated by HX to yield coordinated N_2H_2 (X = Cl, Br for W; Br for Mo. Hydrogen chloride plus $Mo(N_2)_2(dppe)_2$ was found to yield $(MoH_2Cl_2(dppe)_2)$ plus $2N_2$.) It was postulated that the grouping $W-N-NH_2$ existed in [$WCl(N_2H_2)(dppe)_2$]. A crystal structure of [$WCl(N_2H_2)(dppe)_2$]BPh_4 has shown that this grouping is present in the salt[29] and a structure of [$Mo(N_2H_2)F(dppe)_2$]$BF_4.CH_2Cl_2$ has revealed a similar grouping in this molybdenum hydrazido complex.[30] Isotopic substitution ($^{15}N_2$ and ^2H), ^1H n.m.r. and infra red spectroscopy have shown that the form $W-NH=NH$ is present in the seven coordinate [$WCl_2(N_2H_2)(dppe)_2$].[31] The ligand N_2H_2 could not, however, be protonated further, the complex [$WCl_2(N_2H_2)(dppe)_2$] even being recovered from warm concentrated H_2SO_4. One proton could be removed (by mild base)[32] to yield the ligand N_2H. $WX_2(N_2H_2)(dppe)_2$

is reported to be readily converted to $WX(N_2H)(dppe)_2$, the Mo analogue was found to be more sensitive to base and readily converted under an N_2 atmosphere to $Mo(N_2)_2(dppe)_2$.

In 1975 Chatt et al reported the production of ammonia and hydrazine from cis-$W(N_2)_2(PR_3)_4$ plus sulphuric acid in thf or methanol (R = alkyl or aryl).[33] It is of some interest to note that at room temperature this reaction, when PR_3 = PMe_2Ph is light activated, but occurs readily at 60°C without activation by light.

In 1975 it was also reported[32a] that the grouping N_2H_3 had been isolated in the complex $trans$-$WCl_3(NHNH_2)(PMePh_2)_2$, and led to further postulation as to the mechanism of protonation of dinitrogen in complexes of Mo and W to yield ammonia. The possible mechanisms of these reactions have been discussed, and the various reactions summarised in detail in a review article by Chatt.[31]

It has been suggested that the extent of the protonation observed with the various dinitrogen complexes is a result of the varying electron donating properties of the coligands in the complex.

1.6 Reaction with alkyl halides

In 1973 Diamantis investigated the reactions between alkyl halides and $trans$-$W(N_2)_2(dppe)_2$ and found that there existed a light catalysed reaction, yielding the grouping W-N=N-R.[1] This could be readily protonated to yield W-N-NHR. Various alkyl halides were found to yield different groupings, these are detailed (figure 1.4). George and co-workers had also about the same time

$$W(N_2)_2(dppe)_2 \;+\; MeBr \xrightarrow{\;C_6H_6\;} [WBr(N_2Me)(dppe)_2]$$

$$W(N_2)_2(dppe)_2 \;+\; EtBr \xrightarrow{\;C_6H_6\;} [WBr(N_2Et)(dppe)_2]$$

$$W(N_2)_2(dppe)_2 \;+\; t\text{-}BuBr \xrightarrow[\text{thf}]{C_6H_6} [WBr(N_2C(CH_3)_3)(dppe)_2]$$

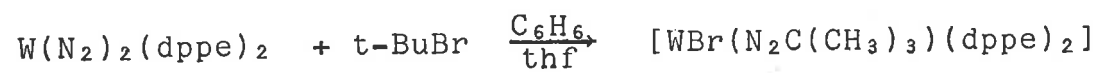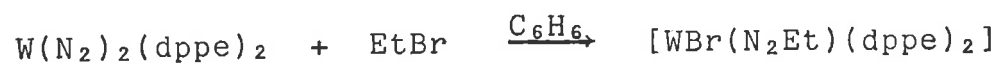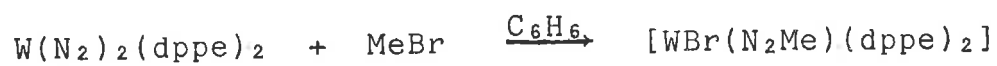$$W(N_2)_2(dppe)_2 \;+\; MeBr \xrightarrow{\text{thf} \quad HBr} [WBr(N_2CH(CH_2)_3OH)(dppe)_2]Br$$

FIGURE 1.4   Reactions between alkyl halides and $W(N_2)_2(dppe)_2$ reported by Diamantis, Chatt et al.[1]

reported a similar reaction involving $Mo(N_2)_2(dppe)_2$ and alkyl halides.[36] In the tungsten system it was found that in thf solvent when R=Me, X=Br, a green product was formed, which has since been found to be a diazobutanol complex $MBr(N_2(CH_2)_4OH)(dppe)_2$.[2] The butanol was believed to be derived from the attack of methyl radicals on thf, resulting in butyl radicals being formed. When R· derived from the alkyl halide was less reactive fewer butyl radicals were produced, some butyl complex was observed with R = ethyl. If CH_2Br_2 was used instead of RX the compound $WBr(N_2CH_2)(dppe)_2Br$ was formed which contains coordinated diazomethane, $N-N=CH_2$.[34]

A crystal structure of $WBr(N-NHCH_3)(dppe)_2Br$ has been reported,[35] the angles W-N(1)-N(2) and N(1)-N(2)-C were found to be 174° and 121° respectively. The bromide ligand was found to be *trans* to the $N-N-CH_3$ ligand. Various other similar structures have been reported, some are shown in figure 1.5.[36,37] Comprehensive tables of structural, electronic spectral, n.m.r. and infra red spectral data have been published.

Diazoalkane complexes have also been formed by the condensation of ketones with the grouping $W-N-NH_2$, to yield $W=N-N=CR^1R^2$ and with the grouping $W-NH-NH_2$ to yield $W-NH-N=CR^1R^2$. The complexes were found to yield secondary amines and ammonia upon reduction by $LiAlH_4$ and hydrazine and azines upon protonation by HBr (anhydrous).[38,39]

Similar complexes have been prepared from *trans*-$Mo(N_2)_2(dppe)_2$[40] and from *cis*-$Mo(N_2)_2(PMe_2Ph)_4$.[41] The novel compounds $MoX(N_2CH_2COOC_2H_5(dppe)_2$ (X = Cl,Br,I) have been produced from *trans*-$Mo(N_2)_2(dppe)_2$ and ethyl

FIGURE 1.5
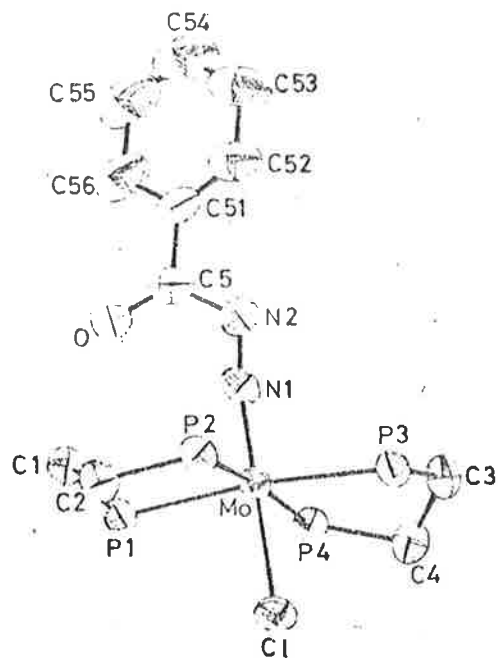
The structure of
MoCl(N$_2$COPh)(dppe)$_2$ from
Sato et al.[37],
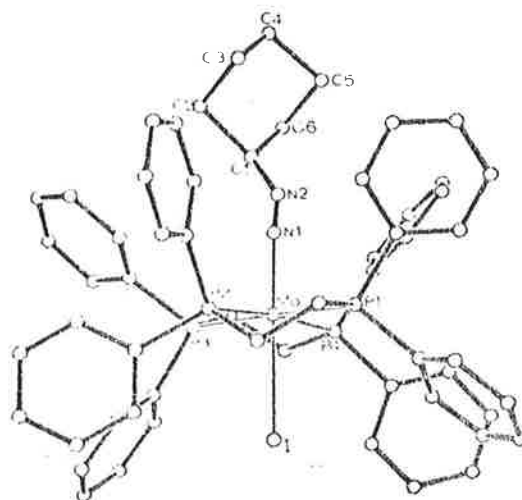
The structure of
MoI(N$_2$C$_6$H$_{11}$)(dppe)$_2$ from
Day et al.[36]
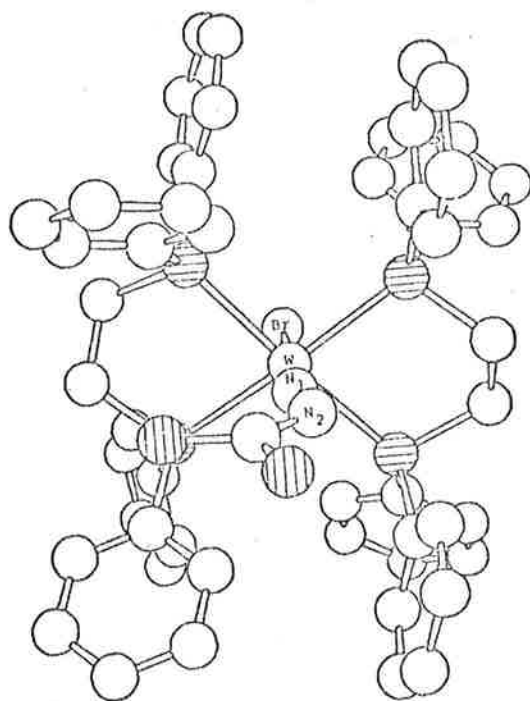
The structure of
[WBr(N$_2$CMe$_2$)(dppe)$_2$]$^+$
from Chatt et al.[73]

haloacetates ($XCH_2(CO)OCH_2H_5$). This reaction is of particular interest in that normally alkyl carbon-chlorine bonds do not add to a metal-N_2 moiety.[42]

The production of amines has previously been reported to occur upon either reducing $MBr(N_2R)(dppe)_2$ with $LiAlH_4$ (followed by hydrolysis by MeOH or acid) or by base distillation of $MBr(N_2R)(dppe)_2$.[43] Both amines and ammonia were reported to be produced from $MBr(N_2R)(dppe)_2$ (M = Mo, R = Bu, C_6H_{11}; M = W, R = Bu), upon sodium borohydride reduction at elevated temperature and pressure.[44]

1.7   Other substitution reactions

The dinitrogen coordination site can accept a number of other ligands; some of these such as ethylene bind reversibly,[17] others bind so strongly that the parent complex cannot be reformed.[45]

Organonitriles have been found to react with $Mo(N_2)_2(dppe)_2$ to yield $Mo(N_2)(RCN)(dppe)_2$.[46] When R = Me, or Et, the parent complex could be formed by treating the derivative by bubbling N_2 through a solution, however, when R was a substituted benzonitrile this could not be achieved, the benzonitrile being tightly bound to the metal centre. These monodinitrogen complexes were found to react with benzoyl chloride to give $MoCl(N_2COPh)(dppe)_2$ in very low yield.

The substitution kinetics for the reaction of Mo and W dinitrogen complexes with nitriles has been studied, and it has been shown that for the tungsten diphos complex the reaction requires light, while for the molybdenum diphos
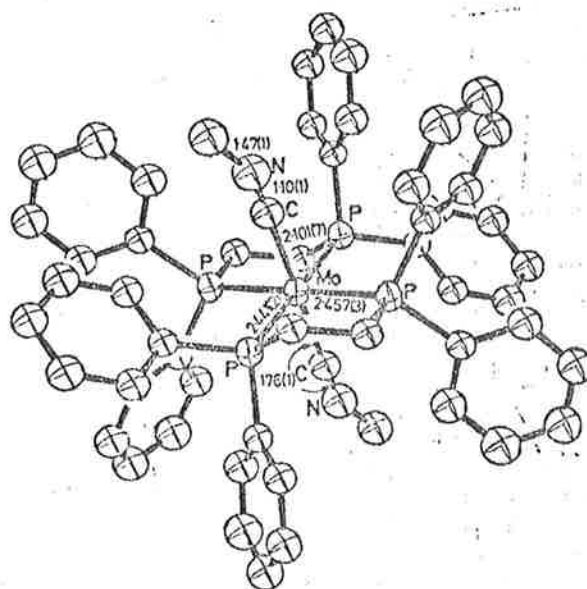
FIGURE 1.6   Structure of *trans*-Mo(CNMe)₂(dppe)₂.   From
             J. Chatt, A.J.K. Pombeiro, R.L. Richards
             and G.H.D. Royston, *J.C.S. Chem. Comm*,
             1975, 17, 708-709.[48]

complex the reaction occurs by a mechanism involving an initial rate determining dissociative step.[47]

Chatt et al have reported the formation of carbyne like ligands by protonation of ligating isonitriles and have produced an X-ray structure of $Mo(CNMe)_2(dppe)_2$[48] (figure 1.6), while Leigh and Pickett have studied the electrochemistry of organonitrile dinitrogen complexes of $Mo(N_2)(RCN)(dppe)_2$ and $W(N_2)(RCN)(dppe)_2$.[49]

Thiols and sulphonyl halides have been found to react with $Mo(N_2)_2$ according to the following scheme[45]:

$$Mo(N_2)_2(dppe)_2 + 2RSH \longrightarrow Mo(SR)_2(dppe)_2 + H_2 + 2N_2$$
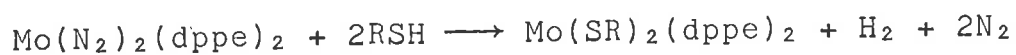
Carbonyl diphos complexes have been prepared by reacting CO with $Mo(N_2)_2(dppe)_2$[50] and by reduction of $WCl_4(dppe)$ under CO. In the former case $trans\text{-}Mo(CO)_2(dppe)_2$ is formed initially, this then isomerises to the cis isomer.[51,52] Ashwood has isolated $trans\text{-}Mo(CO)_2(dppe)_2$[3] by reacting $trans\text{-}Mo(N_2)_2(dppe)_2$ with CO at 0°C using visible light catalysis using techniques developed in this work. In this work $trans\text{-}W(CO)_2(dppe)_2$ has been produced in the same way, upon warming this compound it isomerises to the cis form.

A monodinitrogen-monocarbonyl-molybdenum-diphos complex has been isolated (formed from dmf plus $Mo(N_2)_2(dppe)_2$ under nitrogen).[53] This mixed complex can also be formed from $Mo(N_2)_2(dppe)_2$ in refluxing benzene containing benzyl propionate and can in turn be used to produce the five coordinate $MoCO(dppe)_2$.[54]

1.8 Reviews of metal dinitrogen complex chemistry

The general field of metal dinitrogen complexes has been the subject of a number of reviews which have covered; preparation and properties,[55] bonding of N_2 to transition metals,[56] molecular orbital calculation,[57] and formation of N-C bonds.[58]

Others have considered the mechanism of nucleophilic attack on coordinated N_2,[59] the relationship between structural factors and redox potentials of dinitrogen complexes[60] and the binding of N_2 hydrides to molybdenum.[61]

1.9 Mechanism of reaction of $M(N_2)_2(dppe)_2$ with alkyl halides

The nature of the mechanism of the reaction between $M(N_2)_2(dppe)_2$ and alkyl halides has been the subject of much speculation, some based on purely theoretical beliefs,[62] other based on solid experimental evidence.[63]

Budge[62a] has elaborated upon a theory due to Feltham[62b] and suggested a halide catalysed mechanism (figure 1.7) for the reaction of $M(N_2)_2(dppe)_2$ with acyl halides and HBr. He also suggested that the light catalysed reaction of $M(N_2)_2(dppe)_2$ with CH_2Br_2 occurs via a charge transfer from metal to ligand (involving two electrons) resulting in the formation of a M(II) centre which then undergoes an increase in coordination number from 6 to 7. This results in coordination of $BrCH_2Br$. Metal assisted bond cleavage and ligand migration then occur, and result in the grouping $BrWN_2CH_2Br$. The terminal Br is then eliminated, to yield the diazomethane ligand.
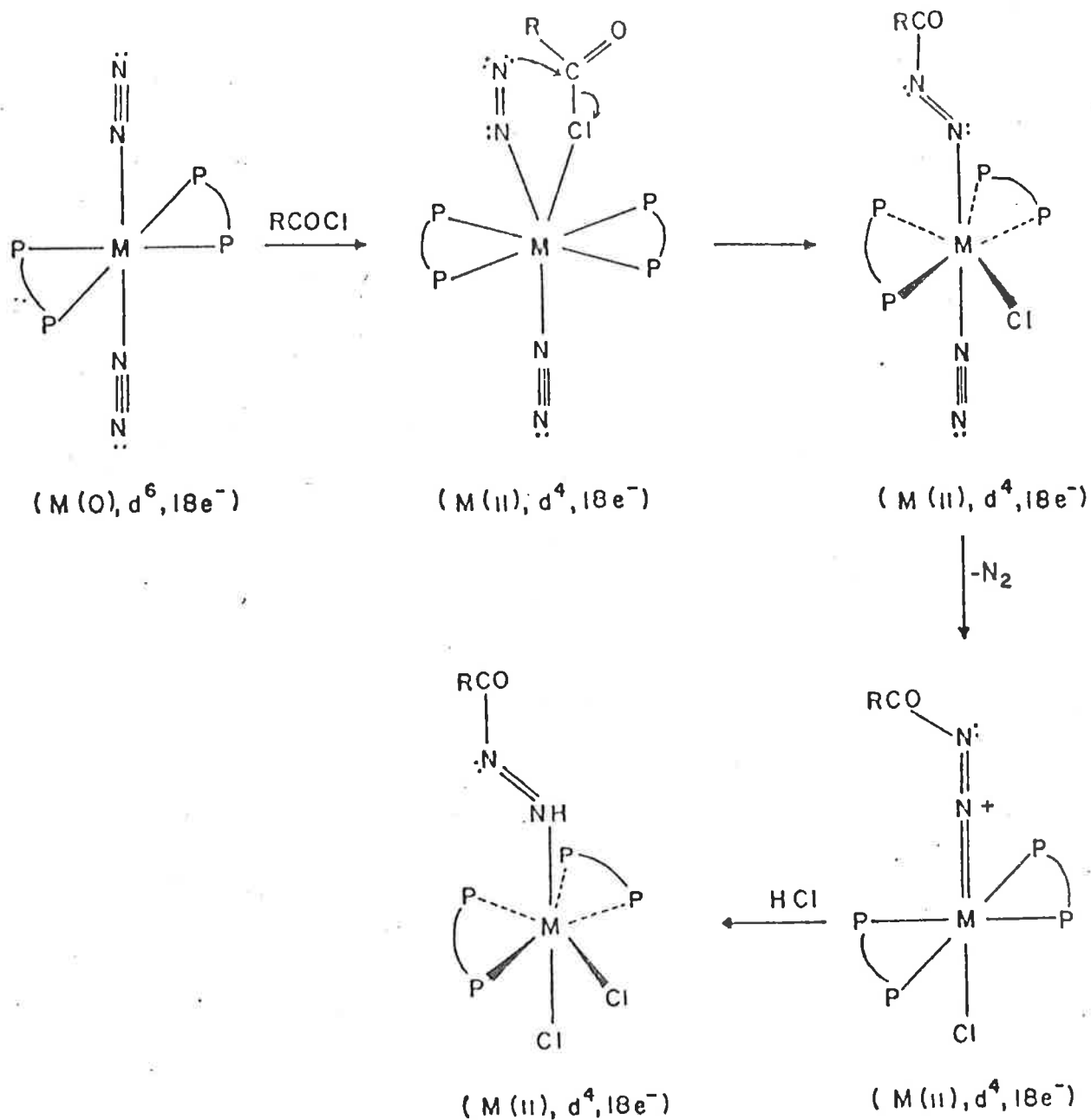
FIGURE 1.7 Mechanism postulated by Budge[62a] for the photochemically induced reaction between *trans*-M(N₂)₂(dppe)₂ and RCOCl (M=Mo, W).

A similar mechanism was also suggested for the formation of the tungsten diazobutanol complex (figure 1.8), however, for reasons discussed below this would appear unlikely, and the more probable mechanism is a variant of that suggested by Chatt.[63,64]

A charge transfer mechanism has also been suggested by George.[65]

Chatt[63,64] has drawn together preparative results and e.s.r. studies of the reaction of $M(N_2)_2(dppe)_2$ with RX, and suggested the mechanism below.

$$M(N_2)_2(dppe)_2 \rightleftharpoons M(N_2)(dppe)_2$$
$$\downarrow$$
$$(RX)M(N_2)(dppe)_2$$
$$\downarrow$$
$$XM(N_2)(dppe)_2 + R$$
$$\downarrow$$
$$XM(N_2R)(dppe)_2$$
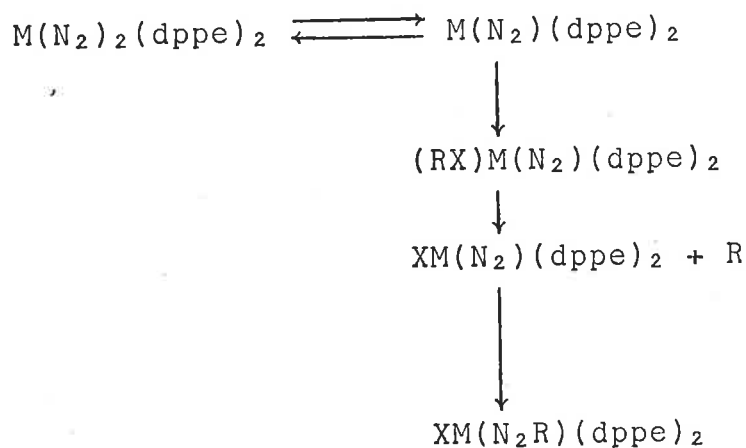
The following observations were made[63]:

(1) Light is required in the tungsten system, not in the molybdenum.

(2) Redox potentials for $Mo(N_2)_2(dppe)_2$ and $W(N_2)_2(dppe)_2$ are similar.

(3) Charge transfer spectra for $Mo(N_2)_2(dppe)_2$ and $W(N_2)_2(dppe)_2$ are similar.

(4) Reaction in thf with a 100 fold excess of alkyl halide is pseudo first order in $M(N_2)_2(dppe)_2$.*

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* The light catalysed reaction tends to appear first order because I_{abs} decreases during the process of the reaction, thus the rate (equal to $I_{abs}\phi$) decreases proportionately to the amount of complex used.
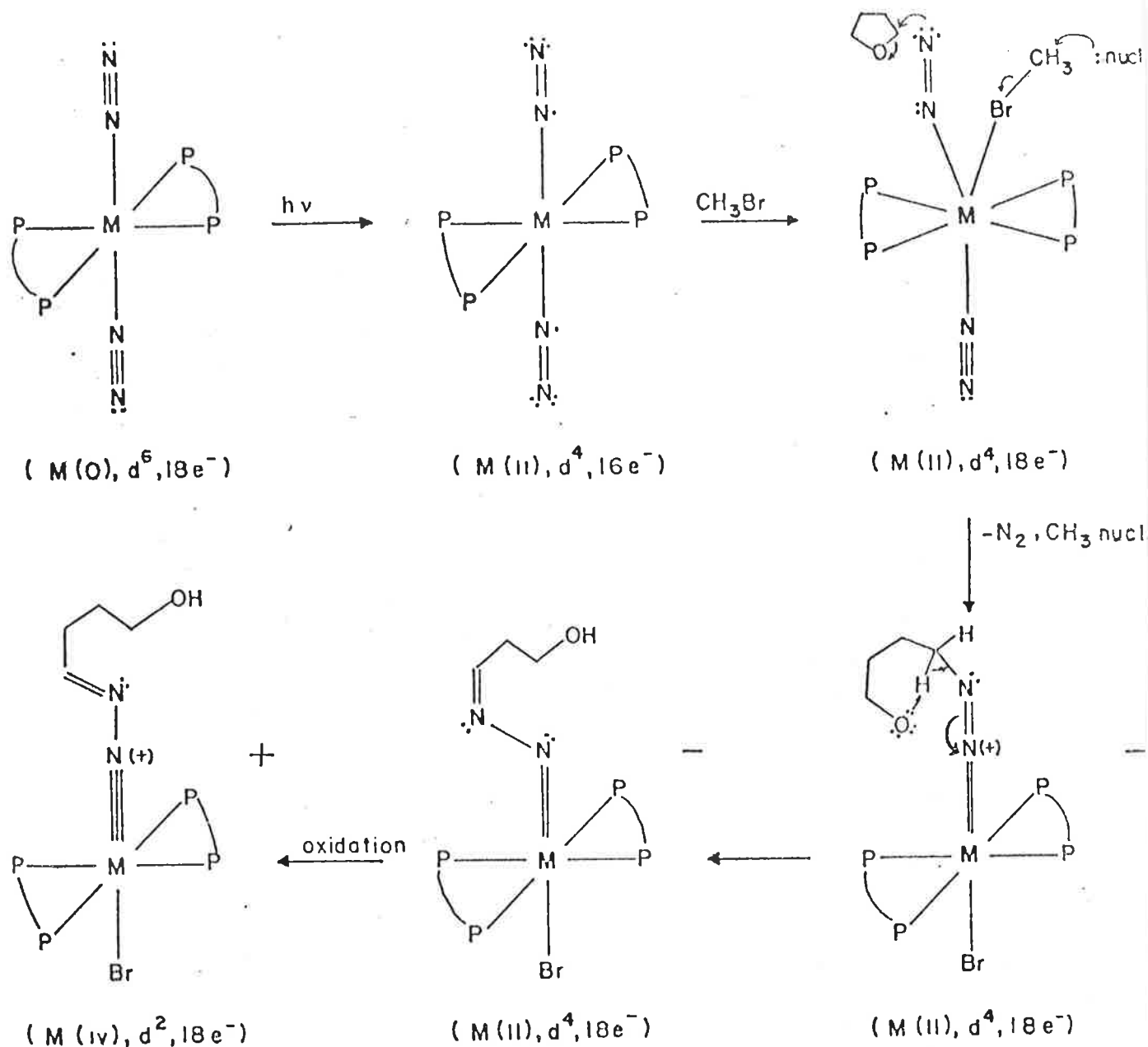
FIGURE 1.8 Mechanism postulated by Budge[62a] for the photochemically induced reaction between trans-M(N₂)₂(dppe)₂ and thf in the presence of CH₃Br in dinitrogen saturated thf solution. (M=Mo, W).

(5) One mole of N_2 is evolved whether the reaction is carried out under N_2 or argon.

(6) The observed rates are sensibly independent of R. for Me, Et or Bu.

(7) The CO substitution

$$M(N_2)_2(dppe)_2 + 2CO \longrightarrow M(CO)_2(dppe)_2 + 2N_2$$

requires light activation for W, not for Mo.[*]

(8) $^{14}N_2/^{15}N_2$ isotope exchange occurs slowly in the diffuse daylight for Mo, but not W.[*]

(9) The kinetics of

$$Mo(N_2)_2(dppe)_2 + PhCN \longrightarrow Mo(N_2)(PhCN)(dppe)_2 + N_2$$
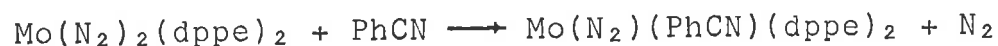
are typical of dissociative mechanism.

(10) When R· is highly reactive it can react with thf, when not very reactive R_2 can form.

(11) R· can be trapped using nitrosodurene and observed by e.s.r.

(12) 6-Br-hexene reacts with $M(N_2)_2(dppe)_2$ to yield 1,5 cyclised ligand in the complex $BrM(N_2CH_2\overline{CH(CH_2)_2CH_2})(dppe)_2$.
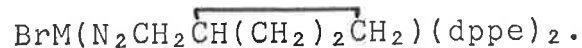
(13) The radical ·$BrCH_2CH_2Br$ has been observed in the reaction of $BrCH_2CH_2Br$ with $Mo(N_2)_2(dppe)_2$.

Further discussion[64] of these points has been published and rates of the reaction of $Mo(N_2)_2(dppe)_2$ with various substrates in the dark determined. All rates were found to lie around $k = 1.3 \pm .2 \times 10^{-4}$ sec^{-1} (20°C).

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[*] The Mo exchange reaction will occur in total darkness, for tungsten Rate $\propto I_{abs}\phi$, for molybdenum Rate $\propto (k_x + I_{abs}\phi)$.

In general, the results obtained by Chatt et al and the conclusion drawn, are in accord with this work, except that in this work an initial release of two dinitrogen ligands is postulated followed by a rapid uptake of one N_2 group, e.g.

$$W(N_2)_2(dppe)_2 \longrightarrow W(dppe)_2 \longrightarrow W(N_2)(dppe)_2$$

From this stage on the mechanism is believed to be identical to that shown above.

Carter[66] has studied the U.V./visible spectra of $Mo(N_2)_2(dppe)_2$ and has reached conclusions sensibly in agreement with those reached in this work and by Ashwood.[3] Carter assigned the absorbance in the far U.V. to intra-ligand bands, the peak at *ca.* 300 nm to $M \longrightarrow N_2$ charge transfer, and the envelope trailing into the visible to d-d and MLCT bands. These results were sensibly in accord with those reported by Caruana and Kisch.[72]

1.10 Photochemistry of inorganic complexes

The photochemistry of inorganic complexes has been the subject of a number of reviews,[67] the photochemistry of complexes of the heavier transition metals has also been discussed.[68] Wrighton[69] has reviewed the photochemistry of metal carbonyls, the field is interesting in some of the similarities to the photochemistry of metal dinitrogen complexes. He has also considered mechanistic aspects of the photochemical reactions, of coordination compounds.[70] The monograph by Balzani[71] has been used extensively for references in this work.

The theory of photochemical reactions is discussed in chapter three, however, a few concepts are discussed below.

The rate of a photochemical reaction is governed purely by the number of quanta of light absorbed, multiplied by ϕ, the quantum yield. Quantum yield simply reflects the probability of an excited species (which has absorbed light) reacting. The quantum yield for a reaction at any wavelength is normally independent of factors such as light intensity, although P or T changes may change ϕ.[71]

Photochemical reactions of metal complexes fall into a number of classes (1) Photosolvolysis (2) photoreduction (of metal centre) (3) photooxidation (of metal centre) (4) photooxidation (of metal complex, concomitant with photoreduction of solvent). The type of reaction which occurs can be influenced by the type of transition which is induced by absorption of light.

In this work the reactions observed generally appear to involve d-d transitions which result in loss of ligands, probably followed by solvolysis. Such reactions have been observed in many metal complexes, such as in metal hexacarbonyls, $M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO$.[69]

The test as to whether a reaction is photochemical or thermal is simply to isolate the reaction system from light, and compare the rate observed with that observed in the light. Three possible cases can occur:

(1) photochemical reaction, no thermal reaction.

Rate $\propto I_{abs}\phi$.

(2) Thermal reaction, no photochemical reaction.

Rate $\propto k_1[A]$. (First order reactions)

(3) Thermal reaction plus photochemical reaction.

Rate $\propto k_1[A] + I_{abs}\phi$.

In this work both cases 1 and 3 have been observed, as well as the usually encountered case 2. $W(N_2)_2(dppe)_2$ undergoes the reaction

$$W(N_2)_2(dppe)_2 \longrightarrow W(dppe)_2 + 2N_2$$
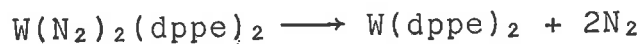
only in the light, while the reaction

$$Mo(N_2)_2(dppe)_2 \longrightarrow Mo(dppe)_2(N_2)_{2-x} + xN_2$$
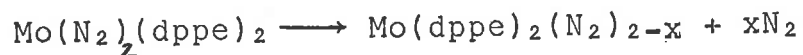
occurs in the dark, but is accelerated by visible light irradiation.[3] Conclusive evidence of the photochemical nature of both the Mo and W reactions has been achieved using the technique of flash photolysis.

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CHAPTER 2

2.1 Preparation and characterisation of W(N₂)₂(dppe)₂

2.1.1 Preparation

Various syntheses of *trans-Bis*(dinitrogen)-*bis*(bisdiphenylphosphinoethane)tungsten(0) have been reported in the literature.[1,2,3] It was found that the reaction of WCl₄(dppe) with dppe, N₂ and sodium amalgam (*ca.* 2%) readily yielded the orange *bis*-(dinitrogen) *bis*-(diphos) complex, however it had been reported that magnesium will reduce WCl₄(dppe) in a more convenient synthesis.[2] This was achieved in this work provided that strictly anaerobic and moisture free conditions were used. If the reaction mixture became contaminated with water or air the principal product was a yellow compound postulated to be W.Cl.₂(dppe)₂ The following method was used to prepare W(N₂)₂(dppe)₂. W(Cl)₄(dppe) was prepared by the standard procedure from WCl₆,[2] and dried thoroughly in vacuo. This product (*ca.* 10 g.) was placed in a two litre flask with Mg (*ca.* 15 g.), dppe (*ca.* 6 g.) and a magnetic stirrer. The flask was evacuated using a rotary vacuum pump with a liquid nitrogen trap for approximately 30 minutes, while attached to the solvent still. Dry, freshly distilled thf (dinitrogen saturated, *ca.* 200 cm³.) was introduced into the flask, and the flask filled with dinitrogen and removed from the still. A flow of dry high purity dinitrogen was maintained through the reaction vessel while the mixture was stirred vigorously for approximately 3 hours. Occasionally a small crystal of iodine was added to start the reaction, however, this was not

normally needed. The resulting dark red/brown solution was filtered, and orange crystals of the product recovered by condensing the mother liquor to 50% of the original volume and cooling overnight at circa 2°C. This crude product was recrystallised from thf to a constant extinction coefficient at 297 nm. Normally three crystallisations were sufficient.

2.1.2 Spectral properties

(i) Electronic and vibrational

The infra red spectrum which was dominated by $\nu(N-N)_{asy}$ at 1945 *to 1950* cm^{-1} (figure 2.1.1) was found to be consistent with that reported in the literature. The symmetry forbidden $\nu(N-N)_{sym}$ was also observed at 2000 cm^{-1} as a very weak broad signal.

It was found that provided strictly oxygen and moisture free conditions were used solutions sufficiently dilute to enable ultra-violet spectra to be determined could be prepared and handled in the light. The U.V./visible spectrum obtained is shown (figure 2.1.2). The absorption between 210 and 260 nm with $\epsilon \doteqdot 6 \times 10^4$ mol^{-1} dm^{-1} was observed in all *bis*(bisdiphenylphosphinoethane) complexes of tungsten studied in this work, and also in dppe alone, and was therefore believed to involve intra-ligand transition with possibly some contribution from charge transfer between ligand and the metal centre.

It was found that during reactions of $W(N_2)_2(dppe)_2$ the intensity of absorption at 297 nm declined at the same rate as the $\nu(N-N)_{asym}$ stretch at 1950 cm^{-1} in the
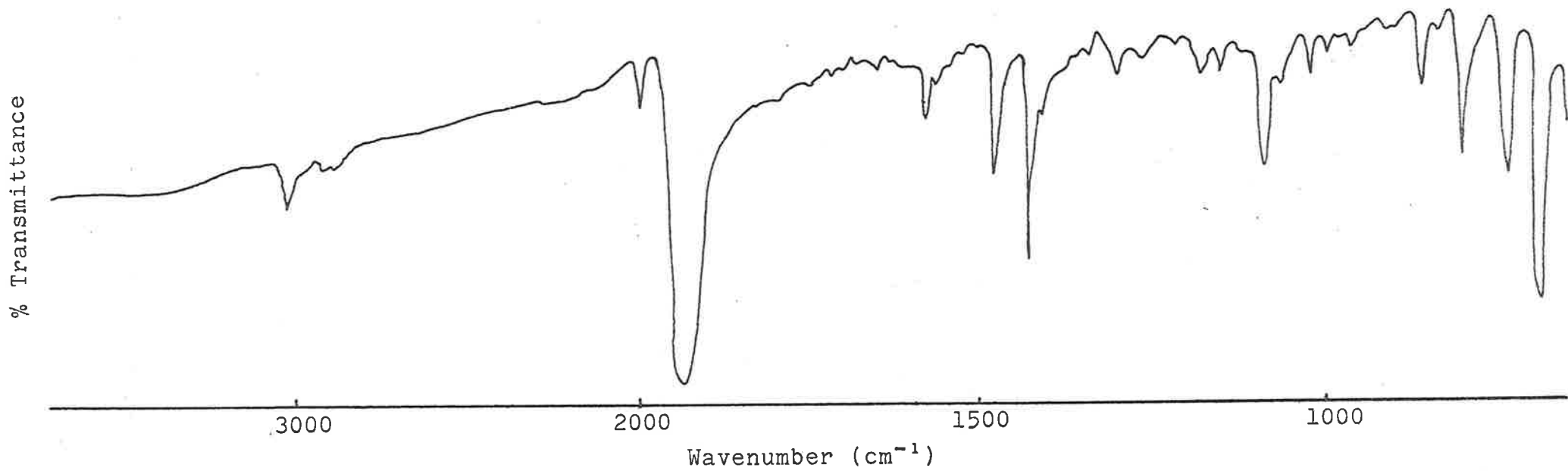
FIGURE 2.1.1   I.R. spectrum of $W(N_2)_2(dppe)_2$ (KBr disc).

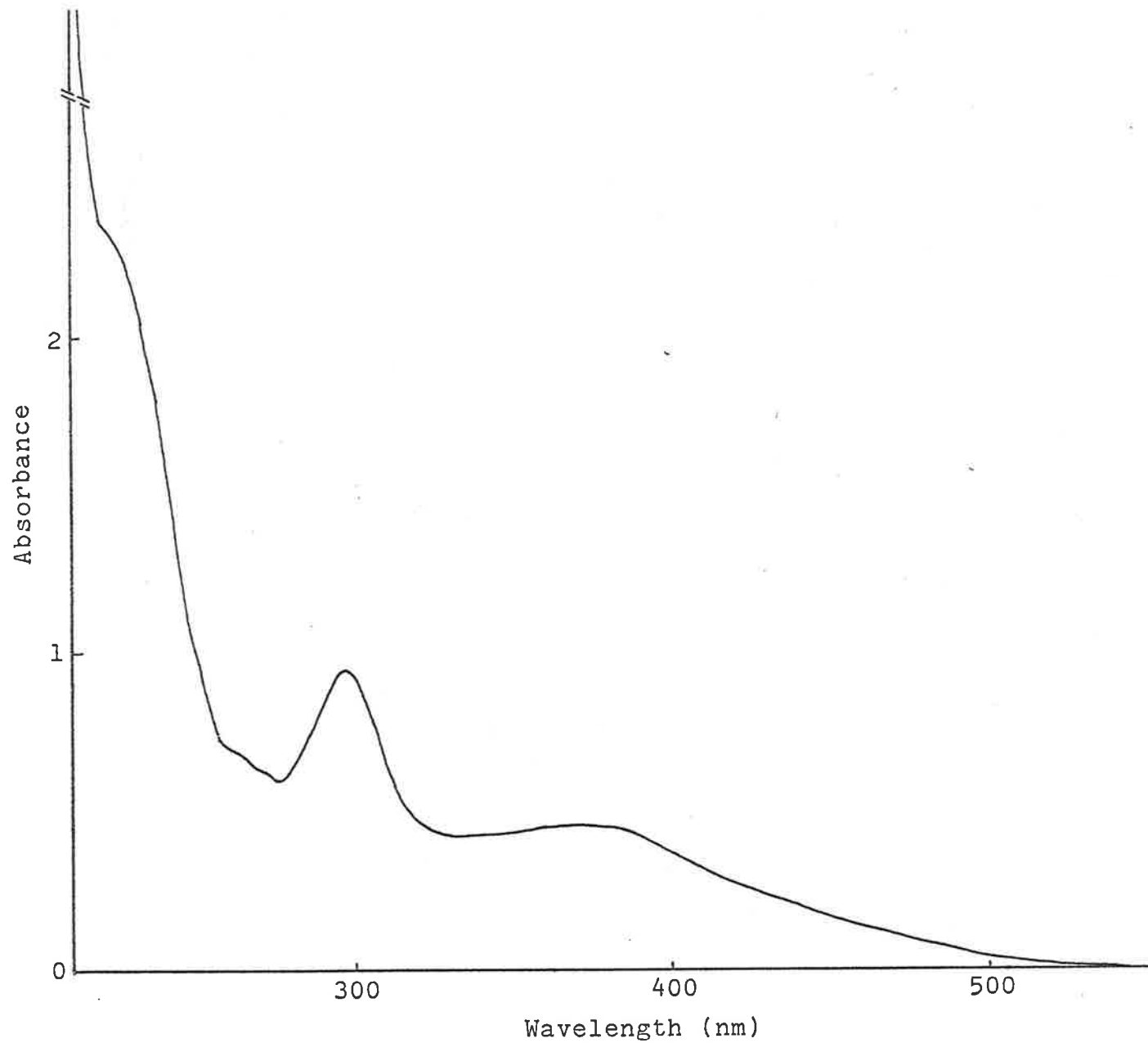FIGURE 2.1.2 UV/visible spectrum of $W(N_2)_2(dppe)_2$ in thf (3.03×10^{-4} molar, 1 mm cell).

infra red spectrum. This absorption was not observed in the spectra of other tungsten diphos complexes, and was therefore believed to involve M$\longrightarrow$N$_2$ charge transfer. This absorption had $\varepsilon = 3.1 \times 10^4$ cm^{-1} dm^3 mol^{-1}. Metal dinitrogen charge transfer bands have previously been observed in the u.v. spectrum of metal dinitrogen complexes; for example at 208 nm in [(NH$_3$)$_5$OsN$_2$]Cl$_2$.[31] ($\varepsilon = 2.5 \pm .3 \times 10^4$ cm^{-1} dm^3 mol^{-1}).

The broad plateau observed between 330 and 520 nm was present in most dppe complexes of tungsten, however, it was generally much less intense unless one other ligand contained a multiply bonded dinitrogen group (e.g. W-N=N-R complexes). The extinction coefficient was found to decrease upon protonating the ligand. A possible explanation is that this plateau involved both d-d transition at the tungsten centre and metal to ligand charge transfer.

Ashwood[4] and George[5] have shown that the related complex Mo(N$_2$)$_2$(dppe)$_2$ has a very similar spectrum, with M$\longrightarrow$N$_2$ charge transfer at 308 nm.

(ii) N.M.R. Spectra

A 90 MHz pulsed fourier transform ^{1}H n.m.r. spectrum (fig. 2.1.3) revealed aromatic signals assigned to dppe and aliphatic signals due to the ethane bridge in the phosphine ligand. The integrals for the two areas were in the ratios 5.1 : 1.0 (Expected 5 : 1).

A 36.435 MHz p.f.t. ^{31}P n.m.r. spectrum of a solution of W(N$_2$)$_2$(dppe)$_2$ in C$_6$D$_6$ revealed a singlet. The chemical shift of this singlet was not measured. A 67.89 MHz p.f.t. ^{13}C n.m.r. spectrum of a solution of
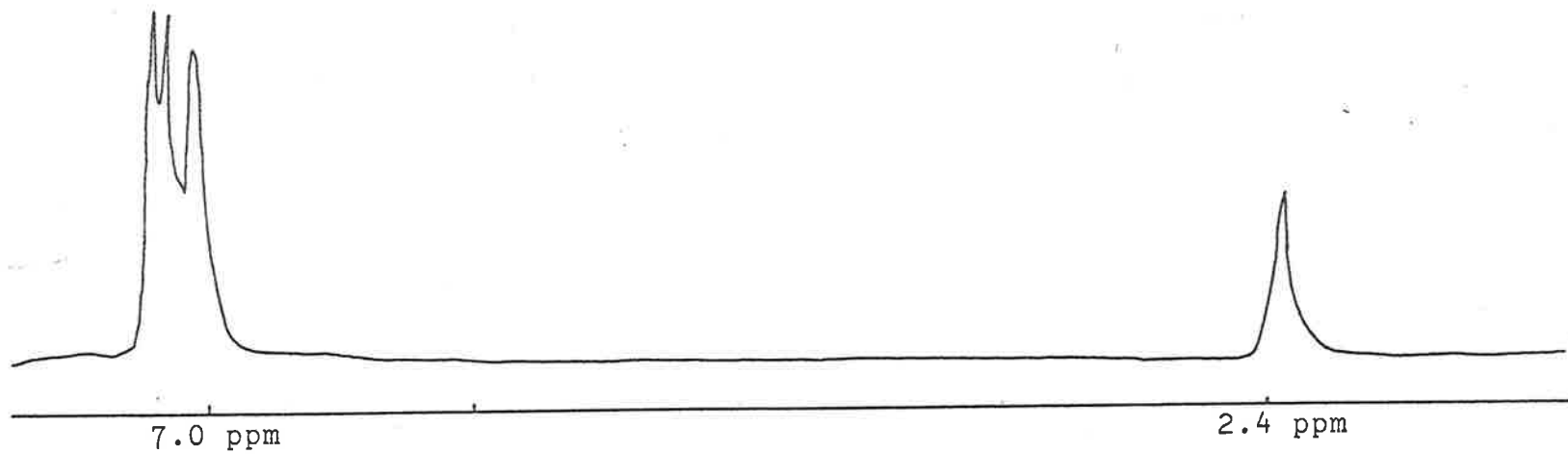
7.0 ppm   2.4 ppm

FIGURE 2.1.3   90 MHz ^{1}H nmr spectrum of *trans*-$[W(N_2)_2(dppe)_2]$ in C_6D_6.

$W(N_2)_2(dppe)_2$ in C_6D_6 (fig. 2.1.4) revealed signals due to the carbons in the phenyl rings and in the ethane bridge of the phosphine ligand. Both phenyl carbon atoms and the bridging carbon atoms experience splitting due to coupling with phosphorus. The bridging ethane carbons give a deceptively simple spectrum, which looks like a classic triplet, but is in fact the result of $^1J_{P-C}$, $^1J_{P-C-C}$ and $^3J_{P-W-P-C}$. This type of anomalous spectrum has been reported previously for ^1H n.m.r. spectra of complexes of dppe.[6]

2.1.3 Chemical Properties

$W(N_2)_2(dppe)_2$ is an "18 electron" diamagnetic, orange coloured complex which is moderately stable and insensitive to air or moisture when in the solid state, unless exposed to intense light.

The complex is probably isostructural with $Mo(N_2)_2(dppe)_2$ [7] (fig. 2.1.5) since they have similar vibrational, electronic and nuclear magnetic resonance spectra and chemical and electrochemical properties.[8]

As has been discussed, the complex reacts with alkyl bromides to yield diazenido complexes, acyl chlorides to yield acylazo complexes and as is discussed below, a variety of other small molecules to yield substitution products where the dinitrogen ligands (or ligand) have been replaced. (Table 2.1)

Diamantis, while at the University of Sussex, had noted that a solution of .5 g. of the dinitrogen complex in *ca*. 50 mls. of thf was stable under irradiation by a 100 watt tungsten filament lamp for 3 hours; accordingly
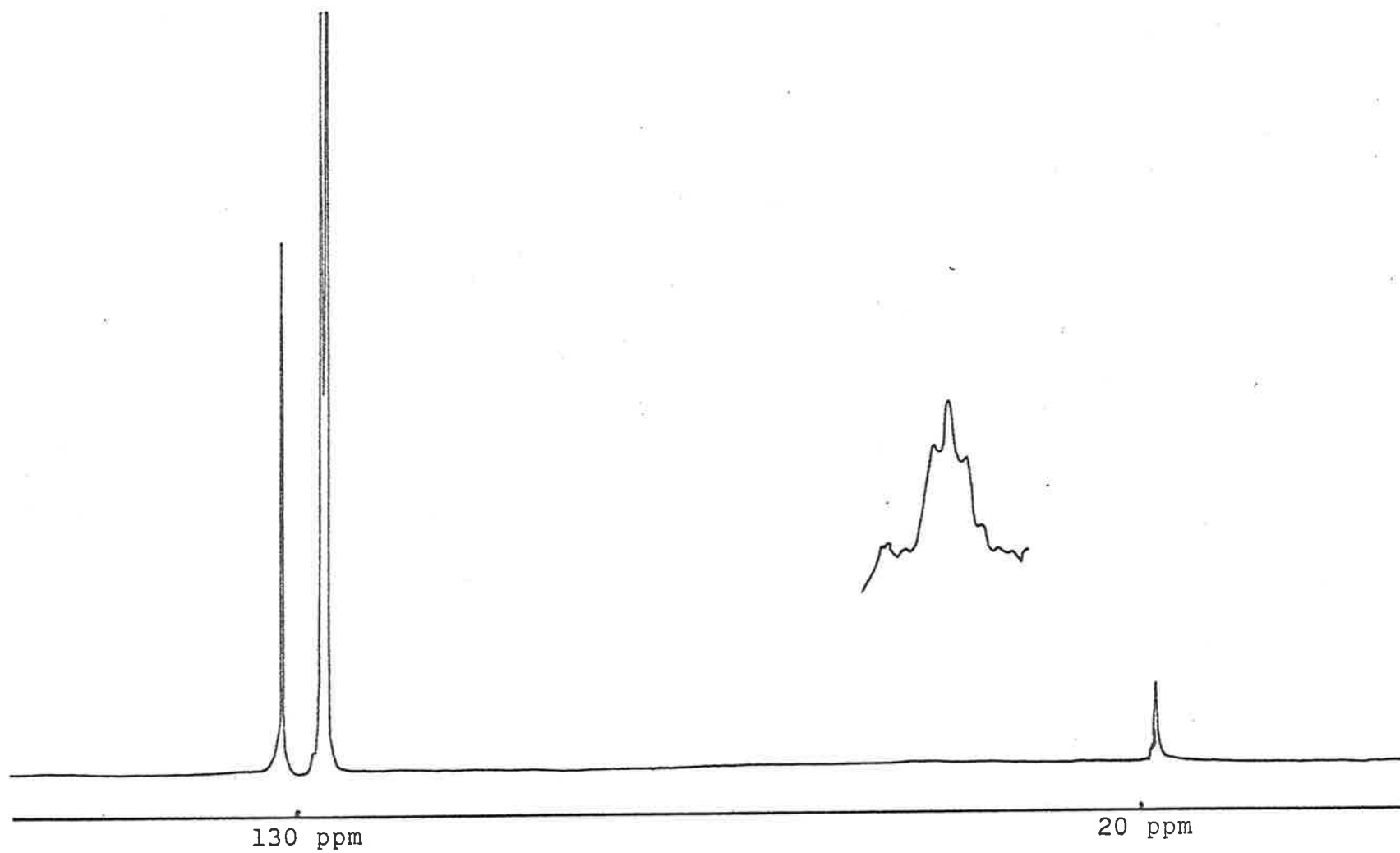
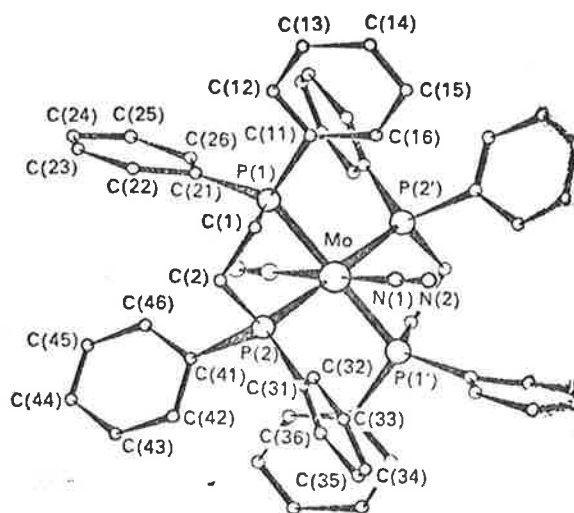FIGURE 2.1.4   67.89 MHz ^{13}C nmr spectrum of *trans*-[W(N$_2$)$_2$(dppe)$_2$] in C$_6$D$_6$.

FIGURE 2.1.5 Structure of *trans*-[Mo(N₂)₂(dppe)₂] (from T. Uchida, Y. Uchida, M. Hidai and T. Kodama, *Acta Cryst.*, 1975, B31, 1197).

Table 2.1.1

Reactions of $W(N_2)_2(dppe)_2$ under a variety of conditions at 30°C.

Reactant, conditions[b]	Reactions observed[a]
N_2 saturated thf solution[c]	*ca.* 5% decomposition in 3 hours
N_2 saturated benzene solution	*ca.* 6% decomposition in 3 hours
Ar saturated thf solution	$t_{\frac{1}{2}}$[d] for decomposition 2 hours
Vacuum, thf solution	$t_{\frac{1}{2}}$ for decomposition 2 hours
$^{15}N_2$, thf solution of $W(^{14}N_2)_2(dppe)_2$	$W(^{15}N_2)_2(dppe)_2$, $W(^{15}N_2)(^{14}N_2)dppe$ plus $W(^{14}N_2)_2(dppe)_2$ isolated after 2 hours
$^{14}N_2$, thf solution of $W(^{15}N_2)_2(dppe)_2$	no reaction observed (in dark)
CO atmosphere, benzene solution	$t_{\frac{1}{2}}$ *ca.* 45 minutes for conversion
CO atmosphere, thf solution	to $t\text{-}W(CO)_2(dppe)_2$
H_2 atmosphere, benzene solution	$t_{\frac{1}{2}}$ *ca.* 40 minutes for conversion
H_2 atmosphere, thf solution	to $W(H)_4(dppe)_2$
N_2O atmosphere, thf solution	$t_{\frac{1}{2}}$ *ca.* 50 minutes
NO atmosphere, thf solution	$t_{\frac{1}{2}}$ *ca.* 50 minutes
C_2H_4 atmosphere, thf solution	$t_{\frac{1}{2}}$ *ca.* 60 minutes

Table 2.1.1 (Continued)

Reactant, conditions[b]	Reactions observed[a]
2, 2-bromomethylpropane, thf solution	$t_{\frac{1}{2}}$ *ca*. 45 minutes formation of $BrWNN-C-(CH_3)_3$
2-bromobutane, thf solution	$t_{\frac{1}{2}}$ *ca*. 45 minutes formation of $BrW(NN-CH-CH_2-CH_3)$ CH_3
1-bromobutane , thf solution	$t_{\frac{1}{2}}$ *ca*. 50 minutes formation of $BrWNN-(CH_2)_3-CH_3$
6-bromohexene, C_6H_6 solution	$t_{\frac{1}{2}}$ *ca*. 50 minutes for formation of,

$$
\begin{array}{c}
\text{H}_2\ \text{H}_2 \\
\text{C—C} \\
BrWNN\!-\!\!C\!-\!\!C \diagup \quad \diagdown \\
\text{H}_2 \quad \text{C—C} \\
\text{H}_2\ \text{H}_2
\end{array}
$$
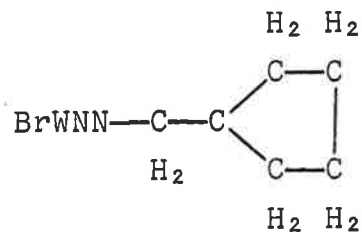
CH_3COCl, thf solution	$t_{\frac{1}{2}}$ *ca*. 55 minutes formation of $BrWNNCOCH_3$
PMe_3, thf solution	$t_{\frac{1}{2}}$ *ca*. 55 minutes
PMe_2Ph, thf solution	$t_{\frac{1}{2}}$ *ca*. 50 minutes
$PHBu_2$	slow reaction ($t_{\frac{1}{2}}$ 6 hours) in light, no reaction in dark
H_2O, thf solution	$t_{\frac{1}{2}}$ for decomposition *ca*. 25 minutes

Table 2.1.1 (Continued)

Reactant, conditions[b]   Reactions observed[a]

air, atmosphere, thf solution $t_{\frac{1}{2}}$ for decomposition $ca.$ 20 minutes

HBr, thf solution   Immediate formation of $\left[BrWN_2H_2(dppe)_2\right]^+$ in the dark

(a) For all reactants other than acid no reaction was observed in the dark, the reactions
    described above occurred under irradiation by two 100 Watt tungsten filament lamps at a
    distance of $ca.$ 60 cm from the reaction vessel.

(b) Typically .4 g. $W(N_2)_2(dppe)_2$ in 60 cm^3 of solvent.

(c) All gases used were flowing slowly over the solution during the reaction, except $^{15}N_2$.

(d) $t_{\frac{1}{2}}$ refers to the time for the concentration of $W(N_2)_2(dppe)_2$ to fall to half the initial
    concentration.

(e) This reaction has been reported to occur without light, however, in the complete absence of
    moisture, light is definitely required to cause the reaction to occur.

initially the test of reproducing this result was used as one of the criteria for purity of the complex.

It was found that this could be achieved provided that air and moisture were excluded from the solution effectively, and therefore reaction vessels used in this work were thoroughly dried by pumping down (after all non volatile solids had been added) while attached to the solvent still.

2.2.1 Reactions of $W(N_2)_2(dppe)_2$ with small molecules

Reactions between $W(N_2)_2(dppe)_2$ in solution and various species were studied initially by measuring the intensity of the $\nu(N-N)_{asym}$ infra red signal in solution. Approximately .5 g. of $W(N_2)_2(dppe)_2$ was dissolved in $ca.$ 50 cm^3. of dry solvent in a round bottomed schlenck flask and stirred magnetically and some reactant added. The rate of the reaction was observed in the presence of light and the absence of a dark reaction was confirmed in each case. The results of such studies with a range of reactant and a variety of conditions are given in table 2.1.1. It was found that in the majority of these reactions $t_\frac{1}{2}$ depended on two factors, (a) the amount of $W(N_2)_2(dppe)_2$ present, and (b) the intensity of light. Upon increasing the amount of $W(N_2)_2(dppe)_2$ the $t_\frac{1}{2}$ increased as a linear function of the mass, (or number of moles) present. The rate of the reaction increased as the irradiating light intensity increased, and decreased to very close to zero in the dark. These observations suggested that the rate of the reaction was controlled by the rate of absorption of photons by $W(N_2)_2(dppe)_2$ in

solution. Since visible light was used in these reactions and the other reactants were colourless, the obvious inference was that $W(N_2)_2(dppe)_2$ was the species involved in the photochemical step, since "only radiations which are absorbed by the reacting system can be effective in producing chemical change".[9]

The results show that a general class of photochemical reactions of $W(N_2)_2(dppe)_2$ exists, and that the photochemical reactions of $W(N_2)_2(dppe)_2$ present a convenient synthetic technique, yielding compounds such as $trans\text{-}W(CO)_2(dppe)_2$ and $BrW(N_2R)(dppe)_2$.

The reaction conditions used, characterisation of the products of the reactions and the significance of these reactions is discussed below.

2.2.2 Stability under N_2, Ar and vacuum

It was found that solutions in dry oxygen free solvent saturated with dinitrogen were stable for a number of hours under a high flux of light (e.g. when 4×10^{-6} moles were exposed to $ca.$ 10^{-8} Einstein/second).[*] However, when the solutions were irradiated under dry, high purity argon or in vacuo the complex decomposed. This was interpreted as signifying the existence of a photostationary state involving the labilisation and reattachment of at least one dinitrogen ligand upon irradiation by visible light.

$$W(N_2)_2(dppe)_2 \underset{N_2}{\overset{h\nu}{\rightleftharpoons}} W(N_2)_{2-x}(dppe)_2 + xN_2$$

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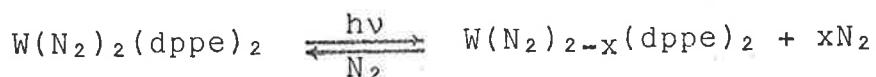
[*] Except when the solvent contained a reactive group; such as CH_2Cl_2 or $CHCl_3$.

In the presence of solvated dinitrogen the reverse
reaction was facilitated, but when $[N_2]_{solv}$ was low, as was
the case when the solution was under argon or in vacuo, the
reverse reaction was slowed down, allowing the intermediate
to react with any other species in the solution. It was
found that if dinitrogen was reintroduced into a vessel
containing a solution under argon or in vacuo, which had
been irradiated, no increase in the $\nu(N-N)_{asym}$ occurred,
that is, the intermediate was short lived (lifetime less than
ca. 1 minute). It was found that traces of moisture or
air could cause solutions under dinitrogen to decompose
when irradiated, thus water and oxygen probably inhibit
the reverse reaction by reacting with the active
intermediate. Solutions were found not to be as
sensitive to air or moisture in the absence of light.

2.2.3 Reactions with isotopically labelled dinitrogen

Irradiation of a solution of $W(N_2)_2(dppe)_2$ under
an atmosphere of $^{15}N_2$(48% $^{15}N-^{15}N$; 6% $^{15}N-^{14}N$; 46% $^{14}N-^{14}N$)
resulted in the appearance of 3 new bands in the infra red
spectrum in the region 2200 to 1800 cm^{-1}, and an increase in
the intensity of the (forbidden) $\nu(N-N)_{sym}$ band (fig. 2.2.1).
The new bands were observed at 1904, 1885 and 1986 cm^{-1},
and were assigned to $\nu(N-N)_{asym}$ for $W(^{15}N_2)(^{14}N_2)(dppe)_2$,
$\nu(N-N)_{asym}$ for $W(^{15}N_2)_2(dppe)_2$ and $\nu(N-N)_{sym}$ for
$W(^{15}N_2)(^{14}N_2)(dppe)_2$.

The shift in frequency caused by isotopic
substitution can be approximated by $\nu_2 = \nu_1 * \sqrt{m_1/m_2}$,
however this rule is known to break down for
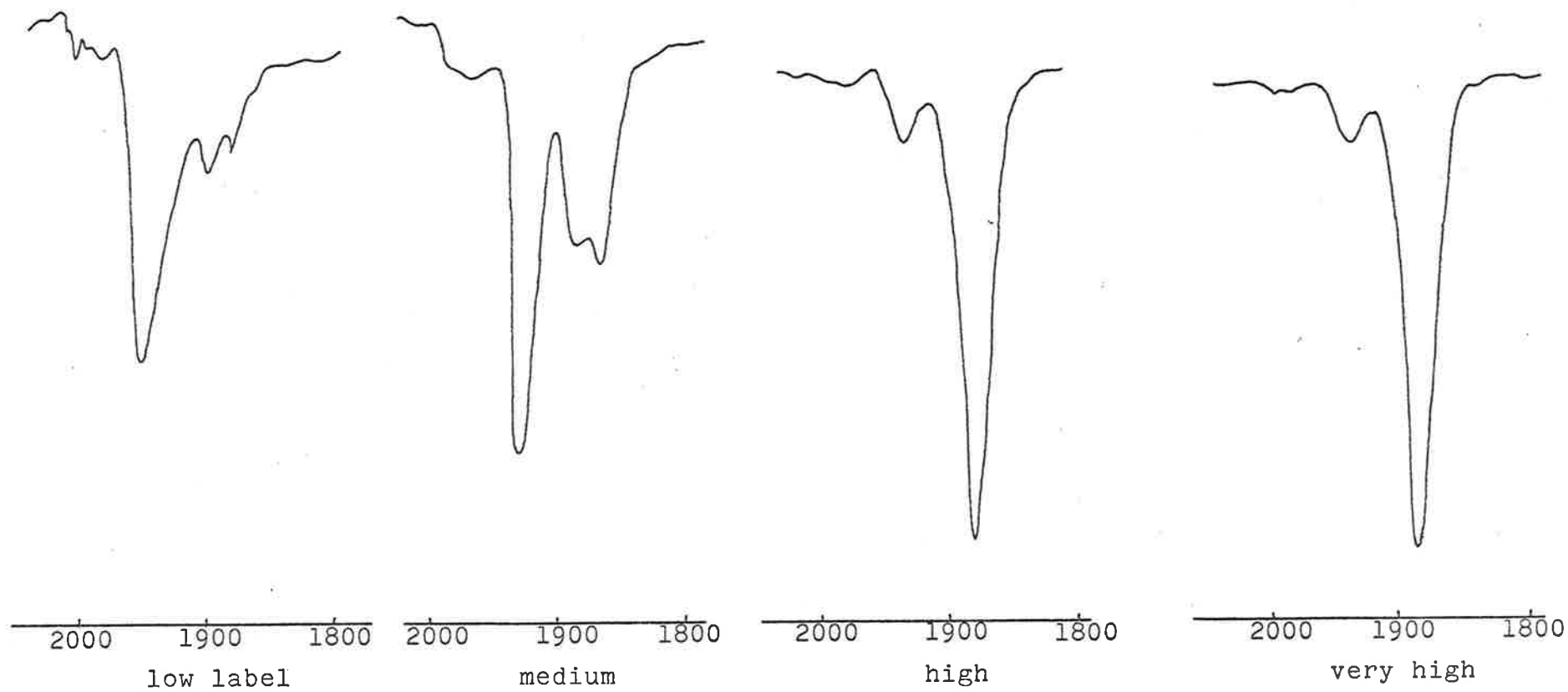unsymmetrically labelled complexes.[10] (That is,

low label   medium   high   very high

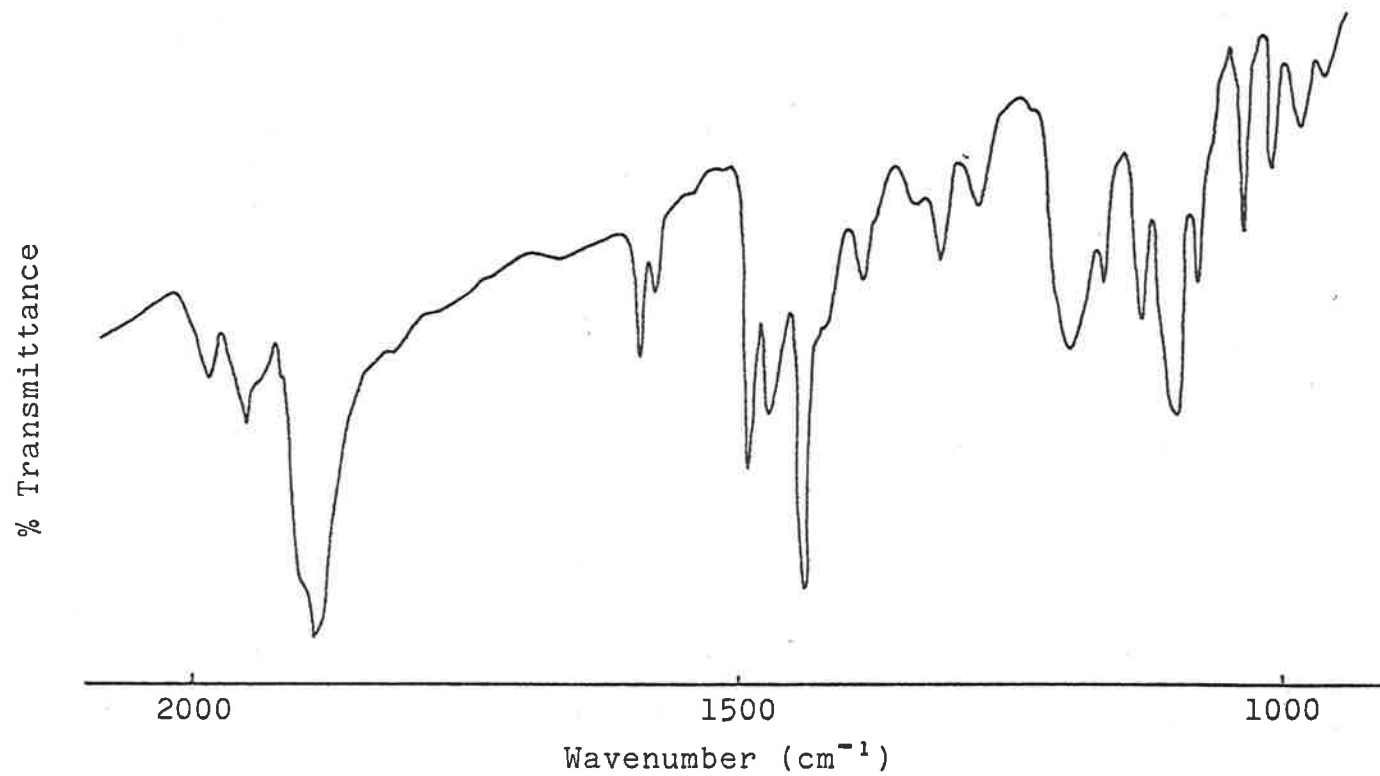FIGURE 2.2.1a   Process of $^{15}N_2$ labelling.

FIGURE 2.2.1b   Infra-red spectrum of $^{15}N_2$ isotopically labelled
trans-[W(N_2)_2(dppe)_2] (Kbr disc).

unsymmetric with respect to the mode of the vibration being considered.) Similarly, for a symmetric substitution the intensity of the absorption of the substituted product is very similar to that of the unsubstituted compound, however, a change in symmetry upon labelling changes the intensity of the absorption bands. Thus when $W(N_2)_2(dppe)_2$ is substituted by two $^{15}N_2$ ligands, the expected $\nu(N-N)_{asym}$ is $\nu_2 = 1948^*\sqrt{56/60} = 1882$ cm^{-1}. The intensity of this band would be expected to be similar to that for $\nu(N-N)_{asym}$ in $W(^{14}N_2)_2(dppe)_2$. This agrees with the observed change in the spectrum upon labelling.

The very weak $\nu(N-N)_{sym}$ which occurs at 2000 cm^{-1} in the unlabelled complex would be expected to shift to 1932 cm^{-1} in the doubly labelled complex: a shoulder was observed at *ca.* 1920 cm^{-1} in samples of labelled dinitrogen complex containing considerable quantities of $W(^{15}N_2)_2(dppe)_2$. The stretch at 1986 cm^{-1} was assigned to $\nu(N-N)_{sym}$ in $W(^{15}N_2)(^{14}N_2)(dppe)_2$ for the following reasons:

(a) It was observed in samples which had considerable quantities of $(^{15}N_2)W(^{14}N_2)(dppe)_2$ as judged by the relative intensities of the $\nu(N-N)_{asym}$ signals.

(b) As mentioned above, unsymmetrical labelling can lead to the breakdown of the selection rules "forbidding" the symmetric stretch.

(c) This band was not present in a sample which was reacted with a 90% $^{15}N-^{15}N$ atmosphere in three separate exposures. This procedure minimised the effect of dilution of $^{15}N_2$ by $^{14}N_2$ from the complex,

(c) (Continued)

and led to a very high percentage yield of
$(^{15}N_2)_2W(dppe)_2$, and very little $W(^{15}N_2)(^{14}N_2)(dppe)_2$.

2.2.4 Reactions with gaseous molecules other than N_2.

(i) Carbon Monoxide

When solutions of $W(N_2)_2(dppe)_2$ were irradiated
with visible light under an atmosphere of carbon monoxide,
an orange/yellow product was formed, which turned canary
yellow with time. The infra red spectrum of the solution
changed during the course of the reaction as shown in
figure 2.2.2. Initially the $\nu(N-N)_{asym}$ signal at 1945 cm^{-1}
decreased and a new infra red stretch at 1815 cm^{-1}
appeared. During the course of the reaction the intensity
of the 1945 cm^{-1} stretch decreased continuously, while the
peak at 1815 cm^{-1} grew to maximum, and then decreased to
zero intensity after ca. 4 hours (35°C). The other
infra red bands developed in the spectrum during this
time, at 1790 cm^{-1}, and 1857 cm^{-1}. At the end of the
reaction the bands at 1790 cm^{-1}, and 1857 cm^{-1} were the
only signals in the region 1600 to 2500 cm^{-1}. This final
infra red spectrum is consistent with that of the known
cis-$W(CO)_2(dppe)_2$.[1] The observed reaction was interpreted
thus:

$$trans\text{-}W(N_2)_2(dppe)_2 \xrightarrow[h\nu]{CO} trans\text{-}W(CO)_2(dppe)_2$$
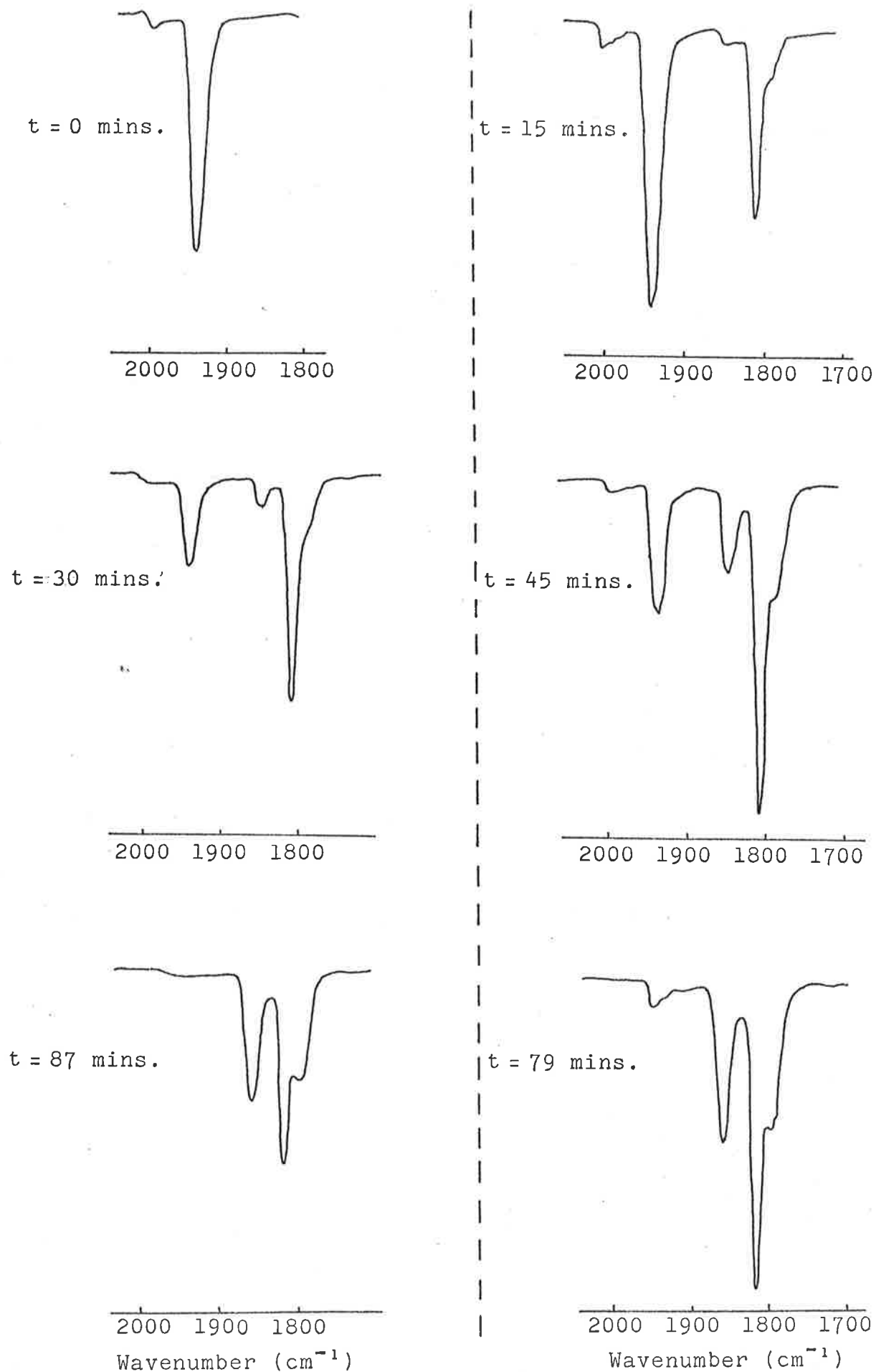
$$\downarrow \Delta$$

$$cis\text{-}W(CO)_2(dppe)_2$$
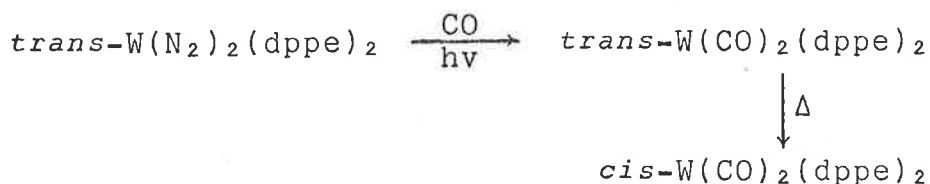
FIGURE 2.2.2   Two independent runs. Reacting
trans-[W(N₂)₂(dppe)₂] with CO under visible
light irradiation.

The proposed scheme was confirmed by irradiating $W(N_2)_2(dppe)_2$ under a CO atmosphere at *ca.* -5°C in thf, benzene or toluene. This enabled the solid *trans*-$W(CO)_2(dppe)_2$ to be isolated.

The infra red spectrum of the *cis* carbonyl complex in KBr was examined in the range 4000 - 250 cm^{-1} (fig. 2.2.3). The peaks at 1857 cm^{-1} and 1790 cm^{-1} were assigned to $\nu(C\equiv O)_{asym}$ and $\nu(C\equiv O)_{sym}$ respectively. The peak observed at 1815 cm^{-1} during the course of the reaction and in the product isolated at 0°C was assigned to $\nu(C\equiv O)_{asym}$ in the *trans* carbonyl species. The symmetry forbidden $\nu(C\equiv O)_{sym}$ for the *trans* isomer was not observed. A mass spectrum of the *cis* isomer was obtained, and revealed a molecular ion centred at 1036 which exhibited the splitting patterns expected for the isotopes of tungsten and carbon in a complex containing one tungsten and fifty four carbon atoms (Appendix B). Peaks were also observed at 1008 [$W(CO)(dppe)_2{}^{+}$] and 980 [$W(dppe)_2{}^{+}$]. Considerable quantities of CO (28) were also observed.

U.V./visible spectrum of the *trans* complex was obtained in thf solution (fig. 2.2.4) under anaerobic conditions. The usual tungsten-diphos absorptions were observed between 200 and 250 nm. No peak similar to the $M(d)\rightarrow N_2(\pi^{*})$ charge transfer observed in $W(N_2)_2(dppe)_2$ was detected.

Although *cis*-$W(CO)_2(dppe)_2$ has been isolated previously[1] this reaction is of some interest in two related respects (a) the ability to use photochemical reactions to attain a geometrical isomer which is thermodynamically unfavourable and (b) the retention of
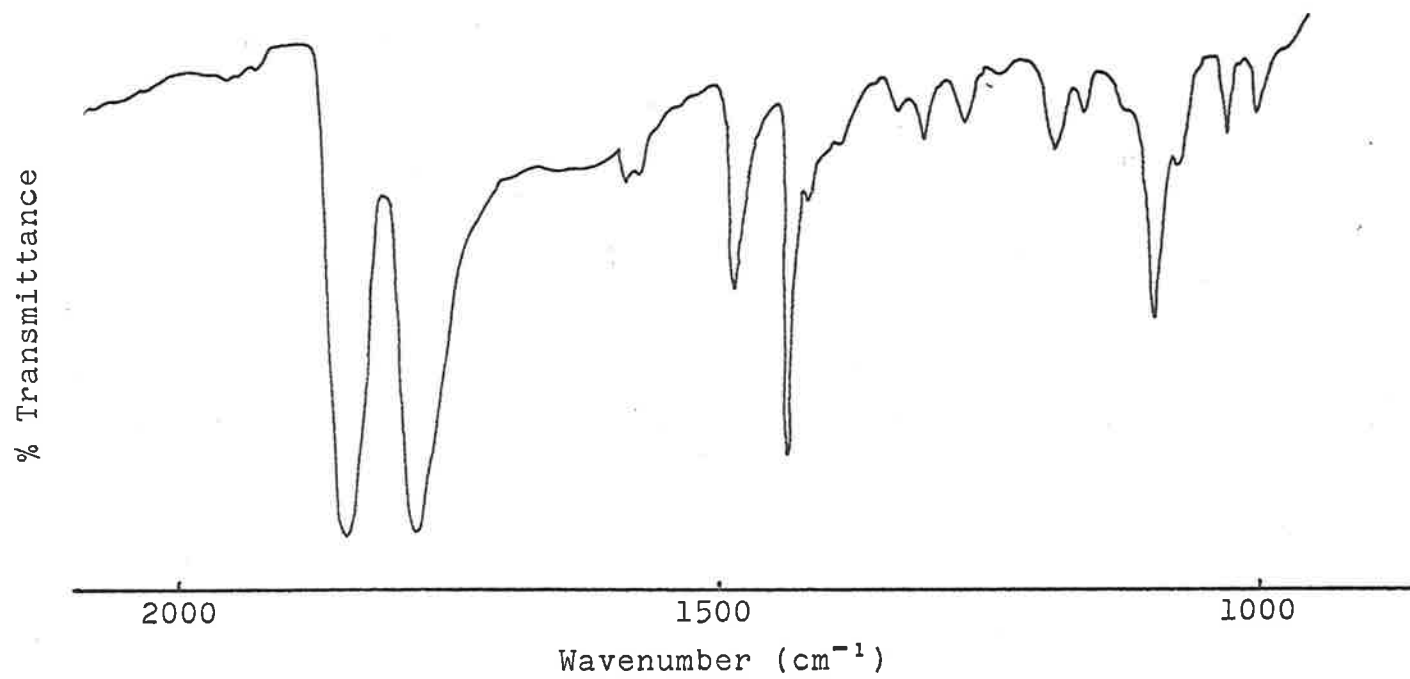
FIGURE 2.2.3   I.R. spectrum of *cis*-[W(CO)$_2$(dppe)$_2$] (KBr disc).
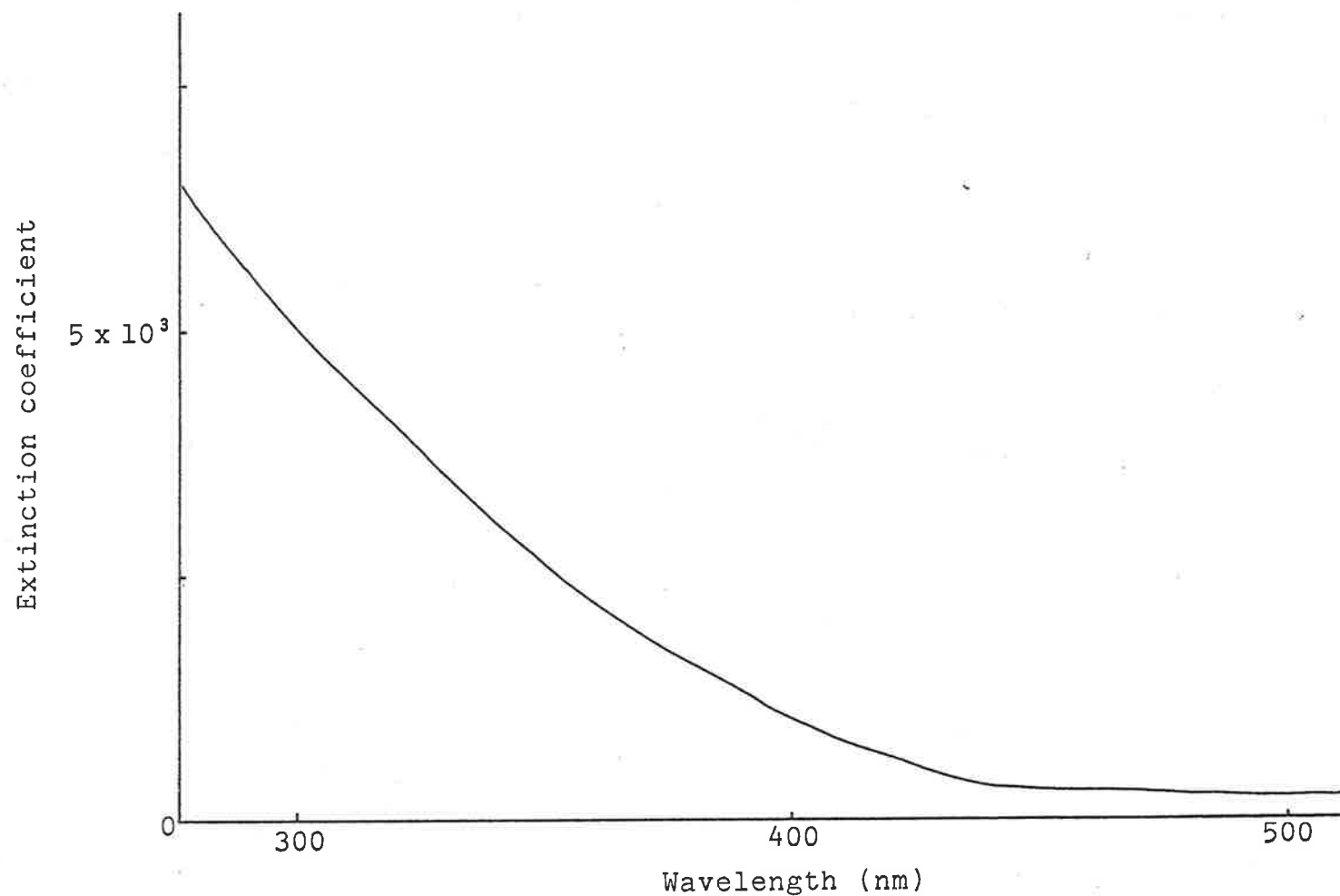
FIGURE 2.2.4 UV/visible spectrum of *trans*-[W(CO)$_2$(dppe)$_2$] in toluene, 1 mm cell.

the *trans* configuration during the course of the photochemical reaction. The isomerisation of the *trans* carbonyl to the *cis* isomer can be explained by conventional π acceptor/donor theory in that CO is a stronger σ donor and π acceptor than is N_2, thus although two N_2 ligands *trans* are not mutually destabilised compared to N_2 *trans* to dppe, the *trans* CO complex is less stable than the complex with CO *trans* to phosphine.[11]

(ii) Dihydrogen, H_2

It was found that dihydrogen could undergo a reaction catalysed by visible light with $W(N_2)_2(dppe)_2$ in thf or benzene solution to yield a yellow microcrystaline substance. An infra red spectrum of the product (fig. 2.2.5) contained signals which could be assigned to dppe coordinated to tungsten, except for a broad stretch at 1890 cm^{-1}. This wavelength is typical of $\nu(W-H)$.[12] A 90 MHz ^1H n.m.r. spectrum, (fig. 2.2.6) revealed signals due to the aromatic group and the bridging $-CH_2-CH_2-$ of the dppe ligand and a weak, broad upfield signal at *ca.* -4 p.p.m. This upfield resonance was assigned to hydride, and the complex tentatively formulated as $W(H)_n(dppe)_2$. (n = 2 or 4). Further evidence was obtained from a 36.43 MHz ^{31}P n.m.r. spectrum which exhibited only one resonance which was partially split by $^1J_{^{184}W-^{31}P}$ (fig. 2.2.7). The central resonance represented 86% of the complex present (with tungsten isotopes other than ^{184}W). The superimposed doublet represented the 14% of the complex with ^{184}W. $^1J_{^{184}W-^{31}P} = 81 \pm 2$ Hz. This spectrum indicates that all four phosphorous atoms in the complex were equivalent.
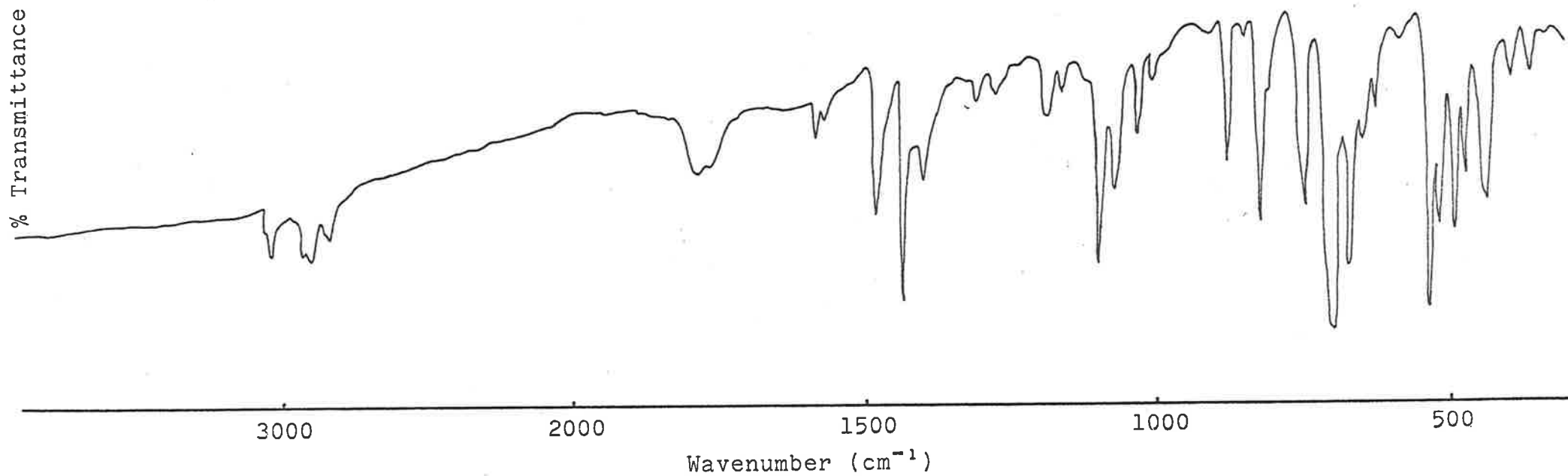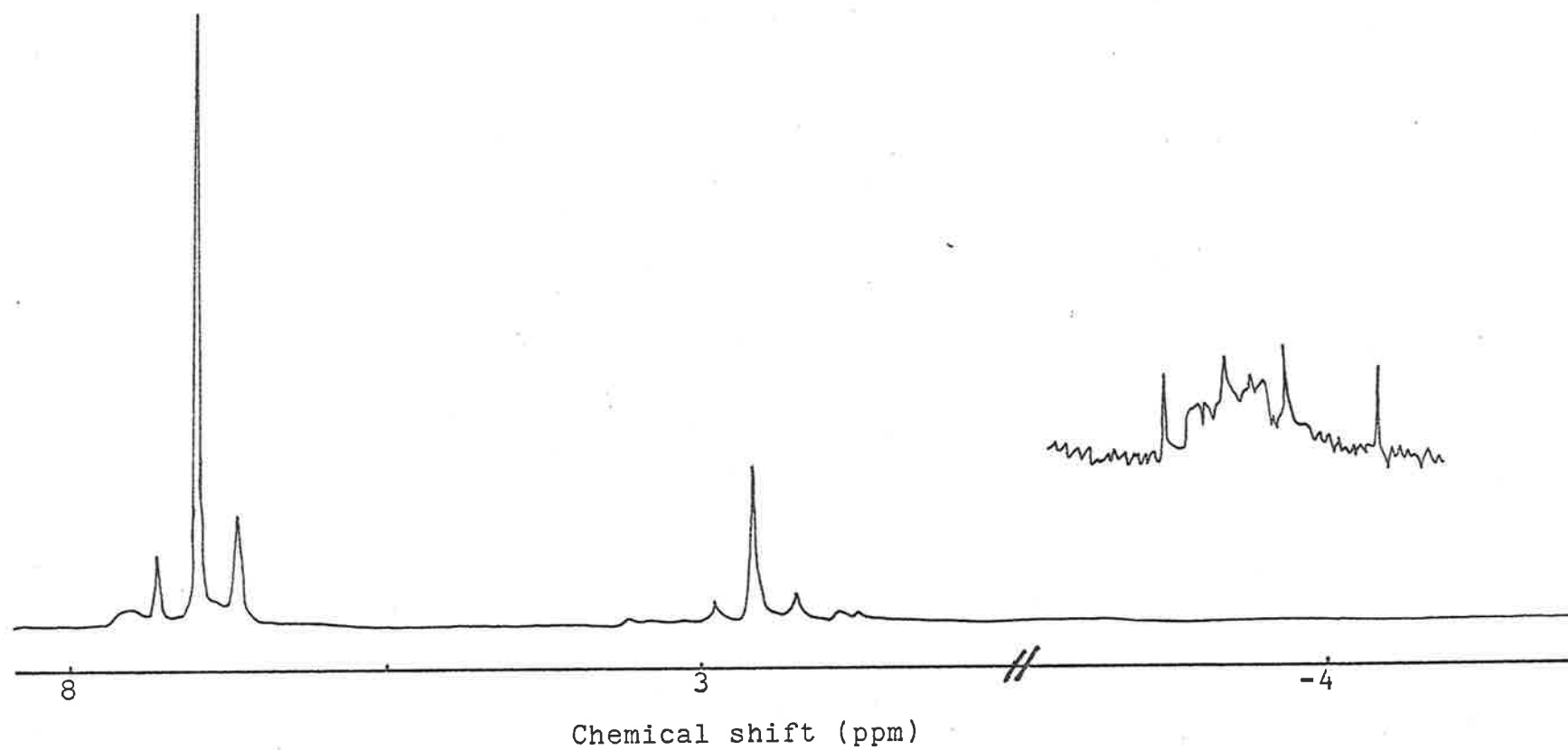
FIGURE 2.2.5 I.R. spectrum of WH₄(dppe)₂ (KBr disc).

Chemical shift (ppm)

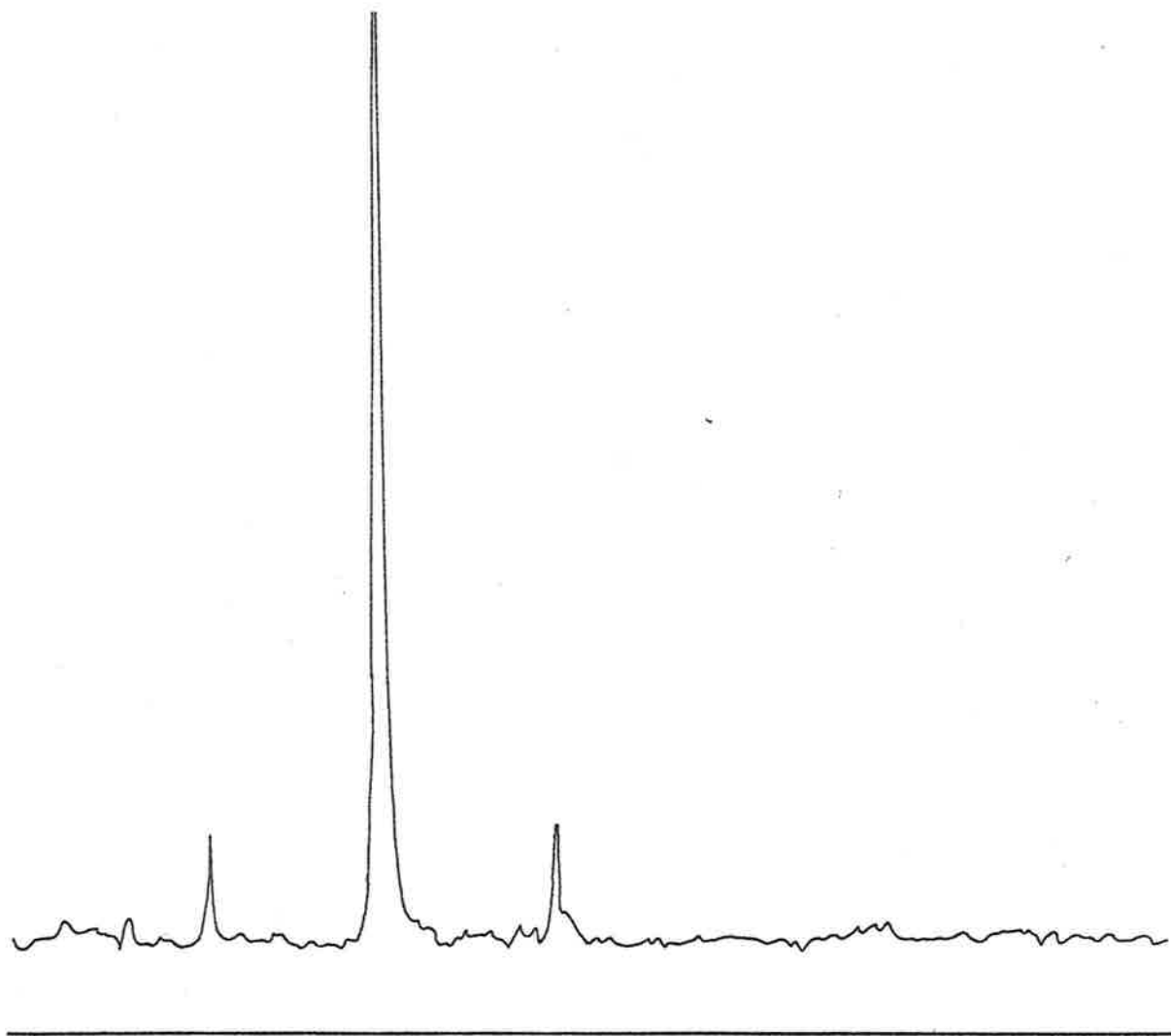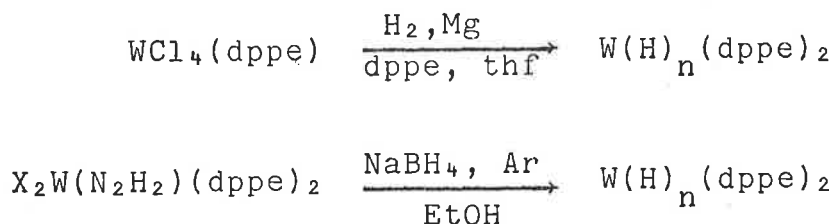FIGURE 2.2.6   90 MHz ^{1}H nmr spectrum of $WH_4(dppe)_2$ in C_6D_6.

FIGURE 2.2.7 ^{31}P nmr spectrum of $WH_4(dppe)_2$.

$W(H)_n(dppe)_2$ (n = 2 or 4) has been reported in the literature as having a broad upfield signal due to hydride in the ^1H n.m.r. spectrum.[12] Previously this compound has been synthesised from $WCl_4(dppe)$ [1] or $X_2W(N_2H_2)(dppe)_2$ [2] (X = Cl, Br), thus:

$$WCl_4(dppe) \xrightarrow[\text{dppe, thf}]{H_2, Mg} W(H)_n(dppe)_2$$

$$X_2W(N_2H_2)(dppe)_2 \xrightarrow[\text{EtOH}]{NaBH_4, Ar} W(H)_n(dppe)_2$$

Full spectral data for this compound had not at that stage, been published. The U.V./visible spectrum of the yellow product exhibited the usual metal-diphos charge transfer peaks at 200 to 250 nm. The plateau of absorbance normally observed in dppe complexes between 300 nm and 450 nm was very weak. In order to confirm that this compound was as formulated, and not a dppe bridged species arising from labilisation of phosphine by light excitation a crystal and molecular structure study was undertaken. (See Appendix A). Although only 7 phenyl rings could be located, and the final R value was .12, the partial structure proposed is chemically reasonable (figure 2.2.9). The hydride ligands could not be found (at the R value obtained any attempt at positioning the hydride ligands would have been meaningless), but the dppe ligands allow room for hydride to coordinate to the metal centre. No atoms other than phosphorus were found within coordination sphere. The structure suggested is quite similar to that found by Guggenberger for $H_4Mo(IV)(P\phi_2CH_3)_4$.[13]
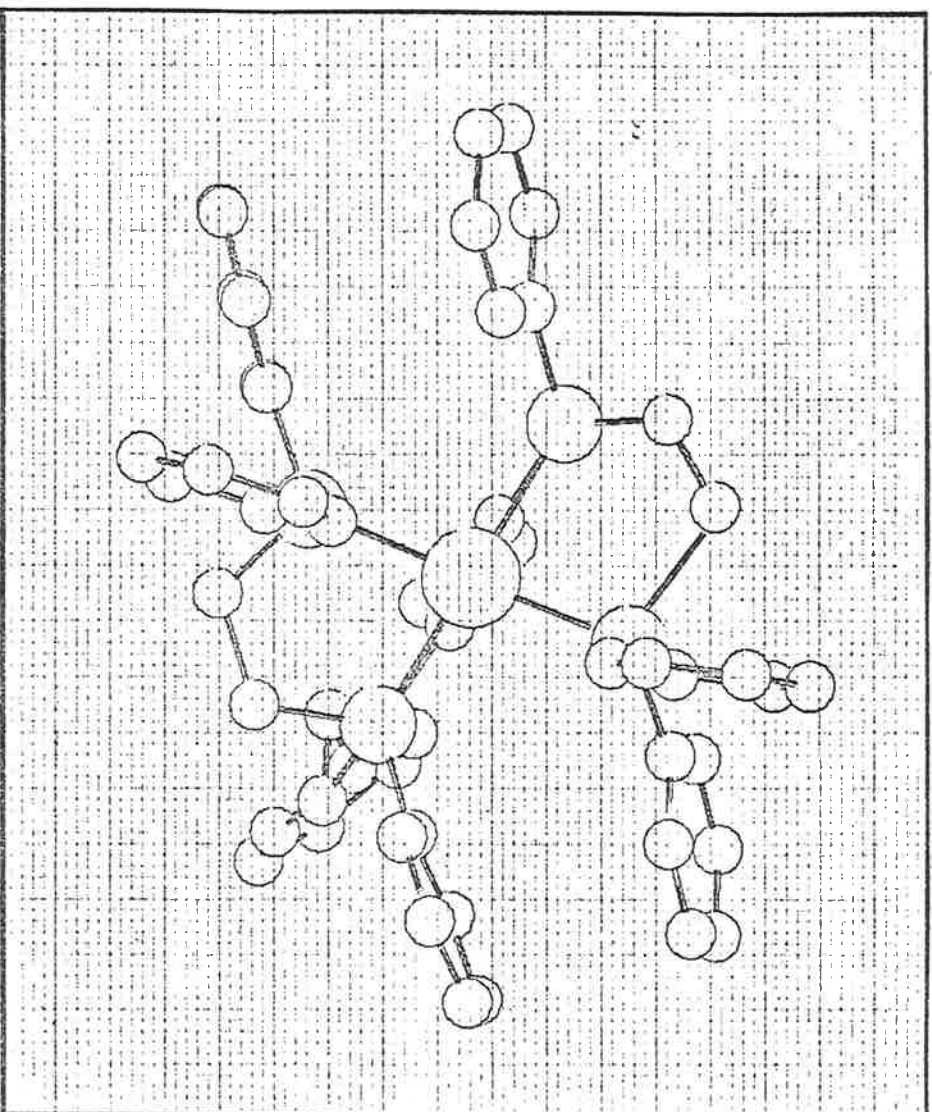
FIGURE 2.2.9 Partial structure determined for $WH_4(dppe)_2$.

64

Both the hydride and carbonyl formation reactions can be readily explained using the scheme of section 2.2.2. The scheme could be expanded thus:

$$W(N_2)_2(dppe)_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} W(N_2)_{(2-x)}(dppe)_2 + xN_2$$

$$\downarrow xL$$

$$(N_2)_{(2-x)}W(L)_x(dppe)_2$$
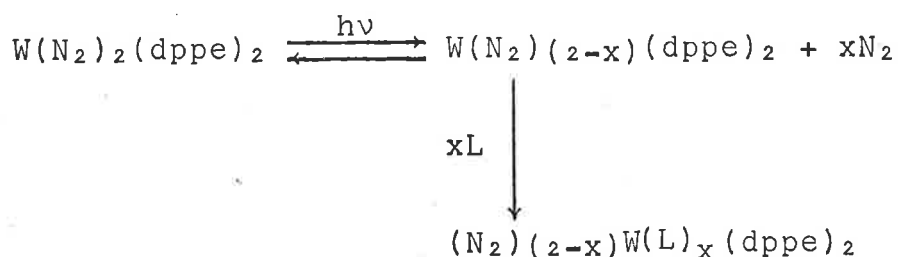
The formation of mixed carbonyl/dinitrogen or hydride/dinitrogen complexes would be expected if only one dinitrogen ligand was exchanged, however, such mixed complexes may be unstable, and could perhaps react further to form the *bis* carbonyl or tetra hydride complexes, via a thermally activated mechanism. However, the stability of the compound $Mo(CO)(N_2)(dppe)_2$[14] argues against this point, and so the appearance of a *bis* carbonyl complex would appear to support the hypothesis that both N_2 ligands are lost from the coordination sphere upon irradiation.

(iii) Nitrous oxide, N_2O

Nitrous oxide complexes have been observed with Ru(II), $[(NH_3)_5RuN_2O]^{2+}_{(aq)}$ is formed from $[(NH_3)_5RuOH_2]^{2+}_{(aq)}$ and N_2O in aqueous solution.[15] This complex then decomposes to yield $[(NH_3)_5RuN_2]^{2+}_{(aq)}$. The use of $^{15}N-^{14}N-O$ and $^{14}N-^{15}N-O$ has allowed the formation of endo and exo labelled $[(NH_3)_5RuN_2]^{2+}_{(aq)}$, both of which undergo rotation of the N_2 ligand to yield, finally, mixtures of endo and exo labelled complex.[16,17] It was of some interest to attempt to prepare the *bis* (nitrous oxide)

bis (diphos) tungsten complex in order to endo or exo label the *bis* (dinitrogen) tungsten complex and study the rotation of the dinitrogen ligand in this compound.

Dry, oxygen free N_2O was introduced into a vessel containing a thf solution of $W(N_2)_2(dppe)_2$. The reaction was monitored by taking infra red spectra of aliquots withdrawn from the reaction vessel. It was found that while the reaction vessel was kept in the dark no reaction occurred, upon irradiating with visible light the intensity of $\nu(N-N)_{asym}$ decreased. An intense peak observed in the solution infra red spectrum at *ca.* 2230 cm^{-1} was assigned to $\nu(N_2O)$ dissolved in thf as it was also present in a spectrum of N_2O in thf alone. A weak absorbance at *ca.* 2560 cm^{-1} suggested that a small quantity of N_2O complex was present, however, no such complex could be isolated. The product isolated had spectra and analysis consistent with dppe oxide plus WO_3. This seemed to indicate that an N_2O complex was formed but decomposed in a way which led to oxidation of the dppe ligand. It was of interest that this oxidation of ligand did not occur until after irradiation of the complex by visible light, suggesting that possibly a mechanism such as depicted below was involved.

$$W(N_2)_2(dppe)_2 \underset{N_2}{\overset{h\nu}{\rightleftharpoons}} W(N_2)_{(2-x)}(dppe)_2 + x(N_2)$$

$$(N_2O) \downarrow$$

$$(N_2O)W(N_2)_{(2-x)}(dppe)_2$$

$$\downarrow$$

oxidation products.
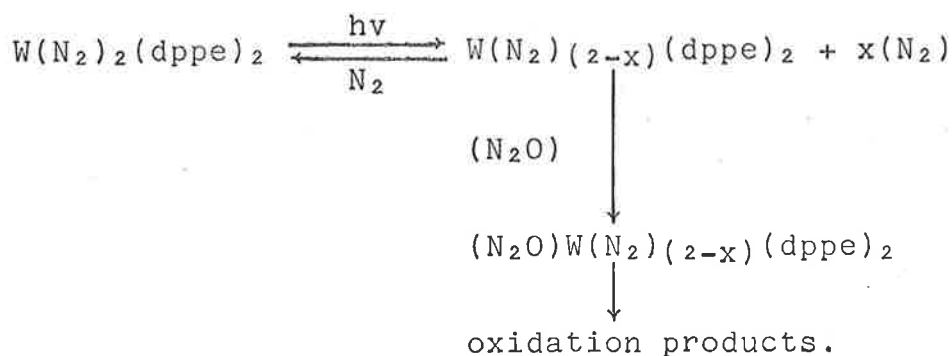
(iv) Nitric Oxide, NO

An attempt was made to produce a nitrosyl *bis* (diphos) tungsten complex from the *bis* dinitrogen complex. A thf solution of $W(N_2)_2(dppe)_2$ was reacted with oxygen and moisture free nitric oxide. No appreciable reaction was observed over ninety minutes at 35°C when the reaction mixture was kept in the dark. Upon irradiating the solution with visible light the complex reacted with NO, the reaction being essentially complete after thirty minutes. However, no product could be isolated with a $\nu(N-O)$ band in the infra red spectrum, nor was a $\nu(N-O)$ band observed in the solution spectrum during the reaction. Thus, if an NO complex was formed it must have rapidly decomposed.

(v) Ethylene, C_2H_4

An ethylene *bis*(dppe) complex of molybdenum has been reported as being formed from $Mo(II)(acac)_2$, dppe and $AlEt_3$ under argon in toluene as solvent.[18] It was further reported that this complex could react (reversibly), with N_2 to yield $Mo(N_2)_2(dppe)_2$. It seemed reasonable therefore that $W(N_2)_2(dppe)_2$ could react with C_2H_4 in a photochemical reaction to form an analogous ethylene tungsten complex. It was also of interest to note that the molybdenum ethylene complex could react thermally with ArX or RX to yield $MoX_2(dppe)_2$.[19]

$$Mo(C_2H_4)(dppe)_2 \xrightarrow{\text{ArX,RX}} MoX_2(dppe)_2$$
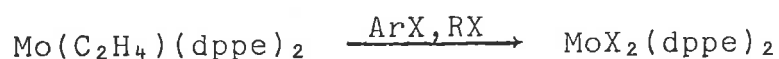
This suggests that a mechanism such as depicted below occurs, with metal assisted R-X bond cleavage occurring in a similar way to the mechanism suggested for the reaction of $W(N_2)_2(dppe)_2$ with RX.[20]

$$Mo(C_2H_4)(dppe)_2 \longrightarrow Mo(dppe)_2(solv) + C_2H_4$$
$$\downarrow RX$$
$$(RX)Mo(dppe)_2$$
$$\downarrow$$
$$R. + XMo(dppe)_2$$
$$\downarrow$$
$$\tfrac{1}{2}R_2$$
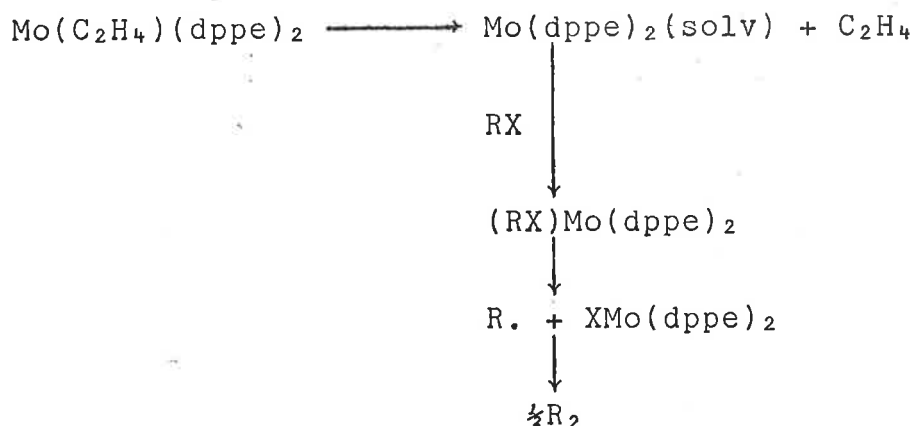
In an attempt to prepare a tungsten ethylene complex a solution of $W(N_2)_2(dppe)_2$ was saturated with C_2H_4, and the reaction rate monitored using the solution infra red spectra of aliquots withdrawn during the course of the reaction. It was found that no reaction occurred after several hours in the dark. Upon irradiating with visible light the intensity of the $\nu(N-N)$ stretch decreased rapidly, and a pale cream coloured compound was isolated. However, there was no indication in the infra red or n.m.r. spectra of the presence of coordinated C_2H_4, merely signals which could be assigned to dppe.

2.2.5 Reaction with Alkyl and Acyl Halides

(i) Butyl Bromides

Three butyl bromides were used in this work, 1-bromobutane , 2-bromobutane , and 2,2-bromomethylpropane (tertiary butyl bromide). All three resulted in formation of similar products when mixed with a solution of $W(N_2)_2(dppe)_2$ and irradiated by visible light. No

reaction was observed in the dark. The rate of the preparative reaction was found to increase linearly with light intensity.* These reactions which have been reported[21] yield initially, under dry conditions, the diazenido complex (II). This can be converted to the hydrazido (2-) complex (III) by the addition of $HBr_{(aq)}$, or anhydrous HBr.

$$W(N_2)_2(dppe)_2(I) + RBr \longrightarrow BrWN_2R(dppe)_2(II) + N$$

$$Et_3N \updownarrow HX$$

$$[Br_2WN_2HR(dppe)_2](III)$$
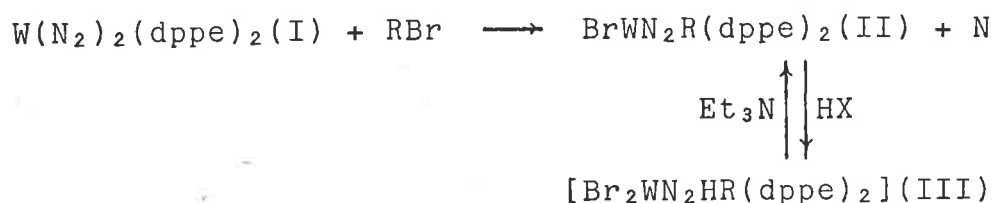
The hydrazido (2-) complex can be converted to the diazenido complex by use of mild base, such as Et_3N. The infra red spectra of the complexes were essentially the same as those reported in the literature. U.V./visible spectra were obtained in thf and benzene for the diazenido and hydrazido (2-) complexes when formed (in situ); spectra of the hydrazido (2-) complex were also run in CH_2Cl_2 by dissolving the solid (figure 2.2.10). Solutions of the diazenido complex were yellow, while the hydrazido (2-) complex was virtually colourless in solution. The spectrum of the hydrazido (2-) complex is quite similar to the spectrum of $[Br_2W(N_2H_2)(dppe)_2]$. The difference in extinction coefficient at 297 nm between the dinitrogen complex and all of the diazenido complexes ($\epsilon \doteqdot 9 \times 10^3$ cm^{-1} mol^{-1} dm^3) provided a convenient means by which the progress of the reactions between $W(N_2)_2(dppe)_2$ and alkyl halides could

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* As the measurement of absolute light intensity under preparative conditions is difficult this cannot be stated *in this section* absolutely.
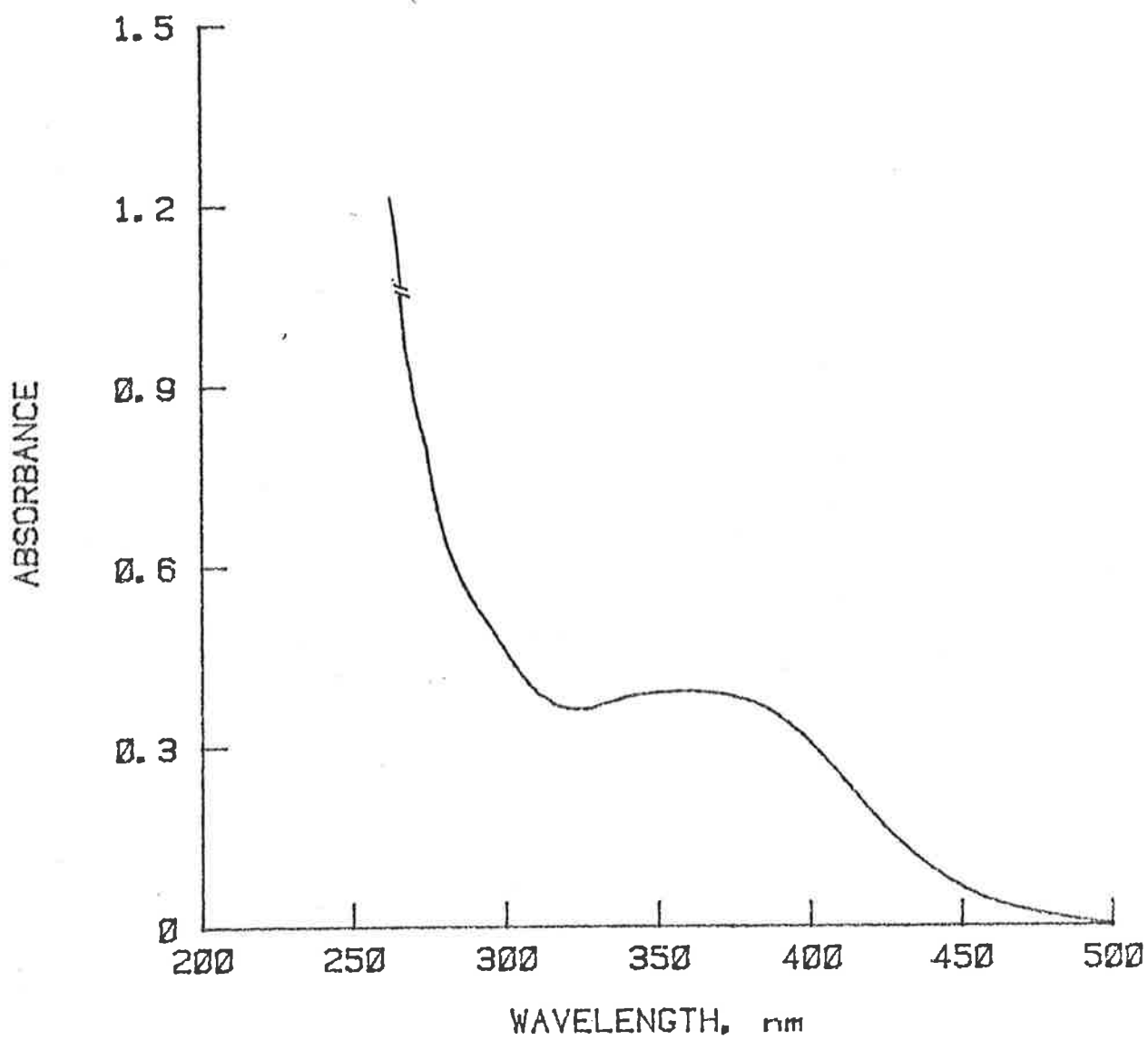
FIGURE 2.2.10 UV/visible spectrum of diazenido butyl
derivative.

be followed. Nuclear magnetic resonance spectra of the complexes (figures 2.2.11 and 2.2.12) were found to be consistent with those reported in the literature.

(ii) Ethyl bromide and Methyl bromide

The reactions of Ethyl bromide and Methyl bromide with $W(N_2)_2(dppe)_2$ were observed to occur on the preparative scale only in the light, and to halt when radiation ceased. Due to the nature of the product mixtures formed in thf and the difficulty of working with these volatile alkyl halides, it was not felt to be productive to investigate further these well characterised preparative reactions. Quantum yields for these reactions were however obtained (see section 3.2) as were U.V./visible spectra of the product mixtures.

(iii) 6-Bromo-1-hexene

Since this reaction was investigated other workers have reported details of the reactions of 6-bromohexene with $W(N_2)_2(dppe)_2$.[20] It has not, however, previously been stressed that this reaction, like the other reactions involving alkyl halides is a light catalysed reaction which does not occur in the dark at 35°C.

6-bromo-1-hexene is used to investigate reaction mechanisms involving organic radicals in order to determine the minimum radical lifetime. This can be achieved since the following reaction occurs.[22]

FIGURE 2.2.11 ^{1}H nmr spectrum of $[W(N_2nBu)Br(dppe)_2]$.

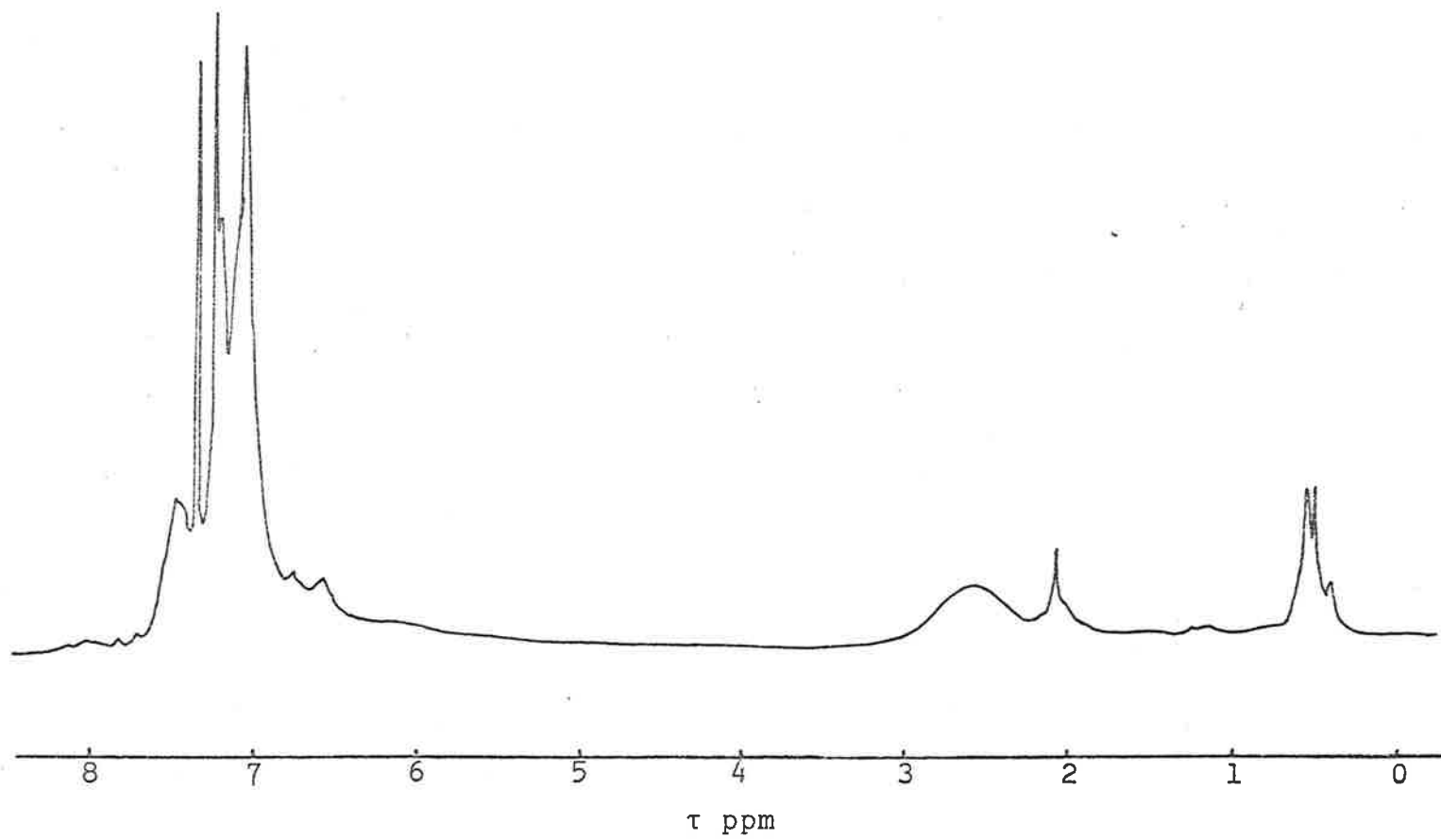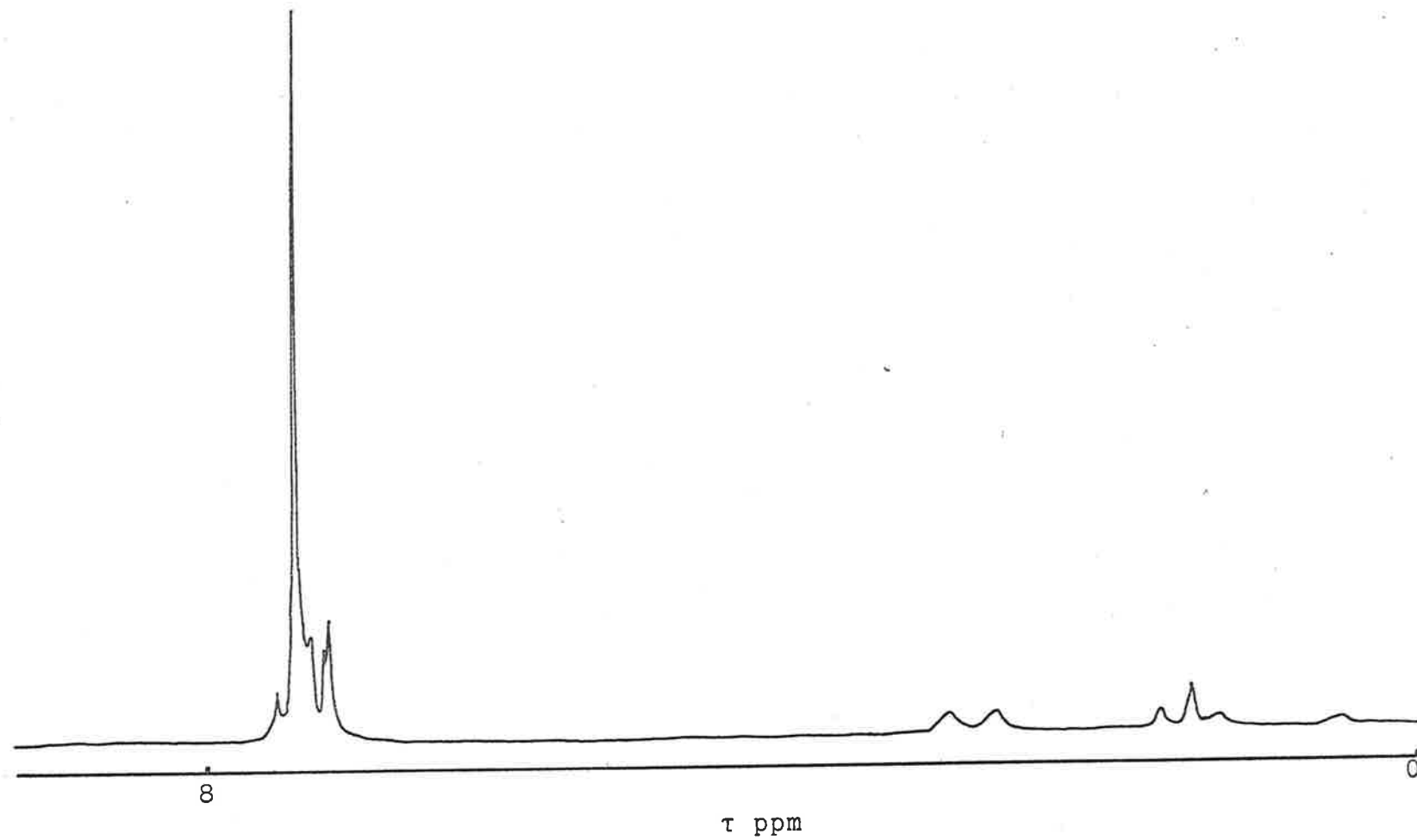FIGURE 2.2.12   ¹H (270 MHz) nmr spectra of 6-bromo-hexene derivative.

τ ppm

$$CH_2 = CH-(CH_2)_3-CH_2Br \xrightarrow{\text{homolysis}} Br^{\cdot} + CH = CH-(CH_2)_3-\overset{\cdot}{C}H_2$$

cyclisation

$k > 10^5$

(sec^{-1})

$${\cdot}CH-CH \Big\langle {\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{}}} $$
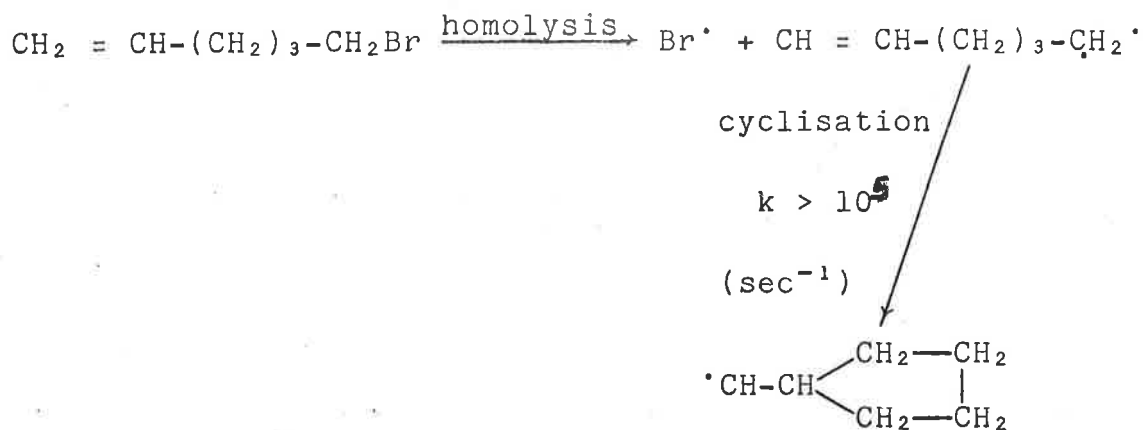
It has been suggested that in the reactions of $W(N_2)_2(dppe)_2$ with alkyl halides $R^{\cdot}$ is formed and then migrates into the solvent before reacting with the dinitrogen ligand of a tungsten complex. If this was the case, and the radical species existed in solution for more than 10^{-4} seconds the radical reactions with the dinitrogen ligand would be predominantly the 1,5 cyclised product. Accordingly, $W(N_2)_2(dppe)_2$ was reacted in C_6H_6 with 6-bromo-1-hexene, and isolated as the alkyl hydrazido (2-) form by the addition of anhydrous HBr (gas) to the reaction mixture.

The ^1H n.m.r. (figure 2.2.12) and the infra red spectrum (figure 2.2.13) were similar to those observed for other alkyl hydrazido (2-) complex as was the U.V./visible spectrum. The former are consistent with spectra later reported by Chatt et al.[20]

A ^1H n.m.r. spectrum revealed signals due to dppe and signals which could be assigned to the cyclised form of the ligand plus the proton on the alkyl hydrazido (2-) group. A ^{13}C n.m.r. (figure 2.2.14) revealed five non equivalent carbon nuclei in the aliphatic region, one of which was split into a "quintet", as was found for the ethane bridge
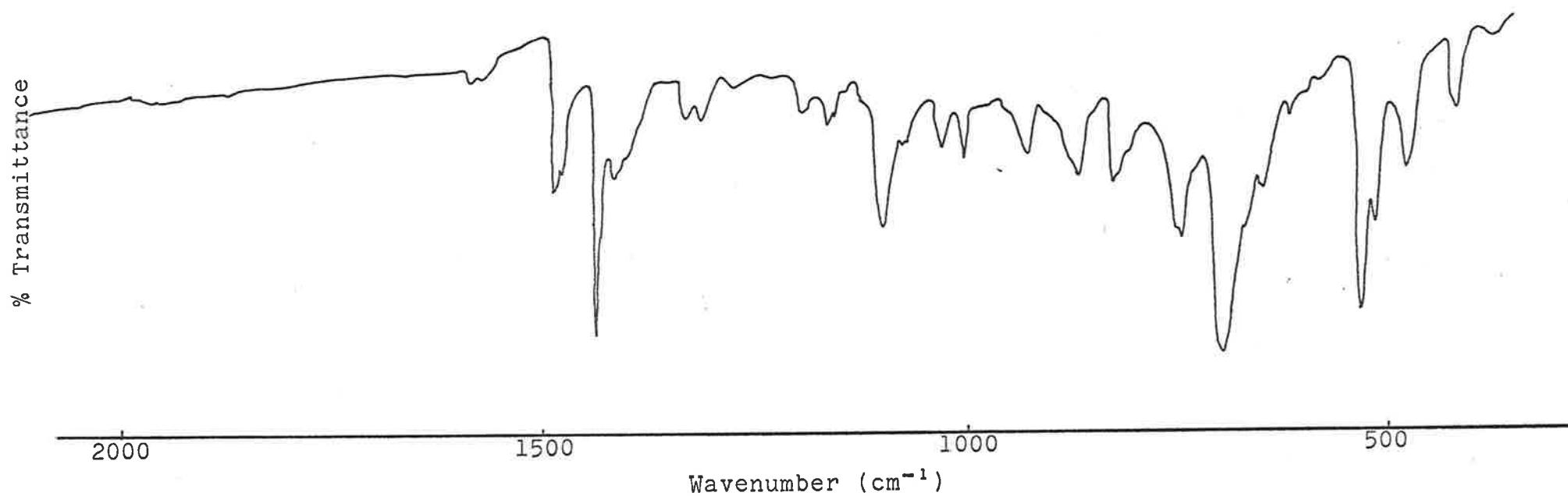
FIGURE 2.2.13   I.R. spectrum of 6-bromo-hexene derivative (KBr disc).

CD₂Cl₂

130 ppm

50 ppm
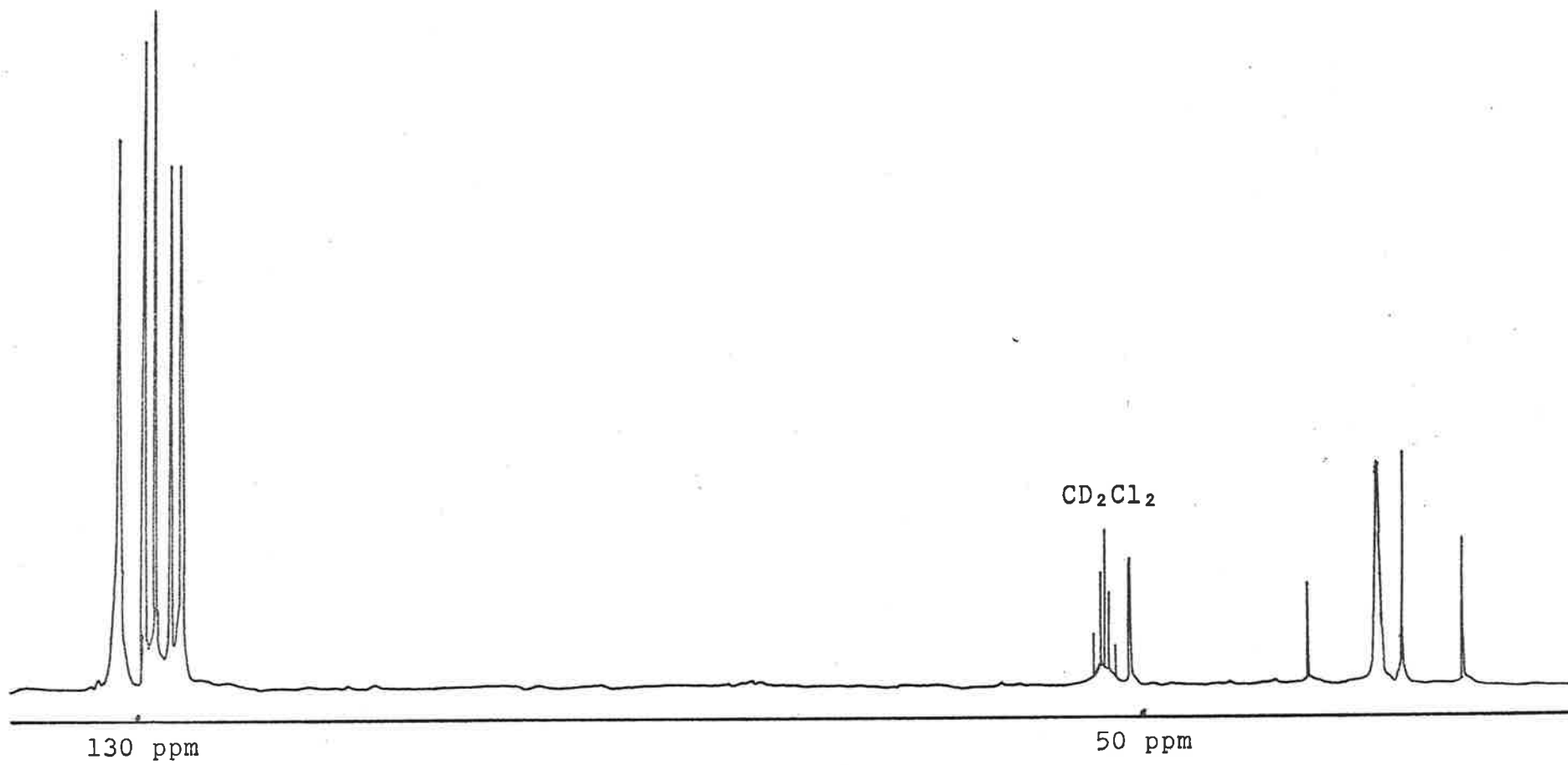
FIGURE 2.2.14 ^{13}C nmr spectrum of 6-bromo-hexene derivative.

of dppe in the parent dinitrogen complex and in the $PHBu_2$
derivative. Signals were also observed in the aromatic
region due to the phenyl rings of the
1,2 bis(diphenylphosphino)ethane ligand.

This evidence proved quite conclusively that the
complex formed had the 1, 5 cyclised alkyldiazenido
ligand attached, rather than a hex-6-ene group, since the
cyclised hexene had four non equivalent carbon atoms,
while the straight chain form has six. This is consistent
with a mechanism involving loss of R˙ after homolytic
cleavage, followed by radical attack on the N_2 ligand
trans to the Br.

(iv) CH_3COCl

It has been reported that acyl chlorides react with
$W(N_2)_2(dppe)_2$ in thf or benzene solution under ordinary
laboratory conditions,[23] (presumably with no irradiation
other than normally prevailing in that laboratory.) However
in this work it has been found that in moisture and
oxygen free solvents the reaction will not proceed in the
dark. When CH_3COCl was mixed with a .4 g. of $W(N_2)_2(dppe)_2$
in 60 cm^3 of thf   it was found to react at a rate
dependent on light intensity. When the irradiation
ceased and the reaction vessel shielded from stray light,
the reaction was found to halt (fig. 2.2.15), showing
that the reaction proceeded cleanly, and did not produce
an appreciable concentration of any species which reacted
with $W(N_2)_2(dppe)_2$ in the dark.
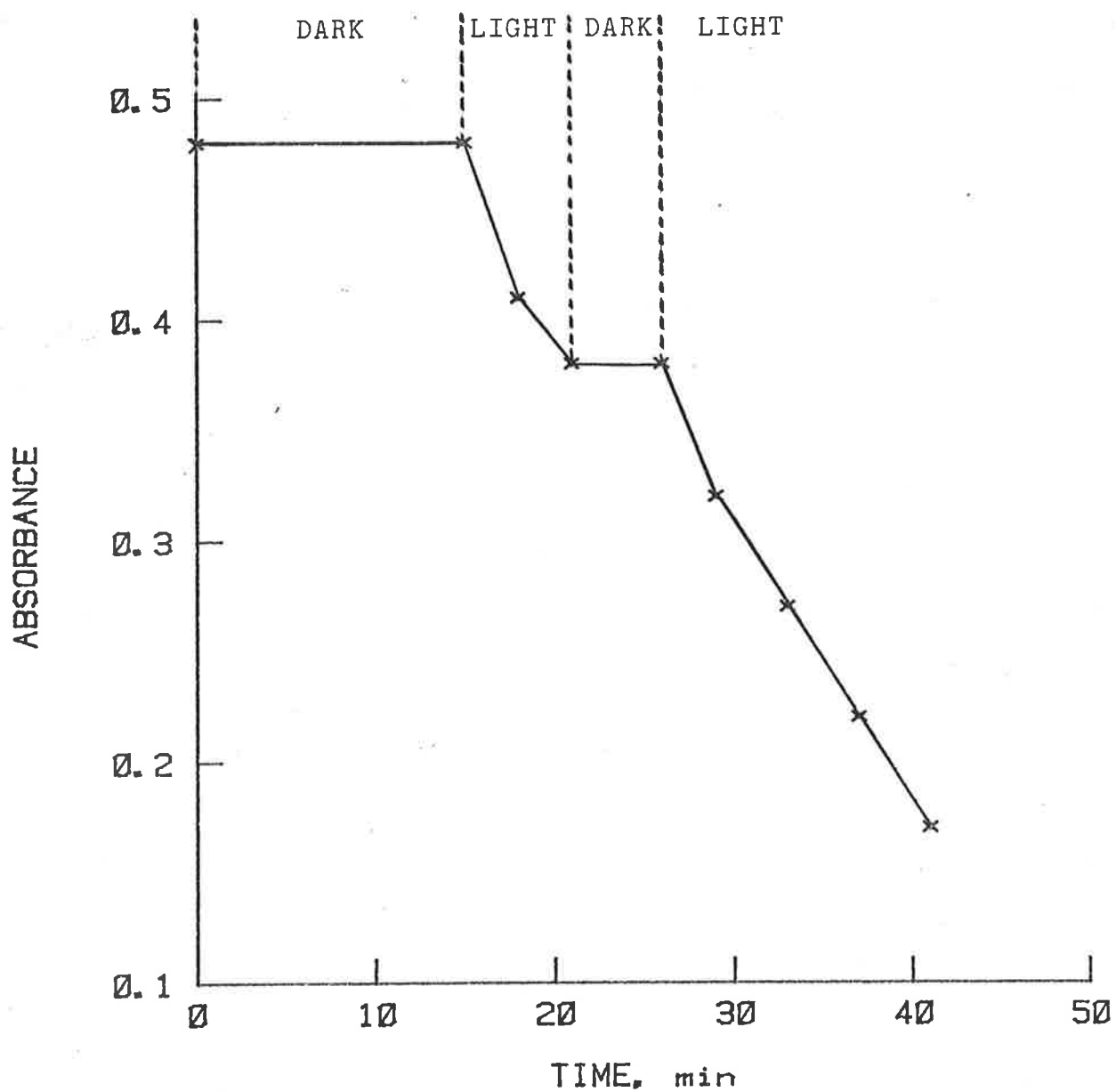
FIGURE 2.2.15   Change in absorbance of $W(N_2)_2(dppe)_2$ due
to reaction with RCOCl under
dark/light/dark conditions.

The infra red (figure 2.2.16) spectrum of the acyl hydrazido (2-) complex produced was sensibly the same as those reported in the literature.

2.2.6   Reactions of $W(N_2)_2(dppe)_2$ with phosphines

It was postulated that since light labilised at least one dinitrogen ligand to produce an intermediate which probably had a solvated coordination site it could be possible to produce a monodinitrogen complex with a monodentate phosphine occupying the sixth coordination site.   Initially substitution was attempted by irradiating a solution of $W(N_2)_2(dppe)_2$ and triphenylphosphine in thf with visible light, however no appreciable reaction was found to occur.   Further reactions were attempted with smaller, less bulky phosphines PMe_2Ph, PMe_3 and "PBu_3".   It was later found that the probable substituent in the latter case was $PHBu_2$, present as 6% of the butyl phosphine. PMe_3 and "PBu_3" gave products of some interest.   The synthesis and characterisation of these products is described below.

PMe_2Ph reacted with $W(N_2)_2(dppe)_2$ in a light catalysed reaction, but gave a mixture of orange coloured products which were difficult to separate by crystallisation and decomposed rapidly on all chromatographic columns used (florasil, alumina, silica).   None of these products had a $\nu(N-N)$ signal in the infra red spectrum.   The products were found to be extremely air and moisture sensitive.
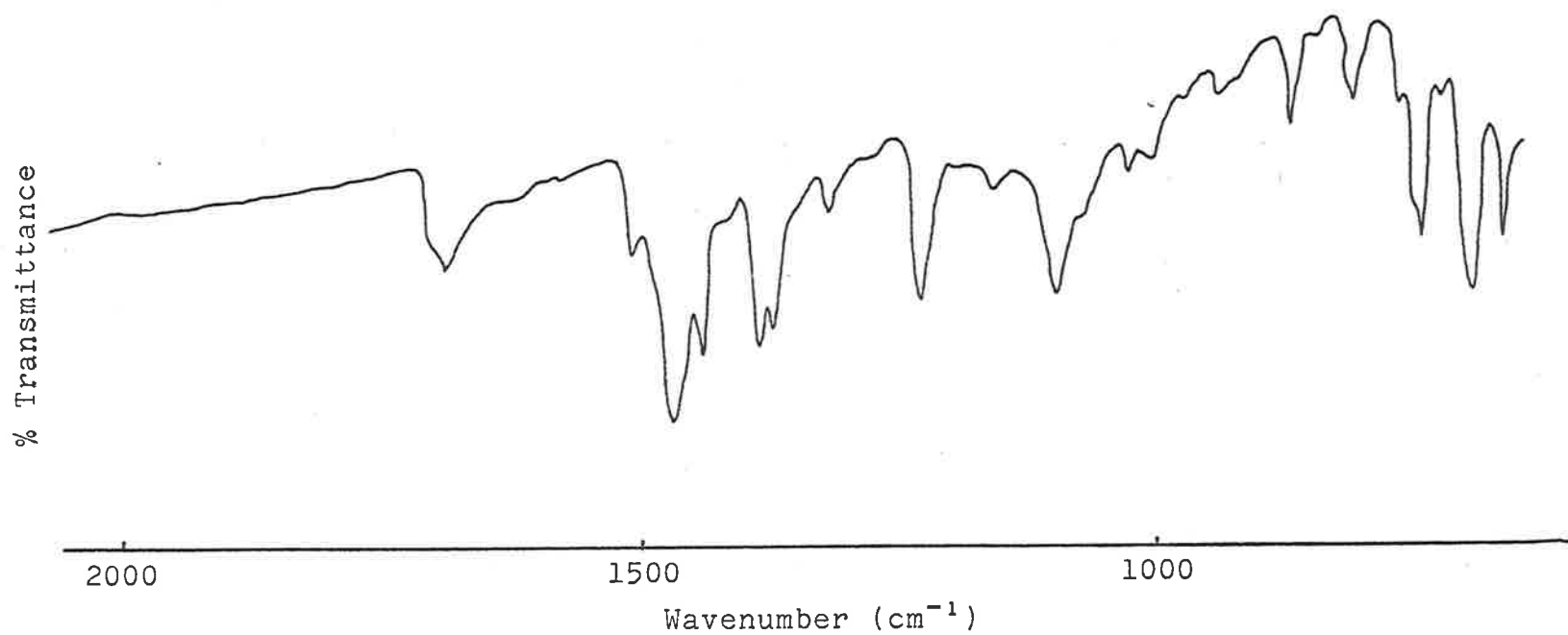
FIGURE 2.2.16   Infra-red spectrum of product of reaction of $W(N_2)_2(dppe)_2$ and RCOCl (KBr disc).

2.2.7 Reactions with Trimethyl Phosphine

(a) Preparation

PMe$_3$ was obtained as the AgNO$_3$ adduct, AgNO$_3$PMe$_3$.[24] This was converted to AgIPMe$_3$ and pyrolysed in vacuo. The resulting PMe$_3$ was distilled onto a frozen thf solution of W(N$_2$)$_2$(dppe)$_2$ at liquid nitrogen temperature. An atmosphere of N$_2$ was introduced into the apparatus and the solution thawed, the reaction mixture stirred and irradiated using a 100W tungsten filament mirror backed lamp. Over three hours the orange solution became a dark red colour. The solution was evaporated in vacuo and left overnight at ca. 2°C under a dinitrogen atmosphere. A red microcrystaline product was isolated and washed with a small volume of cold thf. The complex was found to be extremely sensitive to air and moisture, and decomposed upon dissolution in incompletely dried solvents. It was also found to decompose in solvents containing halogen, e.g. CH$_2$Cl$_2$, CHCl$_3$.

(b) Characterisation

Infra red spectra. An infra red spectrum of the red product had an intense signal at 1920 - 1930 cm^{-1} (KBr) or 1918 cm^{-1} (nujol). Other signals, characteristic of dppe and PMe$_3$ were observed (fig. 2.2.17). No other signal was observed in the ν(N≡N) region of the spectrum. This suggested that the complex was a mono dinitrogen complex, with PMe$_3$ occupying the sixth coordination site, and that the signal at 1920 cm^{-1} could be assigned to ν(N≡N).
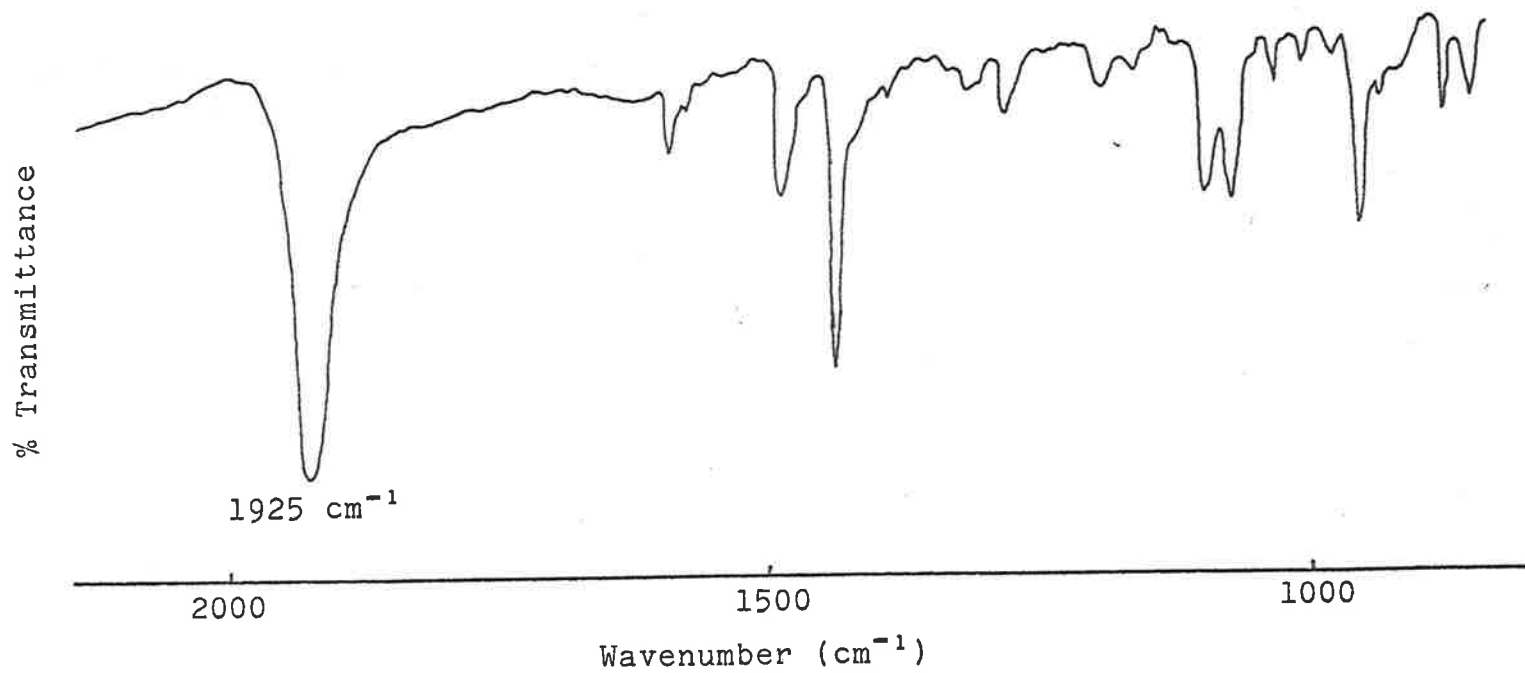
FIGURE 2.2.17   I.R. spectrum of product of reaction between *trans*-[W(N₂)₂(dppe)₂] and PMe₃.

For $(N_2)W(PMe_3)(dppe)_2$ the expected analysis is
C 60.9, H 5.3, N 2.58, P 14.3, microanalysis found
C 57.94, H 5.83, N 2.09, P 12.4. Although all analysis
figures, other than H are low they are reasonably close,
given the extreme sensitivity of this complex to air and
moisture, as the analysis was carried out approximately 7
days after the complex was prepared. Attempts to obtain
^{31}P or ^{13}C spectra were unsuccessful as the preparation
rapidly became contaminated with paramagnetic
substances. A 60 MHz C.W. ^1H n.m.r. spectrum was obtained
(fig. 2.2.18) which had an integral ratio of phenyl (40):
$CH_2-CH_2(dppe)8$: $CH_3(PMe_3)9$, which would appear to suggest
that the complex was $PMe_3(dppe)_2WX$ where X is some group
which did not contain any protons. The U.V./visible
spectrum (fig. 2.2.19) of the PMe_3 product has a broad
moderately intense plateau between 320 and 450 nm which,
as has been pointed out above, would appear to be found
in tungsten diphos complexes containing dinitrogen or a
doubly bonded N=N group. There was also a shoulder at
265 nm, on the edge of the intra ligand band which could
have been due to a M⟶N_2 charge transfer under the
intra ligand envelope.

It was noted that the infra red spectrum of the
complex changed after exposure to air for some time. The
most obvious change was in $\nu(N=N)$, from 1922 - 1930 cm^{-1}
to 1900 cm^{-1}. This suggested that aerial oxidation of
the complex to a W(I) or W(II) complex may have occurred.

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* Analysis carried out by Australian Microanalytical
Service, Melbourne.
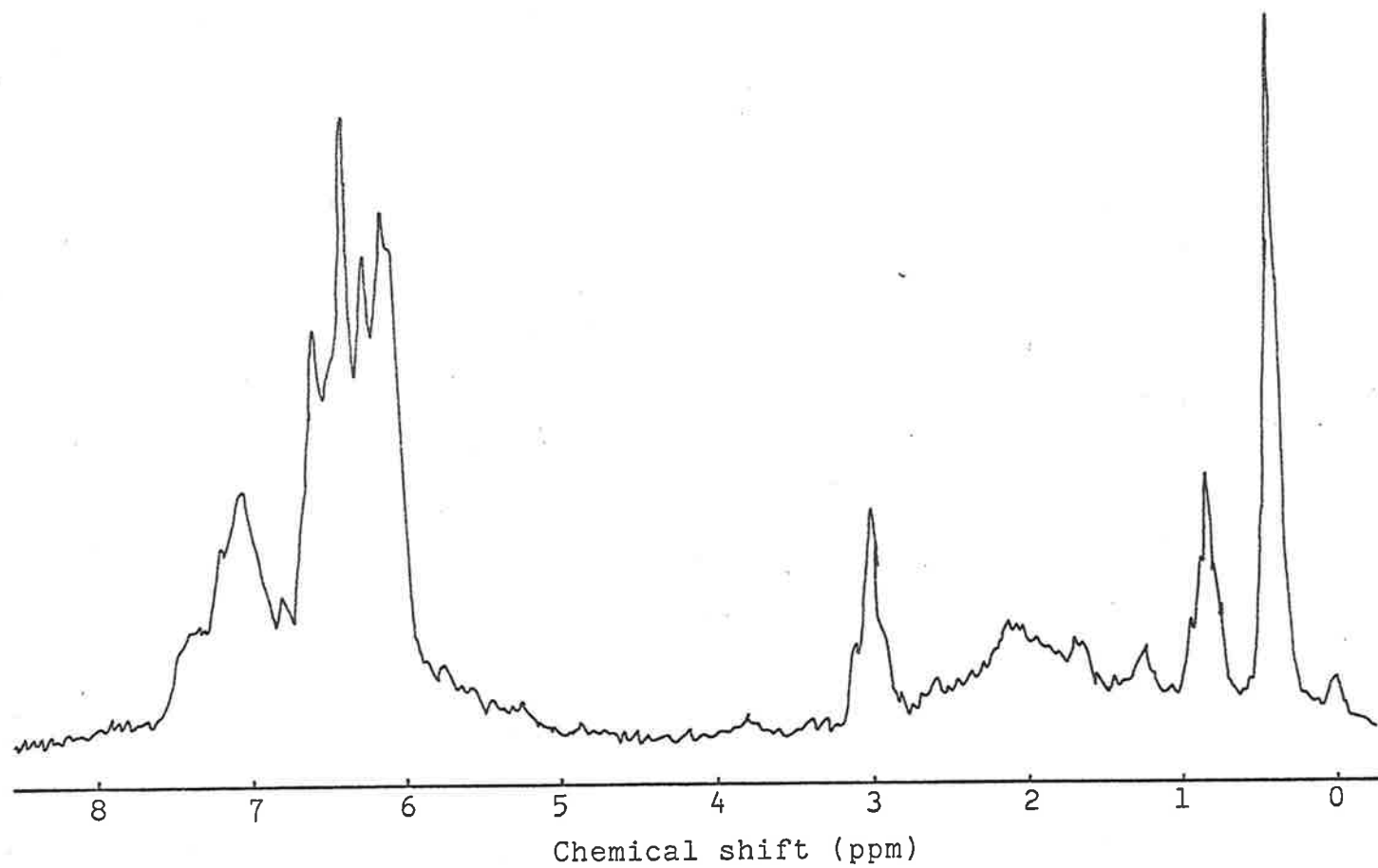
FIGURE 2.2.18 ^{1}H nmr of product of reaction with PMe$_3$.
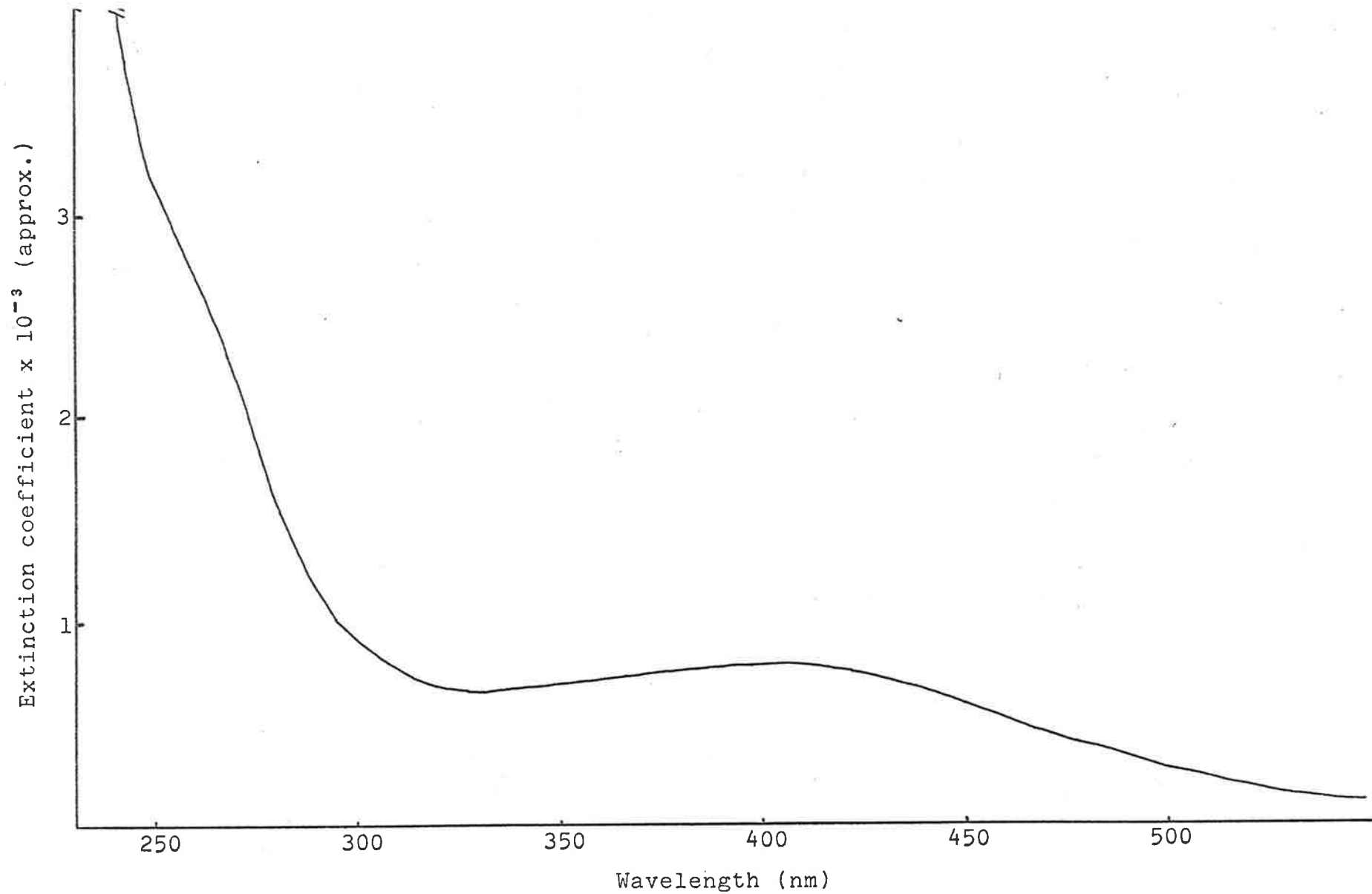
FIGURE 2.2.19   UV/visible spectrum of product of reaction with PMe₃.

The extreme sensitivity of this complex prevented tests for photochemical activity being carried out (e.g. flash photolysis). Reaction of the PMe_3 derivative with CO resulted in the formation of cis-$W(CO)_2(dppe)_2$ plus other tungsten carbonyl complexes. This suggested that the $W(dppe)_2$ grouping was not lost on reacting $W(N_2)_2(dppe)_2$ with PMe_3. The reaction of the PMe_3 derivative with CO appeared to occur more rapidly upon irradiation than in the dark.

2.2.8 Reaction with Butyl Phosphine

(a) Preparation

Typically a solution of $W(N_2)_2(dppe)_2$ in thf was reacted with a large excess of PBu_3. The solution was irradiated for approximately 72 hours using a 150W tungsten filament mirror backed lamp, and the solvent volume was then reduced in vacuo. Green crystals were formed upon cooling. The crude product was recrystallised by temperature gradient from benzene, to yield green rhombic platelets. This product was found to be air and moisture sensitive, and was stored under dry N_2. Solutions were stable only in oxygen and moisture free solvents.

(b) Characterisation

(i) Infra red spectra (fig. 2.2.20) of the green compound gave absorptions which could be assigned to coordinated dppe or PBu_3, except for one weak, broad absorption at 1732 cm^{-1}. This signal is similar to $\nu(M-H)$ observed in $W(H_4)(dppe)_2$.
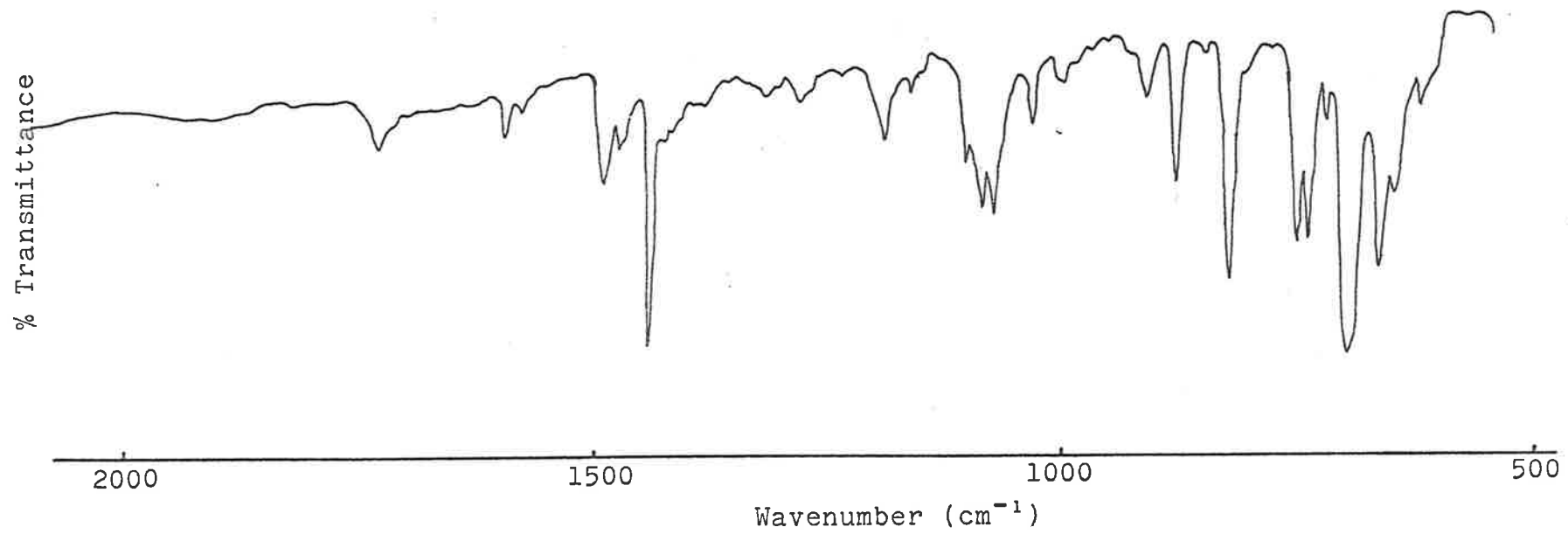
FIGURE 2.2.20 I.R. spectrum of PHBu$_2$ product (KBr disc).

(ii)   A mass spectrum of the complex gave a maximum m/e peak centred at 1129 (minimum mass 1126). Splittings expected for the isotopes tungsten and carbon in a compound containing one tungsten atom and approximately fifty carbon atoms were observed (see fig. 2.2.21). Peaks of significance were also observed at 1048 and 978. A mass of 978 corresponds to $W(dppe)_2$, a similar peak was observed in the mass spectrum of cis-$W(CO)_2(dppe)_2$. The peak at 1048 is $W(dppe)_2 + 70$ which did not fit any obvious grouping. The peak observed at 1129 was the highest despite searches through to m/e of 2500. This mass number was too low for $W(dppe)_2 + PBu_2$, however, it did agree with $W(dppe)_2 + PHBu_2 + H_2$. $(H_2W(dppe)_2PHBu_2)$.

(iii) A 36.43 MH_Z PFT ^{31}P n.m.r. spectrum of the complex in C_6D_6 (fig. 2.2.22) gave two signals, a doublet of intensity 4 at 75.29 ppm, and a quintet of intensity 1 centred at 65.41 ppm relative to uncoordinated dppe. The coupling constants $^1J_{^{31}P-^{184}W} = 138 \pm 2$ Hz was observed for the doublet $^2J_{^{31}P-W-^{31}P} = 28 \pm 2$ Hz. This spectrum is consistent with that expected for an ABX_4 system, (such as $(Bu_3P)W(dppe)_2$), with apparent symmetry C_{2V}. The PBu_3 grouping (or $PHBu_2$) was believed to undergo free rotation about the P-W bond on the n.m.r. time scale, as it did not appear to reduce the symmetry of the complex to C_5, as would be expected if free rotation did not occur.

(iv) A 67.89 MH_Z PFT ^{13}C n.m.r. spectrum of the green compound in C_6D_6 (fig. 2.2.23) revealed aromatic signals assigned to dppe, and the aliphatic signals
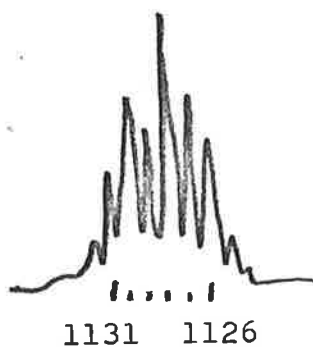
1131   1126

FIGURE 2.2.21   Mass spectrum of product of reaction between $W(N_2)_2(dppe)_2$ and $PHBu_2$.

Theoretical m/e peaks for $WH_2(PBu_2H)(dppe)_2$:

mass no.	relative intensity
1126	13.5%
1127	16.5%
1128	23.7%
1129	12.9%
1130	18.4%
1131	10.6%
1132	3.2%
1133	.7%
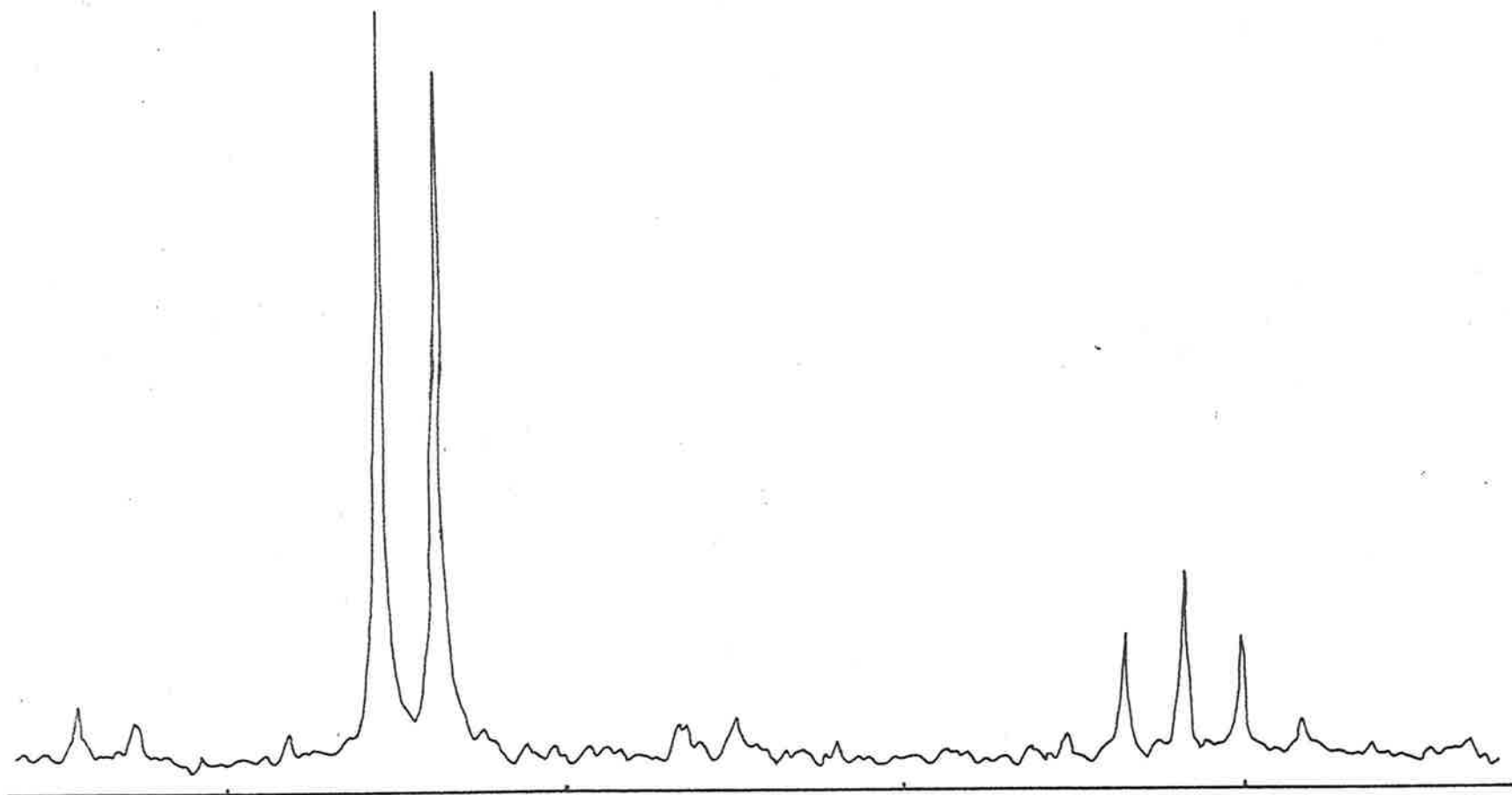
FIGURE 2.2.22 ^{31}P nmr spectrum of PHBu$_2$ product.
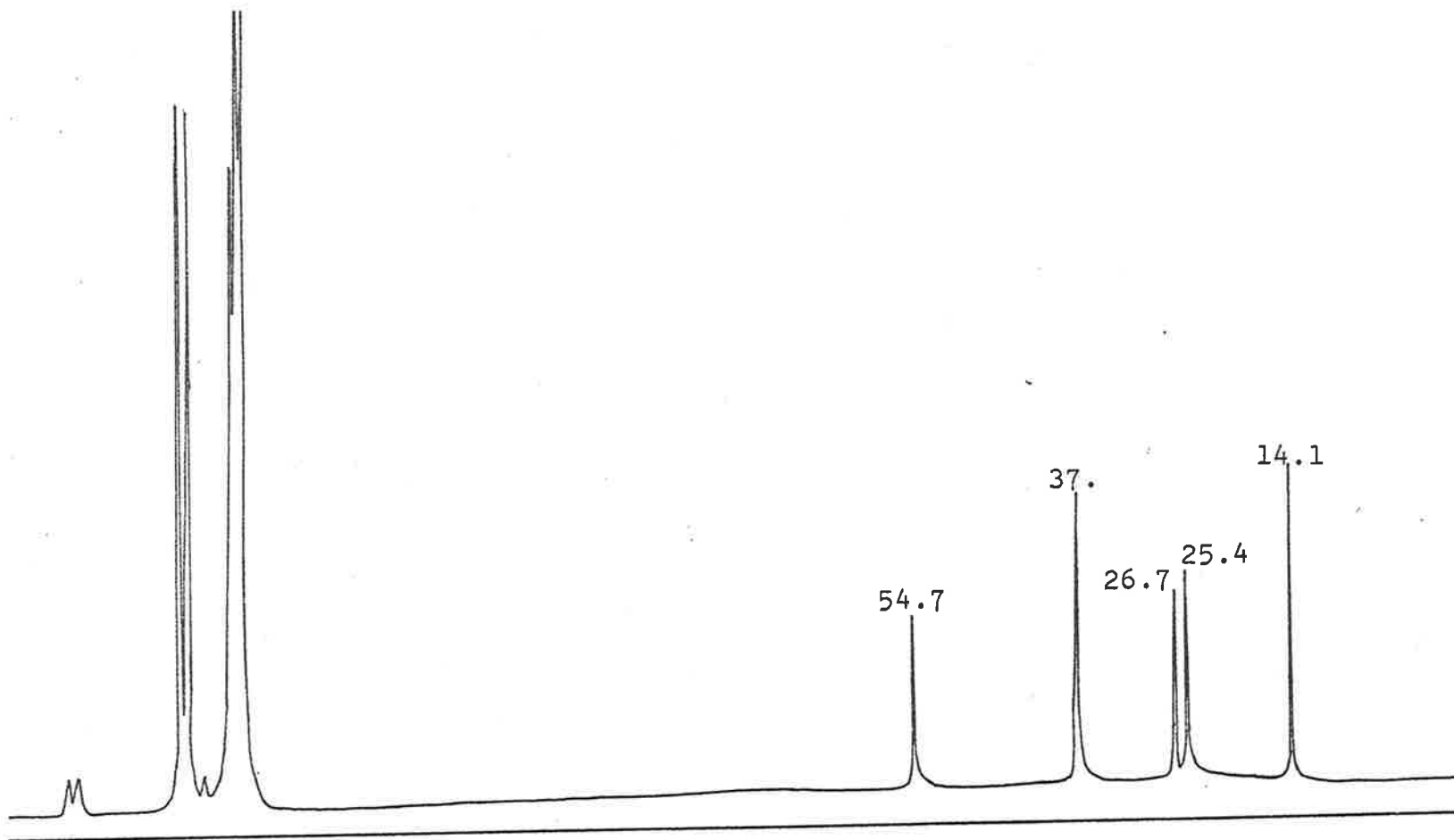
FIGURE 2.2.23 ^{13}C nmr spectrum of PHBu$_2$ product. (Chemical shifts measured with respect to C$_6$D$_6$ and converted to tms = 0.)

(iv) (Continued)

assigned to the bridging $-CH_2-CH_2-$ in dppe plus the butyl groups in PBu_3. No other ^{13}C signals were observed. This suggested that the sixth site on the metal centre was not occupied by a carbon containing ligand.

The bridging ethane in the coordinated dppe which gave rise to a quintet in the ^{13}C spectrum was assigned by comparison with the ^{13}C n.m.r. spectrum of $W(N_2)_2(dppe)_2$, in which the only aliphatic group is $-CH_2-CH_2-$ in dppe. For the dinitrogen complex the bridging ethane groups have δ = 32.17 ppm and $J_{p-c} + J_{p-w-p-c}$ = 10 ± 2 Hz, for the butyl phosphine complex δ = 37 ppm and $J_{p-c} + J_{p-w-p-c}$ = 10 ± 2 Hz.

(v) A 270 MHz PFT ^1H n.m.r. spectrum of the complex in C_6D_6 (fig. 2.2.24) revealed aromatic signals from dppe, aliphatic signals due to "PBu_3" and the ethane bridge in dppe and also an upfield signal characteristic of hydride. The upfield signal, centred at -3.05 ppm was very broad (ca. 250 Hz wide) and of low intensity, typical of tungsten hydride.[25]

Integration of the proton spectrum revealed a deficiency of 9 protons in the signal due to PBu_3, which suggests that possibly the monodentate phosphine is not PBu_3, but $PHBu_2$.

(vi) The space group and cell dimensions of the complex were determined using a precession camera. A section of a rhombic plate was selected which had
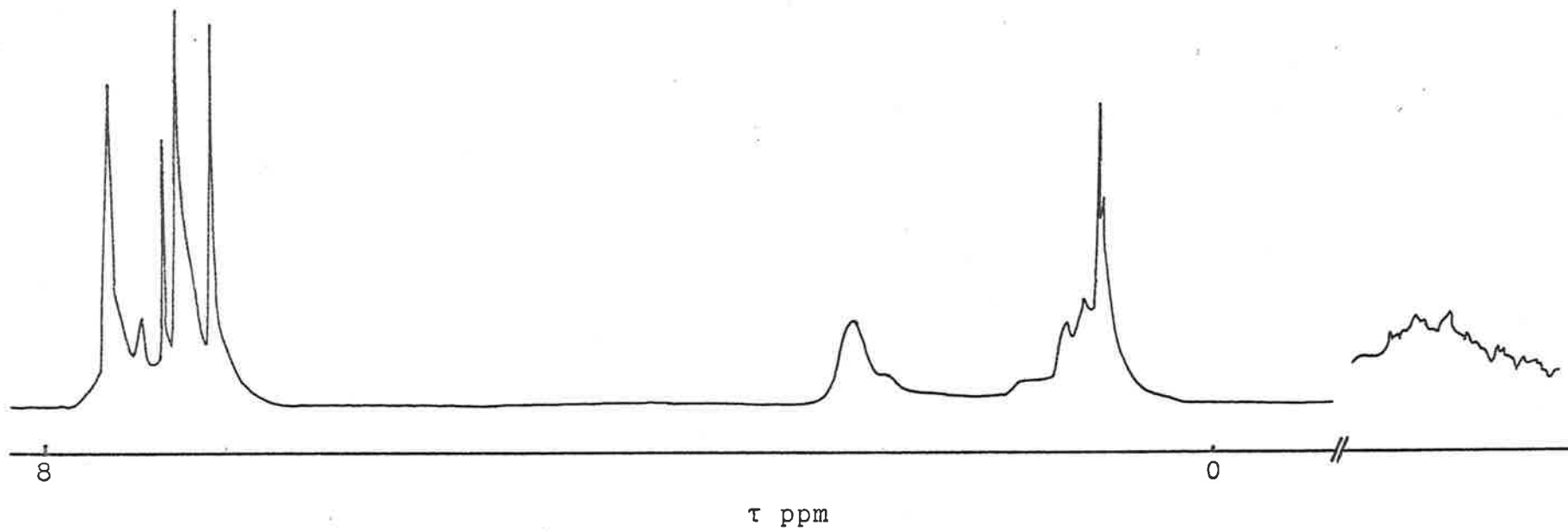
FIGURE 2.2.24 ^{1}H (270 MHz) PHBu$_2$ product.

(vi)   (Continued)

sharp extinctions at 90° under the crossed polars
of a polarising microscope. This was mounted on a
goniometer head with the axis of rotation parallel
to a^* taking b^* as being perpendicular to the plate
face. Precession photographs were taken and revealed
a monoclinic lattice of symmetry 2/m. The following
conditions for reflection were observed.

h0l	h = 2n	l = 2n
h1l	h = 2n + 1	
hk0	h + k = 2n	
hk1	h + k = 2n	

That is, h + k = 2n for all hkl and l = 2n for
h0l. From this it was deduced that the space group
was $C_{2/c}$, number 15.[26] Unit cell parameters were
found to be a = 12.07Å, b = 24.37Å, c = 20.7Å,
β = 78.5°. The volume is given by the equation
V = abc sin β and equalled 5966Å^3. The density was
found by suspending crystals in a mixture of
 1,2dichloroethane and 1,2dibromoethane,
d = 1.438. This led to MW = 5166/n = 1291, if z = 4.
If z = 8, MW = 646, which was less than the mass of
tungsten plus two dppe. It therefore seemed
reasonable to presume Z = 4 which gave the
coordinates of equivalent positions as (0,0,0),
($\frac{1}{2}$,$\frac{1}{2}$,0), (0,y,$\frac{1}{4}$) and (0,$\bar{y}$,$\frac{3}{4}$). These coordinates
have point symmetry 2 which suggested that the
W(dppe)$_2$ grouping lies in the xz plane and that the
W-PBu$_3$ group is colinear with b. The PBu$_3$ (or PHBu$_2$)

(vi)   (Continued)

grouping may be disordered (by rotation about the W-(PBu$_3$) bond) to allow the molecules in the lattice to have apparent symmetry 2.   The sixth coordination site was believed to be occupied by two hydride ligands.

(vii) A spectrum of the complex was obtained in thf under
    u.v. visible

oxygen and moisture free conditions (figure 2.2.25).

(c) Probable formulation

Two formulations were possible based on the above data:

(i) W(H$_2$)(dppe)$_2$(PBu$_3$)

This compound has MW = 1184, which was within the crystallographic molecular weight minus the probable error factor, particularly since there was probably benzene of crystallisation present in the crystal lattice.

The PBu$_3$ used as reactant ("Fluka 98% purum") had a ^{1}H n.m.r. and ^{13}C n.m.r. consistent with that reported in the literature.[27]   However a fully coupled ^{31}P PFT n.m.r. spectrum in C$_6$D$_6$ revealed a doublet at -37.5 ppm relative to the main singlet due to PBu$_3$.   (Literature 32.3 ppm[28] or 33.3 ppm for PBu$_3$,[29] 69.5 ppm for PHBu$_2$.   J$_{P-H}$ = 180 Hz for PHBu$_2$).[30]   The splitting observed was 193 ± 3 Hz.   This doublet was assigned to PHBu$_2$.   An integral revealed that PHBu$_2$ was present as approximately 6% of the ligand. Since PHBu$_2$ is present in small amounts in the starting material possibility (ii) was believed to be the product, and the presence of butyl phosphine explained the source of hydride in the complex.   Obviously the reaction was not a simple substitution, unlike the reaction with,
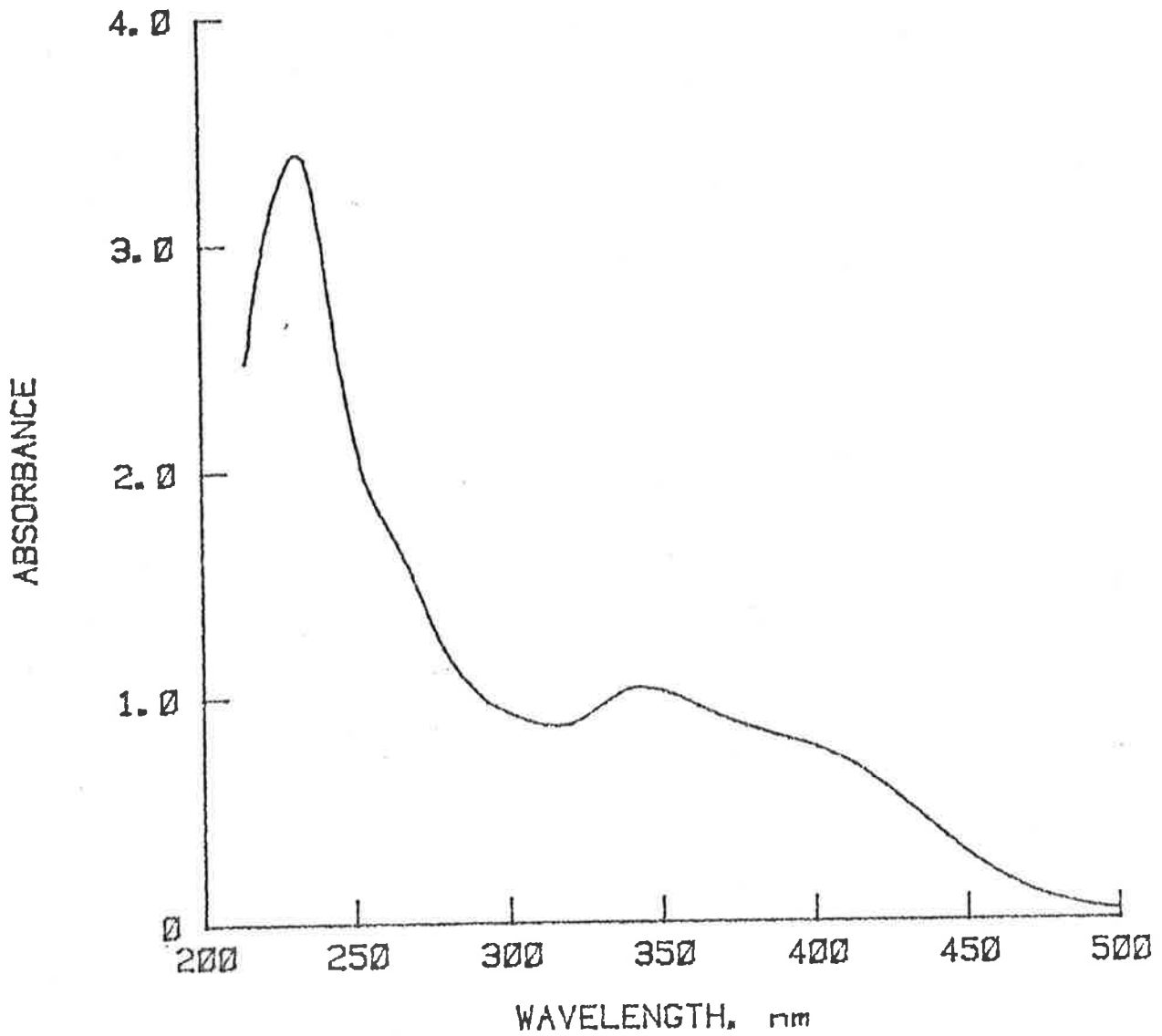
FIGURE 2.2.25a   UV/visible spectrum of PHBu$_2$, reaction region 200-500 nm. (Approx. 9 x 10^{-4} molar, 1 mm cell.)
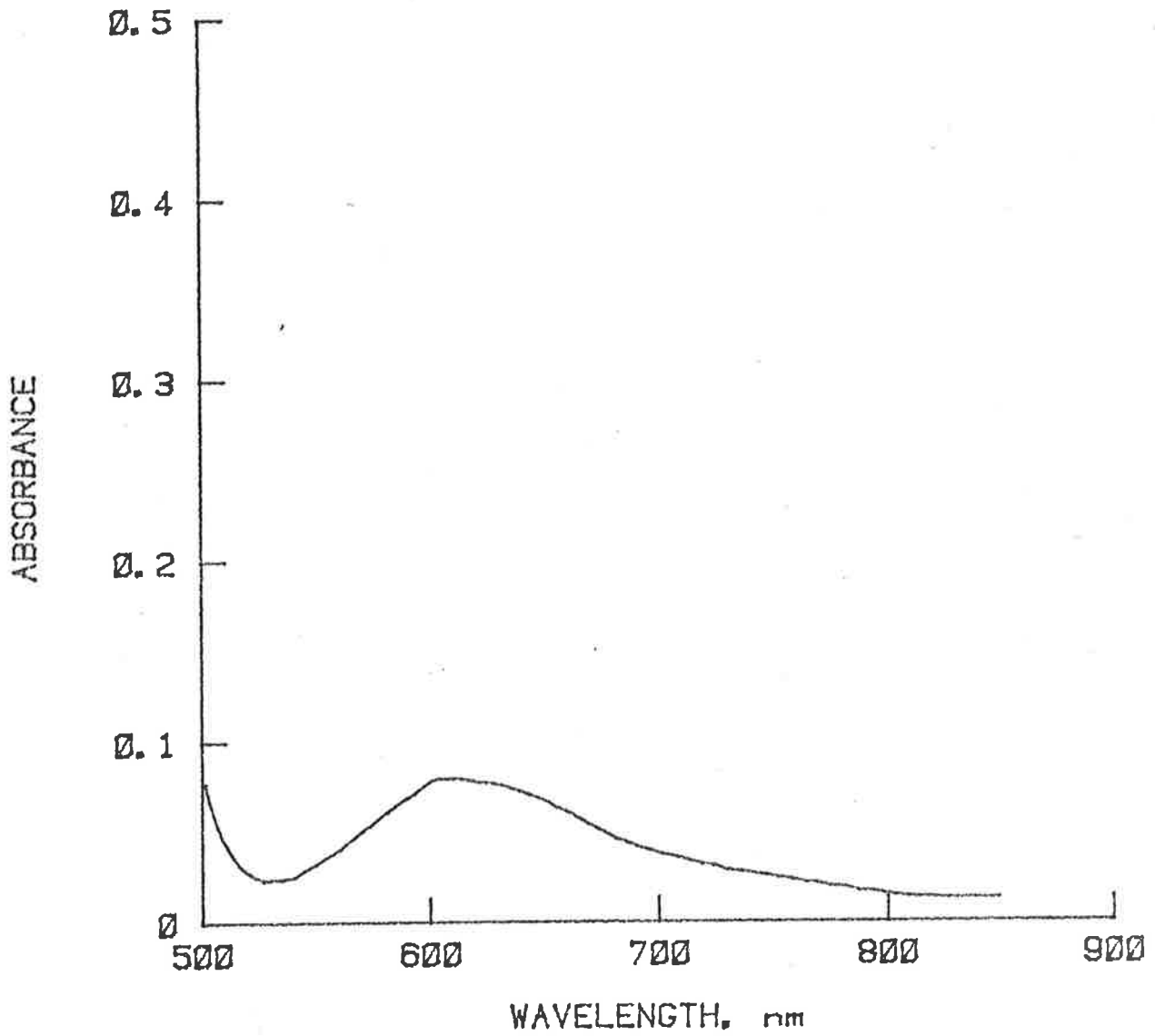
FIGURE 2.2.25b UV/visible spectrum of PHBu$_2$ product, region 500-850 nm. (Approx. 9 x 10^{-4} molar, 10 nm cell.)

for example, CO which only takes approximately three hours under similar conditions of illumination.

(ii) $W(H)_2(dppe)_2(PHBu_2)$

The integration of a n.m.r. spectrum of the complex revealed a smaller number of protons in the section of the spectrum assigned to the butyl phosphine than would be expected for PBu_3, and was in fact consistent with $PHBu_2$.

This formulation had mass no. 1126 for W = 182. An intense peak was observed in the mass spectrum of the green complex which starts at 1126, and was, in fact, the highest mass observed. The splitting of this peak was that expected for a compound with 60C and 1W. This meant that either the formulation was $W(H)_2(dppe)_2(PHBu_2)$, or else the compound was $W(H_2)(dppe)_2(PBu_3)$ and was not volatile in the mass spectrometer ., yet had a fragment at m-56 which was volatile. The latter possibility seemed to be unlikely, but could not be totally discounted.

It appeared that to distinguish between these two possibilities would be extremely difficult without an X-ray crystal structure study being undertaken and refined to a low R value. Since the molecules had symmetry 2 when averaged across the lattice, it would have been necessary to use partial occupancy factors in this structure analysis. Given the air and moisture sensitive nature of the complex it was believed to be unlikely that data collected in an X-ray structure analysis would be good enough to allow such refinement techniques to be validly employed.

2.3.1 Conclusion

The preparative experiment described above demonstrated quite clearly that there was a general class of photochemical reactions which $W(N_2)_2(dppe)_2$ may undergo. These reactions would appear to fall into 2 classes:

(a) Replacement of both dinitrogen ligands, e.g. to produce $trans\text{-}W(CO)_2(dppe)_2$.

(b) Replacement of one dinitrogen ligand by a group which then reacted to release an activated species which then in turn reacted with the other dinitrogen ligand to yield a substituted ligand, e.g.

$W(N_2)_2(dppe)_2 + Ethyl\text{-}Br \rightarrow Br_2W(N_2Et)(dppe)_2$.
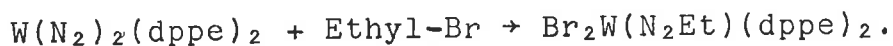
The similarity of the rates of these two types of reaction suggested that the same basic mechanism occurred in each case. The experiments involving isotopic labelling suggested that in dinitrogen saturated solutions a photostationary state existed involving release and recovery of the dinitrogen ligands.

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CHAPTER 3

3.1.0 Photochemistry:

A photochemical reaction may be defined as one which occurs when a molecule is excited by a quantum of light. Two basic rules apply to such processes;[1]

(1) Only radiation which is absorbed by the reacting system can be effective in producing chemical change.

(2) Each light quantum absorbed activates only one molecule.

The absorption of a quantum of light by some species A gives rise to an excited state A^*, which then must, within a relatively short time lose excess energy in order to return to equilibrium with the environment. This can occur in any of four ways:

$$A^* \longrightarrow A' \ (+X) \qquad \text{reaction}$$

$$A^* \longrightarrow A + h\nu \qquad \begin{array}{l}\text{radiative deactivation}\\ \text{(emission)}\end{array}$$

$$A^* \longrightarrow A + \text{heat} \qquad \text{radiationless deactivation}$$

$$A^* + Q \longrightarrow A + Q^* \qquad \text{bimolecular quenching}$$
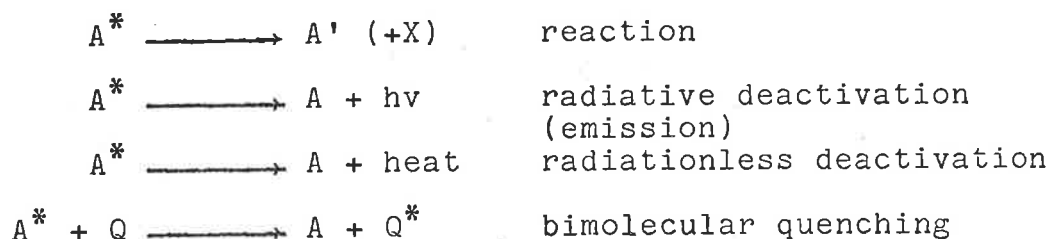
In the last case the quencher must then undergo one of the four processes itself. In the process of absorbing a quantum of light a "vertical transition" normally occurs, due to the Franck Condon principle (electronic transitions are so fast in comparison to nuclear motion that, during the act of the electronic transition, the nuclei do not alter appreciably their relative position or their kinetic energies). (see figure 3.1.1) This means that the species A^* is initially electronically excited and may well also be in a vibrationally excited state.[1] It should be emphasised that the species A^* is essentially a "new" chemical species, rather than a "hot" modification of A, and will
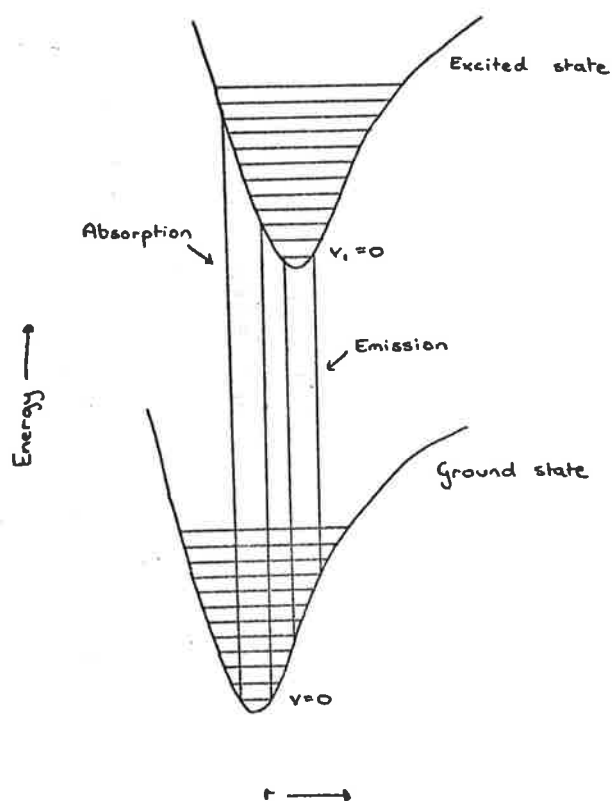
FIGURE 3.1.1   A schematic representation of absorption and emission of light, while obeying the Franck Condon principle.   From Balzani!

have a geometry, chemical and physical properties quite distinct from the initial state. However, in liquid phase a molecule experiences approximately 10^{13} collisions per second with the surrounding molecules, thus dissipating excess vibrational energy very rapidly by the process of vibrational relaxation. The thermally equilibrated excited state ("Thexi state"[2]) is probably the species which then undergoes reaction, emission, radiationless transition to the ground state or intermolecular quenching. Radiative deactivation or emission, which is termed fluorescence if it occurs between states of the same spin multiplicity, phosphorescence if a change in multiplicity is involved, occurs when the excited state returns to the ground state with an emission of light. Selection rules limit the efficiency of this pathway; the most rigorous rule is based on the orthogonality of spin function. However, this rule breaks down for molecules which contain heavy atoms and therefore experience strong spin - orbit coupling. When emission is observed from transition metal complexes it is normally shifted to the red (compared to the irradiating frequency) implying that energy has been dissipated by the process of nonradiative deactivation (vibrational deactivation).

Radiationless deactivation can take place as is shown in figure 3.1.2, which shows hypothetical potential energy curves for the ground state E_0 and for two excited states E_1 and E_2 of a hypothetical diatomic molecule. A vertical transition from the ground state results in the formation of E_2 at a vibrational level $\nu_2 = 6$. A rapid vibrational deactivation will occur, and result in a
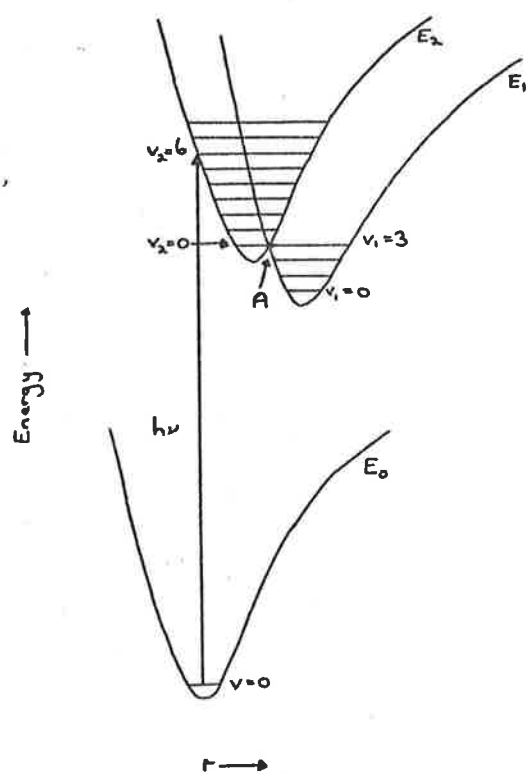
FIGURE 3.1.2   A schematic representation of two excited
states with vibrational energy levels
allowing "crossing over" to take place.
From Balzani!

decrease in ν_2. If some value of ν_1 has a similar energy
to some (low lying) level of ν_2 it will be possible for the
molecule to "cross over" to E_1 with (for example) $\nu_1 = 3$.
Vibrational relaxation will then cause ν_1 to decrease.
Further radiationless deactivation or radiative deactivation
may then occur.

Radiationless transitions must also obey selection
rules based on symmetry and spin, however, spin orbit
coupling which is more pronounced in the presence of a
heavy atom in the molecule, causes the spin selection
rules to break down. Radiationless transitions between
states of the same multiplicity are spin allowed (internal
conversion) and between states of different multiplicity
are spin forbidden (intersystem crossing).

Bimolecular quenching occurs when there is a transfer
of energy from A^* to some quencher Q. An example of this
is in the system $(Ru (III) (bipy)_3)^{3+}_{(aq)}$ plus $Cu^{2+}_{(aq)}$,
where the emission lifetime and intensity from Ru (III)$_{(aq)}$
(on U.V. excitation) decreases with increasing $Cu^{2+}_{(aq)}$
concentration. However, in this work no study has been
made of quenching processes.

In considering the spectrum of a complex it is
convenient to describe the ground state of the molecule as
consisting of "localised" molecular orbitals "belonging"
to metal or ligands. This model is based on the
assumption that the central atom and the ligands are
separated systems which only interact weakly with one
another. Thus a charge transfer transition can be
considered to take an electron from one localised
molecular orbital and move it to another molecular orbital.

Transitions can be considered in a number of classes, ligand field (d - d), ligand to metal charge transfer (LMCT), metal to ligand charge transfer (MLCT), ion pair charge transfer (IPCT) and charge transfer to solvent (CTTS). Intra ligand bands due to transitions between two molecular orbitals, both of which are principally localised on the ligand system may also occur. Generally, "if a band has a rather fixed spectral position independent of the oxidising character of the central metal, it may be assigned to internal ligand transitions".[3] For low valence heavy metals with ligands such as CO, N_2, SCN^- or conjugated carbon containing molecules the MLCT bands are favoured, rather than LMCT, due to the high electron density on the metal centre. The type of transition involved in an excitation has some influence on the chemical reaction of the excited states; d - d transitions tend to lead to solvolysis, LMCT tends to lead to reduction of the metal centre with concomitant oxidation of ligand, MLCT to oxidation of the metal centre with concomitant reduction of the ligand, while CTTS leads to reduction of the solvent with concomitant oxidation of the metal or the complex overall. However, in species where there is the possibility of intersystem crossing or internal conversion one may obtain unexpected products. For example, the products expected from a d - d transition may result from excitation of a MLCT band. Thus the photochemically activated reactions of $W(N_2)_2(dppe)_2$ appear to have a mechanism relatively independent of irradiating wavelength. This is because energy provided by irradiation of MLCT or mixed MLCT/d - d bands may well produce the same excited state.

3.2.0 Quantum yields:

A monochromatic beam of light passing through a solution of a complex generally obeys the Beer Lambert law, $I_{trans} = I_0 \times 10^{-\epsilon cl}$ (ϵ = molar extinction coefficient, c molar concentration, l the cell length). I_0 is referred to in terms of a flux, with units Einsteins (moles of photons) cm^{-2} sec^{-1}, however, when the same size cell is used for calibration and experimental work this can be reduced to Einsteins sec^{-1}. The light absorbed in a cell is given by $I_{abs} = I_0 \times (1 - 10^{-\epsilon cl})$. Quantum yield, ϕ, the proportion of molecules which react on excitation, can be defined by the equation:

$$\text{average rate} = \frac{-d[A]}{dt} = \phi \; I_m$$

where I_m is the average number of Einsteins absorbed by the reactant in unit volume in unit time and [A] the concentration of the reacting species.

In practice the flux emitted from a light source at a particular wavelength is measured by use of a photochemical reaction of known quantum yield, in this work $K_3[Fe(III)(ox)_3] \xrightarrow{h\nu} Fe(II)$, taking care that either almost all of the irradiating light is absorbed (i.e. absorbance $\geqslant 2$) or that the ratio I_{trans}/I_0 is measured. In this work the former approach was always taken. The solution to be studied, in a reaction cell with windows identical to those of the calibration cell is then placed in the light beam and irradiated.

If a reactant is the only absorbing species present, the initial photoreaction proceeds by a zero order rate law. However, as the reaction takes place

the absorbance of the products, at the irradiating wavelength may become non zero, and so

$$\text{rate} = \frac{-d[A]}{dt} = \phi I_0 (1-10^{-\Sigma \epsilon c l}) \frac{\epsilon_A C_A}{\Sigma \epsilon_i C_i}$$

where $I_0 (1-10^{-\Sigma \epsilon c l})$ represents the light absorbed at some wavelength, and $\frac{\epsilon_A C_A}{\Sigma \epsilon_i C_i}$ represents the absorbance due to A relative to the total absorbance at that wavelength. However, if the absorbance of all of the products is much less than that of the starting material, it can be seen that the photochemically induced reaction will have zero order while the absorbance is greater than two. The tendency of the reaction rate to diminish due to absorbance of light by the product is termed the inner filter effect.

Quantum yields do not give any information as to the rates of the steps of the photochemical reaction, (the overall rate measured in quantum yield determination being determined by ϕ and the flux of light) nor is the temperature dependence of ϕ very meaningful in terms of the activation energy.

This can be most clearly seen from the reaction scheme:

$$A \xrightarrow{\text{rate} = I_{abs} \times \phi} A^* \qquad \text{activation}$$

$$A^* \xrightarrow{k_1} \text{products} \qquad \text{reaction}$$
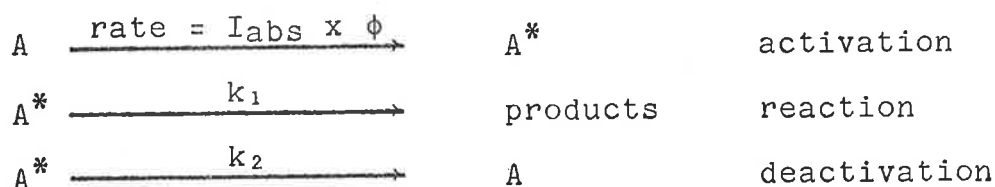
$$A^* \xrightarrow{k_2} A \qquad \text{deactivation}$$

The quantum yield for such a reaction scheme is given by:

$$\phi = \frac{k_1}{k_1 + k_2} \quad \text{and thus the apparent activation energy}$$

$$E_{app} = E_a - \frac{R}{1/T_2 - 1/T_1} \ln \frac{e^{-E_a/RT_1} + k_2/A}{e^{E_a/RT_2} + k_2/A}$$

where E_a is the activation energy of the primary photochemical process.

Thus E_{app} is a function of T and is always less than E_a, the activation energy. The situation is even more complicated, and E_{app} further from E_a when more complex reaction schemes exist.

3.2.1 Quantum yields: experimental

Quantum yields were determined using the apparatus shown diagramatically in figure 3.2.1. The light source used was a 100 W or 150 W quartz iodine lamp (with a parabolic reflector), coupled to an optical wedge. Light was allowed to impinge upon, and leave, the optical wedge via two vertical slits (2 mm wide) which caused a narrow band of wavelengths to be transmitted into a cell mounted in the brass block. Water was circulated through the block in order to thermostat the cell at 25°C. A typical energy spectrum of the beam of light emerging from the optic wedge is shown in figure 3.2.2. The wavelength normally used (*ca.* 420 nm ± 15 nm) was in the region assigned to a mixed d - d/MLCT region of the spectrum. Quantum yields were not measured at much longer wavelengths as the complex does not absorb strongly above 450 nm. The light source was connected to a constant current power supply[*] which was also fitted with a standby load. This allowed the supply to come to, and stay at, a thermally and electronically stable state, and thus

---

[*]Constant current rather than constant voltage was used as the lamp filament resistance was *fairly* constant, once it had reached operating temperature, thus at constant current the power dissipation was also constant. With a constant voltage supply any change in lead or contact resistance would change the current and therefore the power dissipated by the filament.
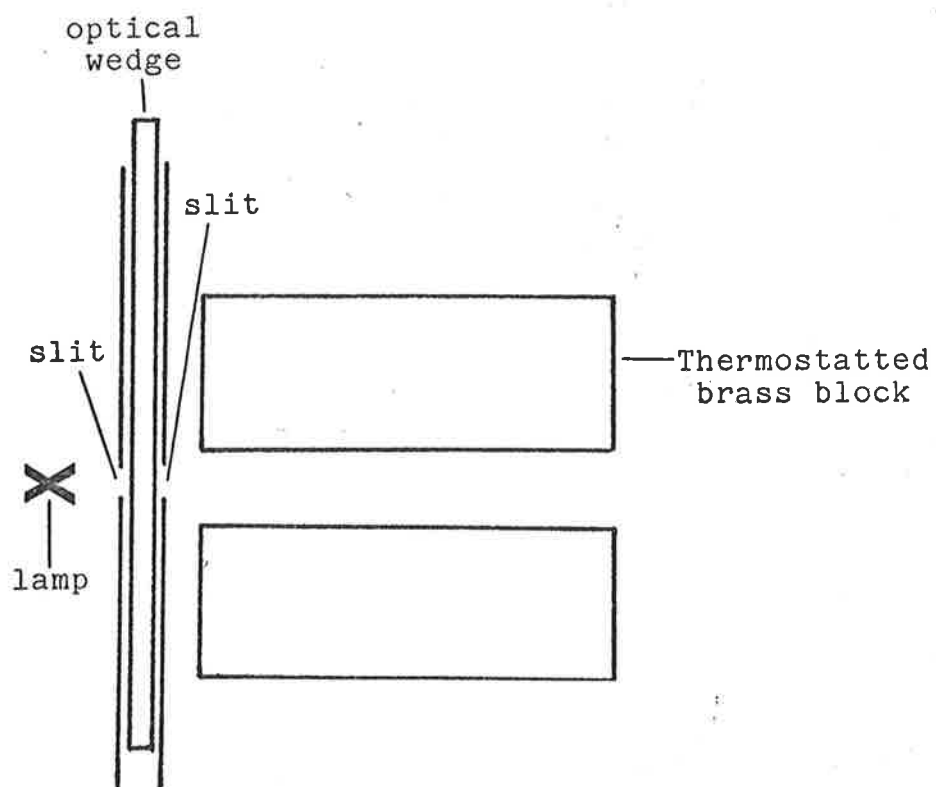
FIGURE 3.2.1 Diagrammatic representation of quantum yield apparatus.
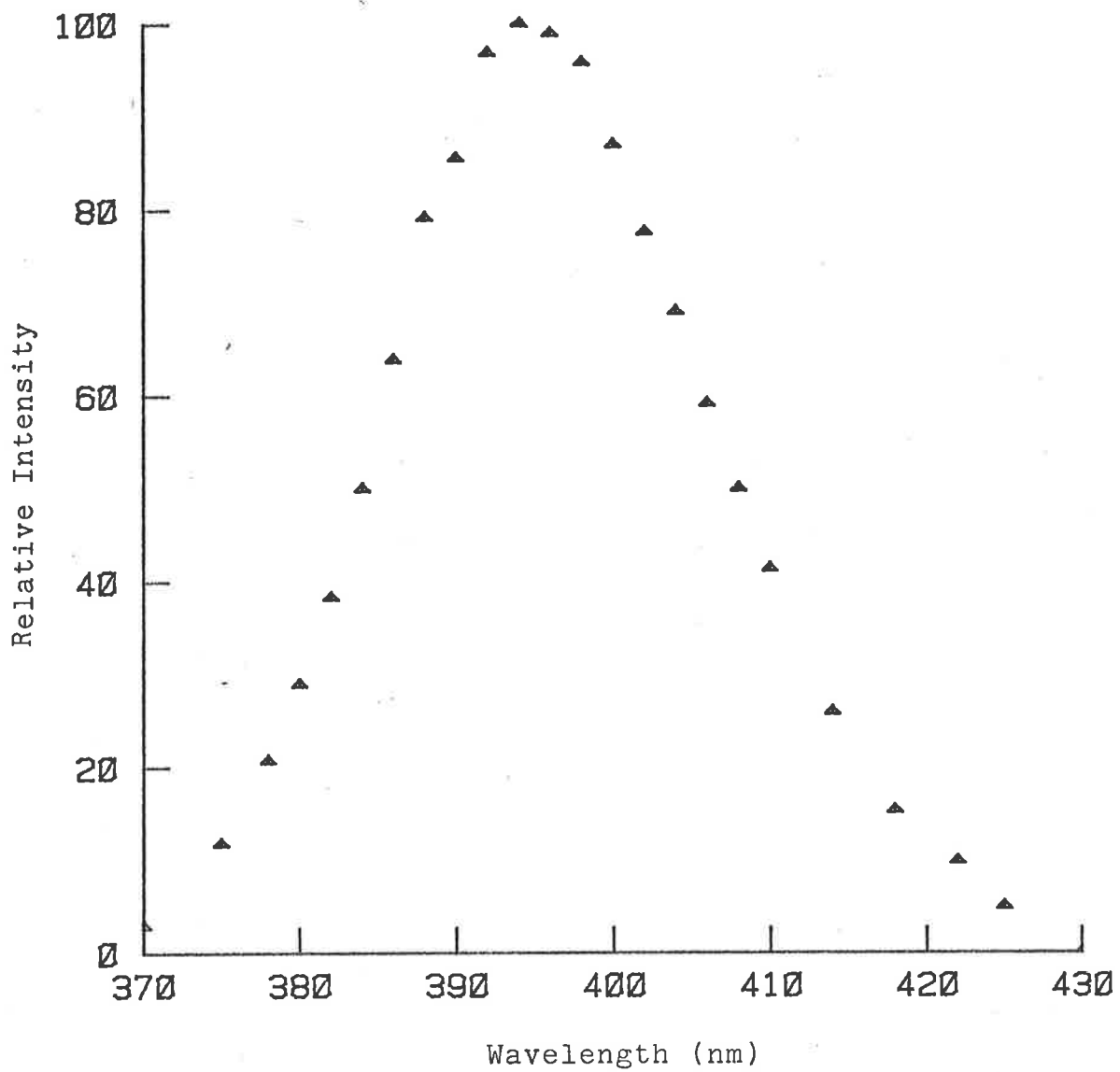
FIGURE 3.2.2   A typical energy spectrum of the output
of the optical wedge/lamp combination
used for quantum yield experiments.

prevented drift of the light intensity during a reaction. The supply/lamp combination was found to be stable over long periods of time (i.e. days) by the use of the ferrioxalate actinometer.

3.2.2 Actinometry

The total incident light on a cell mounted in the brass thermostatted block was measured using solutions of $K_3[Fe(III)(ox)_3]$. The actinometer was prepared by the method of Hatchard and Parker,[4] and was used as a .15 M solution in .05 M H_2SO_4, stored under N_2. The actinometer solution (*ca.* 12 cm^3) was placed in a 40 mm path length quartz cell, and high purity N_2 bubbled through, for 5 minutes before the exposure commenced, and continued until the end of the exposure. The light source was turned on for a known time, ranging from 30 seconds to 10 minutes. The quantity of Fe^{2+} produced was determined by taking a small aliquot (1 to 5 cm^3), mixing with buffer (5 cm^3 .6 M Na Acetate, .18 M H_2SO_4), 1, 10 - phenanthroline (1.%, 2 cm^3) and diluting to 25 cm^3 . The quantity of Fe^{2+} present was determined by reading the absorbance at 510 nm using a Varian Associates 635 dual beam spectrophotometer. The intensity of the absorption of the developer (on that particular spectrophotometer) was determined by constructing a calibration curve using $Fe(II)(NH_4)_2(SO_4)_2$ as a source of Fe^{2+} and identical experimental procedure. The actinometer was found to be extremely sensitive to traces of oxygen, and was handled

under high purity N_2 until the developer was added.[*] This
is because the reaction below occurs.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2Fe^{3+} + H_2O$$

At the concentration of Fe^{2+} produced (10^{-4} M) the extent
of this reaction could be significant, and lead to
incorrect results. Typical values for the quantity of
Fe^{2+} produced were in the range 2 to 5 x 10^{-9} moles
sec^{-1}; since the quantum yield for this reaction is close
to 1 this means that the cell received an integrated
intensity of 2 to 5 x 10^{-9} Einstein sec^{-1}.

The work described in this section was carried out
in a darkroom, illuminated only by two Kodak 40 Watt
safelights with No. 2 filters.

3.2.3 Photolysis of $W(N_2)_2(dppe)_2$

Solutions of $W(N_2)_2(dppe)_2$ for photolysis were
prepared in the following way. A small sample (ca. 3 mg.,
3 x 10^{-6} moles) was weighed accurately on a Cahn
Electrobalance and tipped into a sealed optical cell
assembly (Plate 1), which consisted of 10 mm and
1 mm pathlength cells, joined at a right angle. This cell
was connected via a special adapter to the solvent still.
The cell and filling apparatus were evacuated using a
rotary vacuum pump for ca. 20 to 30 minutes. If any
volatile reactants were to be added, they were distilled
into the collection finger via a sidearm.

---

[*] As has been pointed out in the literature, phen[5] solutions
used for this work should be freshly prepared (i.e. within
ca. 10 days) and should not be left in the light, as long
wavelength ultraviolet photolysis changes the ability of
the phen to form the highly coloured Fe(II)phen complex.

PLATE 1   Cell for quantum yield determinations.
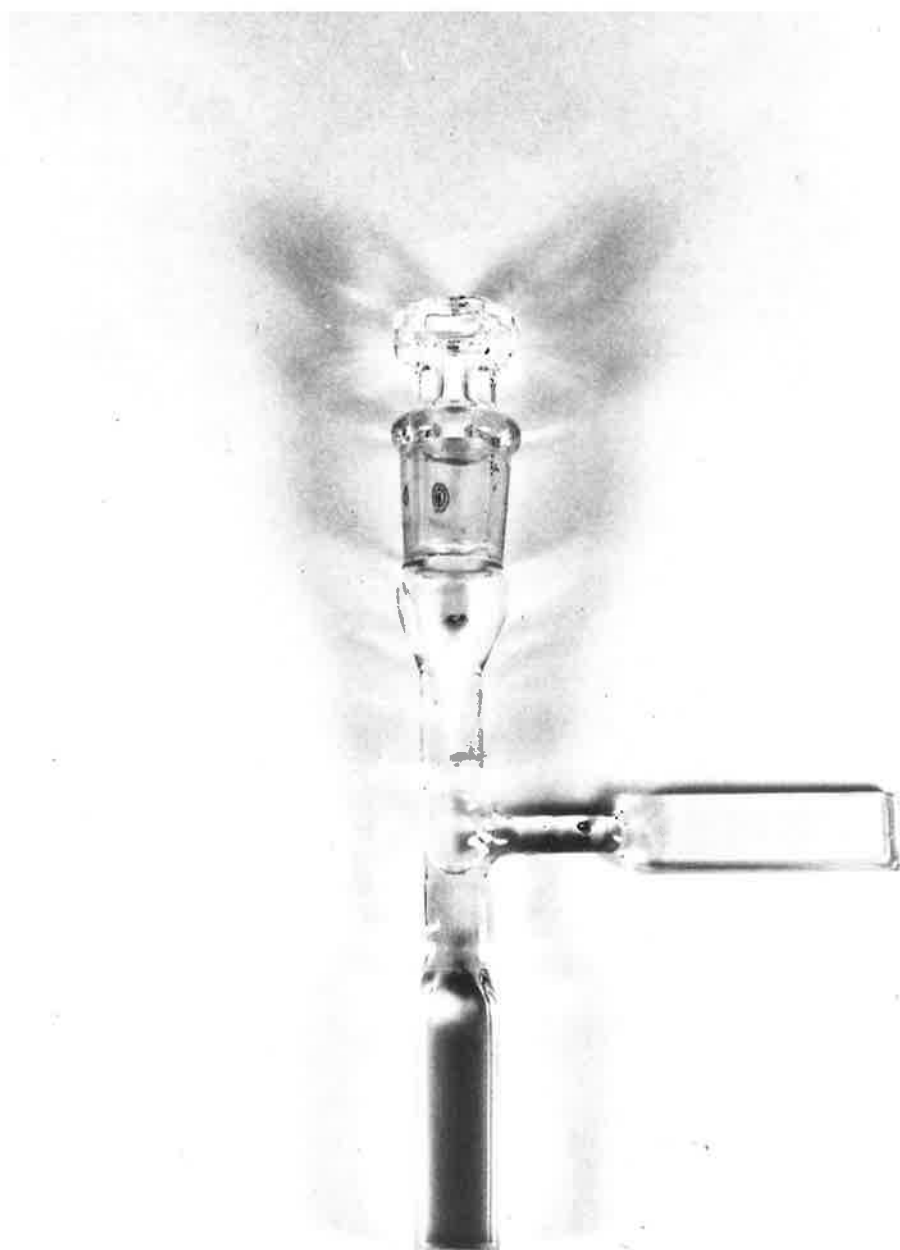
Solvent was then poured into the collection finger, and the apparatus inverted and the cell filled. There was a line engraved on the collection finger to give a rough indication of the volume of solvent (ca. 5 cm^3) being added. The precise volume of solvent was determined from the difference in mass of the empty cell plus stopper and the stoppered full cell. Once the solvent was in the cell a twin oblique tap was opened to allow N_2 to flow into the apparatus, and a dinitrogen stream was maintained over the cell as it was quickly removed and stoppered. The cell was protected from stray light and taken to the darkroom for reaction.

The spectrum of the solution was measured using the 1 mm path cell, while the 10 mm cell was used for irradiation. The entire volume present normally fitted in the irradiation cell, and the reaction was carried out in short intervals. The cell was shaken at the end of each of these before the absorbance at 297 nm was determined relative to that of a 1 mm pathlength cell containing solvent only. The concentration of $W(N_2)_2(dppe)_2$ was calculated by use of the equation

$$A_\infty^{297} = \epsilon_1 C_1 + \epsilon_2 C_2$$

where ϵ_1 and C_1 refer to the starting material and ϵ_2 and C_2 refer to the product. This can be expressed, for a reaction scheme such as

$$W(N_2)_2(dppe)_2 + RX \longrightarrow XW(N_2R)(dppe)_2$$
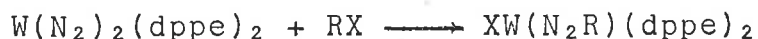
by $A_t = \epsilon_1(c_1 - x_t) + \epsilon_2 x_t$, where A_t is the total absorbance after exposure for time t, c_1 the initial concentration of $W(N_2)_2(dppe)_2$, ϵ_1 the extinction coefficient for

$W(N_2)_2(dppe)_2$ and ε_2 the molar extinction coefficient of the product. (Determined from A_∞^{297}, the absorbance once the reaction had gone to completion.) A plot of x_t, the molarity of the product versus t was found to be linear (see figure 3.2.3) in the initial stages of the reaction (generally $r^2 \geqslant .995$). Quantum yield was calculated by determining the number of moles reacted and dividing by the integrated intensity of the irradiating light for the time period being considered. Quantum yields were found to range from $ca.$ .1 (PMe_3, low [RBr]) to $ca.$ .5 (RBr at high concentrations).

More accurate values of ϕ were determined by using the initially determined value (from $\Delta n/Flux$) as a first approximation in a kinetics simulation programme which corrected for change in I_{abs} due to inner filter affects. A plot of calculated $[W(N_2)_2(dppe)_2]$ versus time was compared to the experimentally observed plot and the initial estimate of ϕ refined. The scheme used was simply

$$W(N_2)_2(dppe)_2 + RBr \xrightarrow[\phi]{h\nu} BrW(N_2R)(dppe)_2.$$
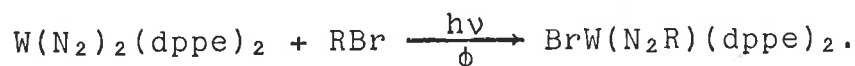
Intermediates were not put into the scheme as steady state concentrations of these species were very low at the flux used, and thus the intensity of light absorbed by the intermediates was very low. The concentration of the intermediates was never greater than the value of the flux of the light as the following scheme shows.

$$W(N_2)_2(dppe)_2 \xrightarrow{h\nu} W(dppe)_2$$

① ② fast ③
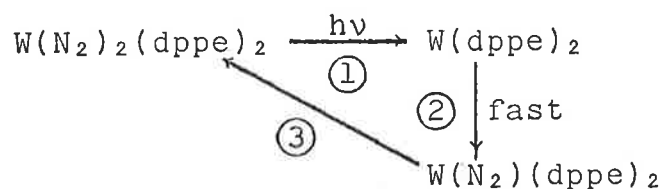
$$W(N_2)(dppe)_2$$

FIGURE 3.2.3   Change in concentration during quantum
yield determination for first 180
seconds. (7.3 cm^3 thf, .19 molar
[lBrBu], 3.3 x 10^{-6} mol s of
$W(N_2)_2(dppe)_2$, 1.05 x 10^{-8} Einstein
$second^{-1}$ flux.)

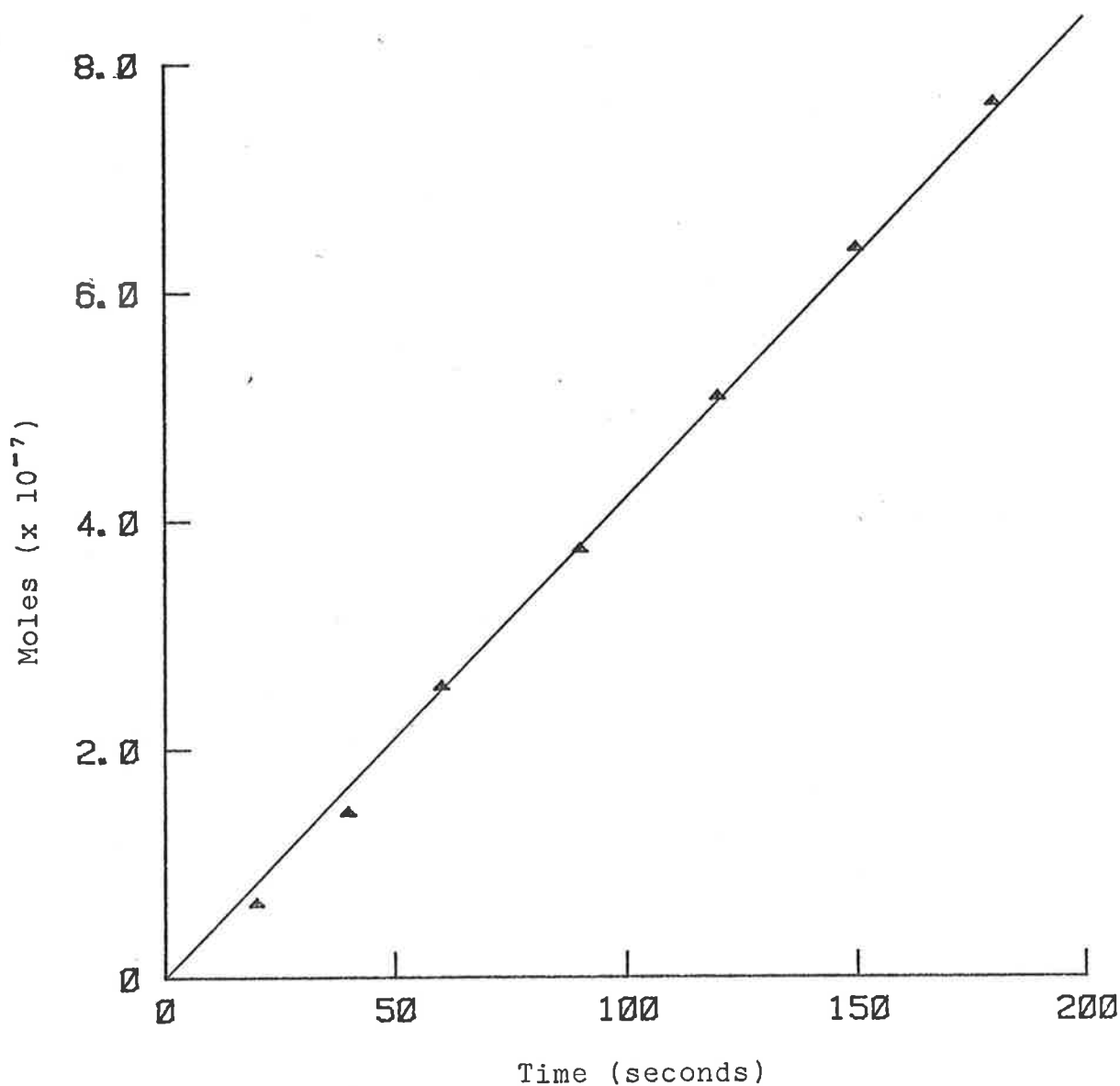In the absence of any other reactions the rate of step ③ must be equal to the rate of step ①. Since k_3 for step 3 is approximately 1. then the concentration of $W(N_2)(dppe)_2$ can be no higher numerically than the rate of formation of $W(dppe)_2$. The rate of formation of $W(dppe)_2$ is given by $I_{abs} \phi_{pr}$ where ϕ_{pr} is the quantum yield of the primary photochemical process. The concentration of $W(dppe)_2$ would be approximately 10^{-2} times the concentration of $W(N_2)(dppe)_2$ as k_2 is approximately 10^2 times k_3. See figure 3.2.4.

3.2.4 Quantum yield results

Quantum yields were measured as a function of the concentration of 1-bromobutane and for various reactions at high concentrations (*ca*. .2 M). The results of the comparison of various reactions are shown in table 3.2.1. The values of ϕ at high alkyl halide concentration for 1-bromobutane and 2,2-bromomethylpropane are averages of 5 measurements at fluxes from 1 to 5×10^{-9} Einstein/second, and with $[W(N_2)_2(dppe)_2]$ varying from $2. \times 10^{-4}$ molar to 1×10^{-3} molar. No consistent variation was found in these values, and so it would appear that ϕ is independent of $[W(N_2)_2(dppe)_2]$ and I_{abs}, the flux absorbed. The maximum value observed was approximately .4 in all cases. This was believed to be due to either of two possible mechanisms.

(1) Relaxation of the initial active intermediate
    $(W(N_2)_2(dppe)_2{}^*)$ back to the ground state occurring
    in 60% of cases, or

(2) Competition between N_2 and RX for the free coordination
    site on the second intermediate $(W(N_2)(solv)(dppe)_2)$.
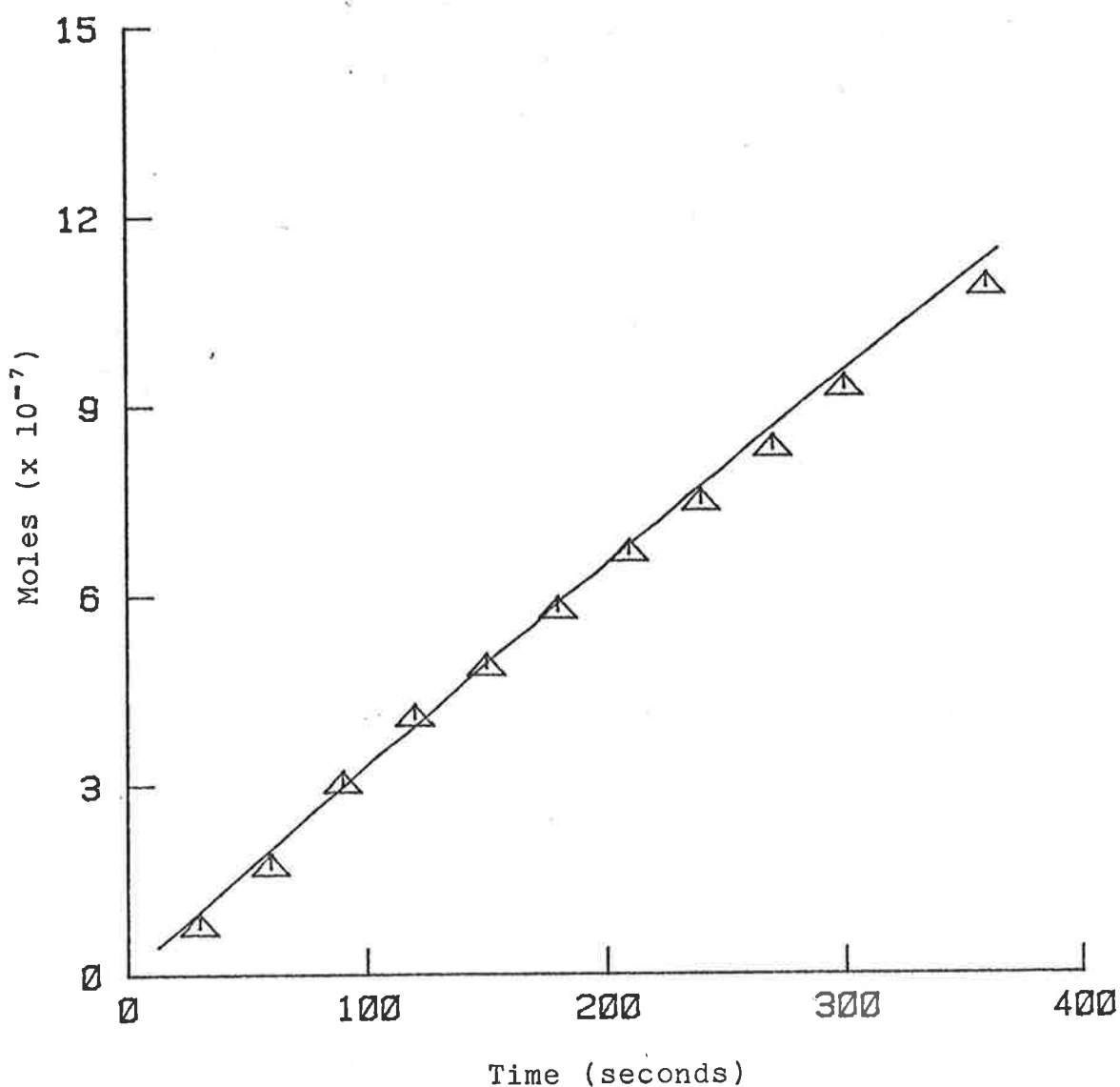
FIGURE 3.2.4   Change in concentration over a longer run
Δ, compared to computer simulated
photochemical reaction —.   (6.6 cm^3 thf,
7 x 10^{-3} molar [1BrBu], 3 x 10^{-6} mol of
$W(N_2)_2(dppe)_2$, flux = 1.56 x 10^{-8} Einstein
$second^{-1}$.)

Table 3.2.1

Quantum yield values for the reaction of

$W(N_2)_2(dppe)_2$ and various species.

Reactant		Quantum yield
2,2-bromomethylpropane	*ca.* .1 M	.48
2-bromobutane	*ca.* .1 M	.38
1-bromobutane	*ca.* 10^{-5} M	.1
	ca. .02 - .2 M	.42
PMe_3	*ca.* .01 M	.10
$PHBu_2$	*ca.* .01 M	.2

All values are based on the disappearance of
$W(N_2)_2(dppe)_2$, rather than formation of product.

Competition studies (dependence of quantum yield versus [RX] (figure 3.2.5)) showed that quantum yield was only dependent on [RX] in the range [RX] = .001 M to [RX] = .03 M. This suggested that relaxation of $W(N_2)_2(dppe)_2$ to the ground state occurred in 60% of all cases without chemical reaction, via either radiationless deactivation or emission. All attempts to find any emission band were unsuccessful apart from emission similar to that found from dppe in benzene or thf solution.

Given the presence of an atom with a large number of electrons in the centre of the complex, the presence of an efficient radiationless deactivation pathway is not unexpected.

3.3.0 Flash Photolysis

Reactions of the type described in chapter 2 showed that there was a general class of substitution reactions of $W(N_2)_2(dppe)_2$ which were photochemically activated, and appeared to involve the dissociation of at least one dinitrogen ligand from the complex. The quantum yield measurements reported above showed how efficiently the light activation was utilised.

These observations implied the existence of a "photostationary state", which occurs when the rate of a photochemical step is equal to the rate of a relaxation process back to a starting material.

$$W(N_2)_2(dppe)_2 \underset{k_r[W(solv)_2]}{\overset{\phi\ I_{abs}}{\rightleftarrows}} W(solv)_2(dppe)_2 + 2N_2$$
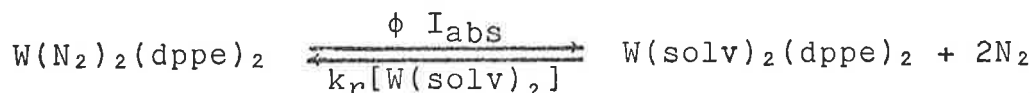
(I_{abs} is the intensity of the light absorbed, ϕ the quantum yield, and k_r the rate coefficient for the reverse step.)
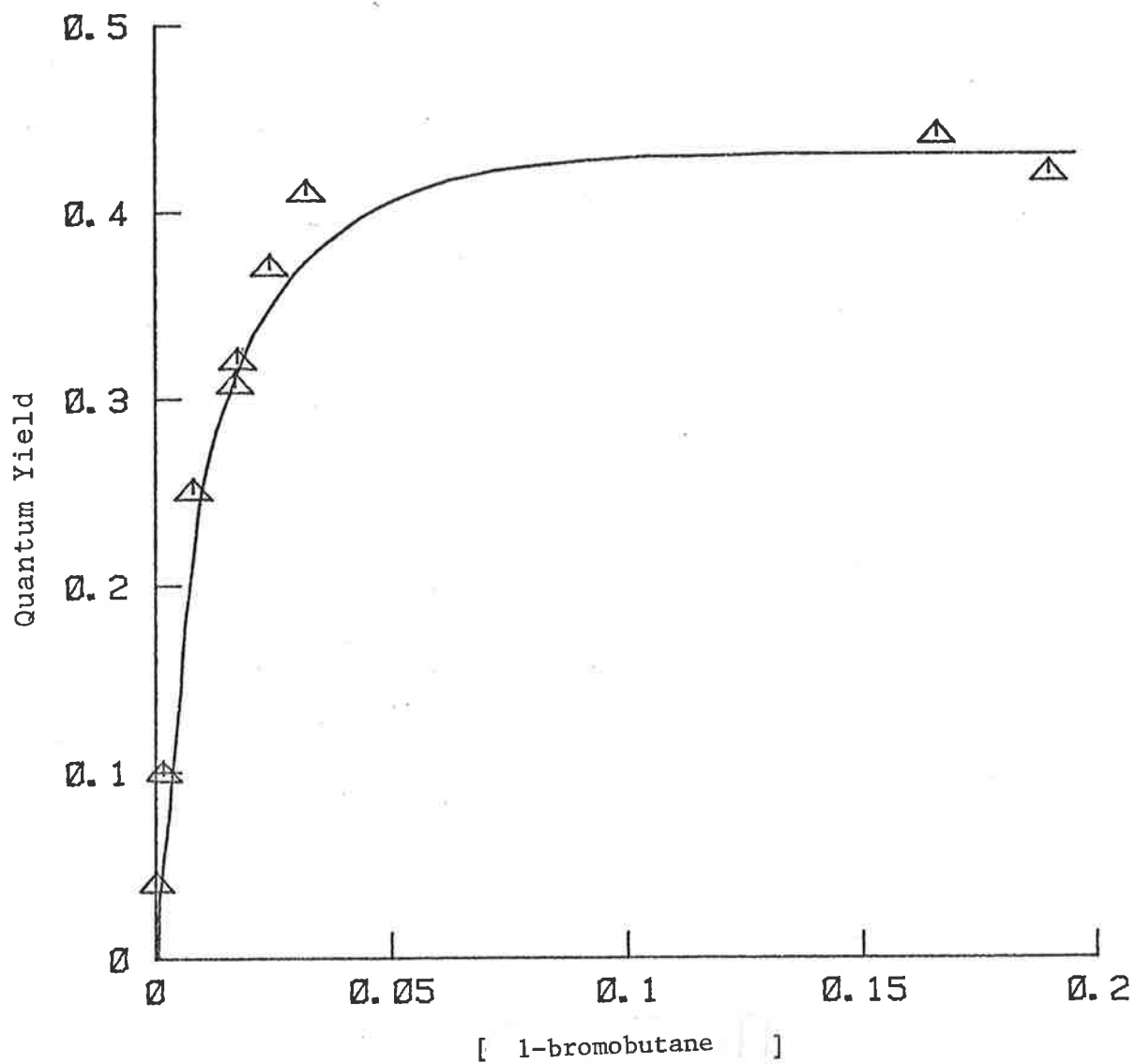
FIGURE 3.2.5 A plot of quantum yield versus concentration, for the reaction between $W(N_2)_2(dppe)_2$ and 1-bromobutane e, in thf solution. All data at 25°C.

Dinitrogen saturated solvent

If the amount of light absorbed can be readily
increased by a large factor, for a short time, and then
decreased again it is possible to observe the return
(or "relaxation") to the initial photostationary state
once the perturbation has been removed. This is one of
the bases of flash photolysis.

3.3.1 Flash Photolysis Experimental Method

(a) Hardware

In this work the apparatus used for flash photolysis
was basically that described by Thornton and Laurence.[6]
Figure 3.3.1 is a block diagram of the flash photolysis
apparatus.

The capacitor had a maximum stored energy of 1000
joules, and was discharged through the xenon oxygen
flashlamp by a mercury ignitron, which was triggered by an
SCR circuit controlled by TTL pulses. The light flash had
a width at half height of 10μ sec. The monitoring light
source was a 75 watt xenon mercury arc lamp (Illumination
Industries Inc.) which emitted a number of intense lines
in the ultra violet region. These were found to be
extremely useful due to the high optical density in the
ultra violet region of the spectrum of the solutions used.
The light from this source was passed through a high
intensity monochromator (Bausch and Lomb), then through
the cell, and finally through another monochromator into
the photomultiplier.

The photomultiplier unit incorporated a fast
voltage follower with low output impedance, and
resistance/capacitance signal conditioning circuits used to
filter noise.
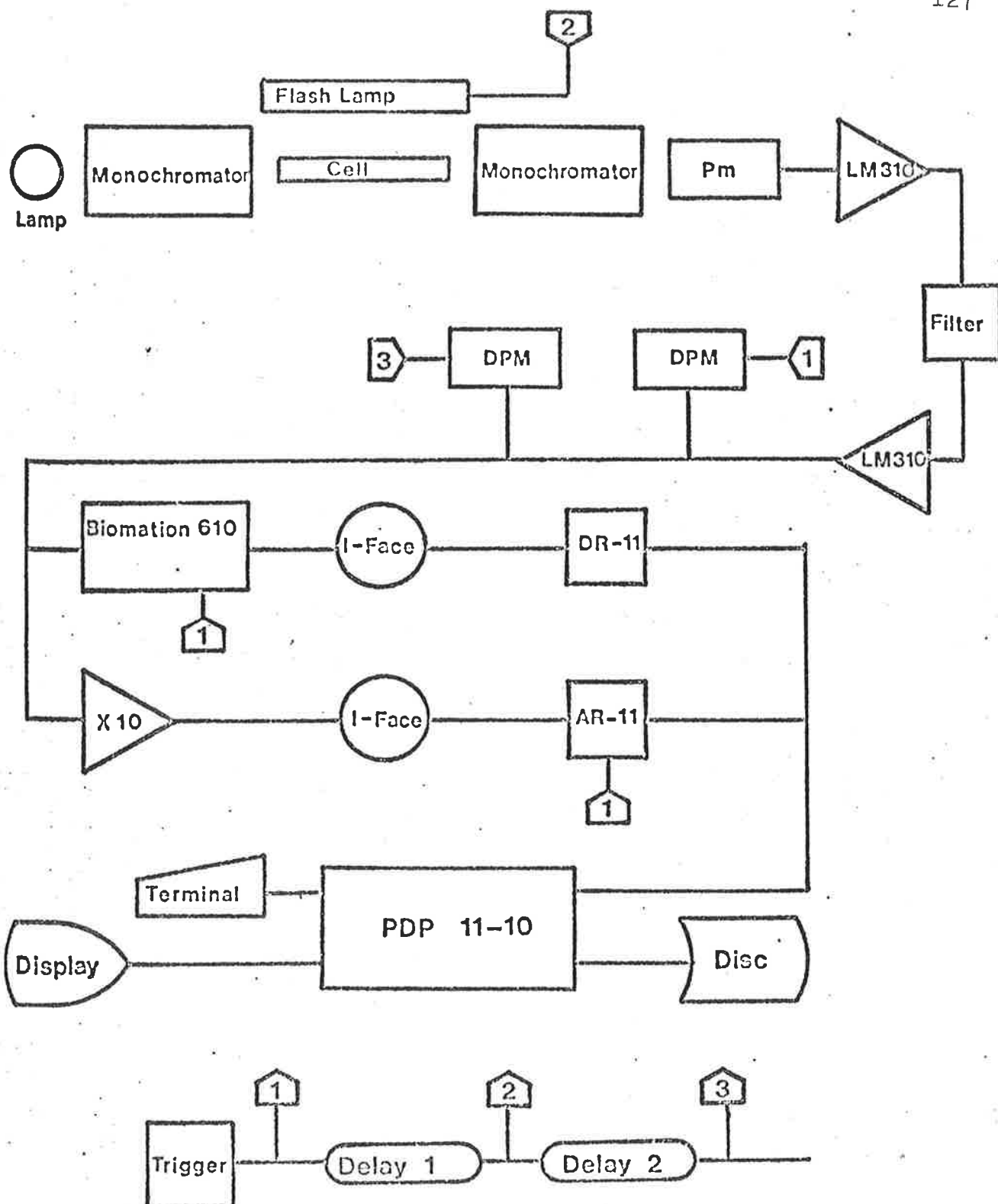
<u>FIGURE 3.3.1</u> Block diagram of the flash photolysis equipment used. From Thornton and Laurence.[6]

The experimental data recorded was the changing transmitted light due to the changing transient concentrations, generally as the system relaxed to the photostationary state. This was recorded using two analogue to digital recorders, one a Biomation 610B, and the other a Digital Equipment Corporation AR-11 real time subsystem interfaced to a PDP - 11/10 computer. The initial transmittance signal was recorded by a digital panel meter which sampled and held the value of the signal on receiving a trigger pulse, usually a short time before the flash lamp was fired.

A pulse generator operated in single shot mode provided master timing pulses. Serial delays were used to generate delayed pulses for triggering the second A-D converter or the flash lamp. DC coupling of the signal allowed observation of slow processes, but necessitated the use of a differential amplifier and a variable DC back off voltage. Most of the initial signal was removed before analogue to digital conversion to allow small changes in transmittance to be followed accurately.

The Biomation 610B was used to record samples at intervals of less than 50 milliseconds. Sample times ranged from 100 nanoseconds to 50 milliseconds and the recorder stored internally two hundred and fifty 6 bit integers. The Biomation was interfaced to the PDP 11/10 computer through a Digital Equipment Corporation DR-11C interface board and a simple interface which provided control latches and inverted the signal from the 610B to make it compatible with those of the DR-11C and the software used. The Biomation 610B was also connected to

an oscilloscope which displayed the contents of the 250 memory locations, as an analogue signal. This was used for setting up and checks on equipment. The DEC AR-11 subsystem was used in this work for recording transients at sample times of greater than 50 milliseconds. The AR-11 converter had a maximum conversion rate of 30 KHz, and provided 10 bit data. A differential amplifier with (switchable) fixed gains of unity, three and ten was interposed between the photomultiplier and the AR-11 input. The sample interval of the AR-11 was under programme control, and the data in the form of a two hundred and fifty element array was stored directly into the computer central memory.

Both the Biomation 610B and the AR-11 converter were triggered in advance of the firing of the flashlamp, in order to monitor V0, the initial transmittance. Timing was arranged so that approximately twenty five samples were taken of V0 before the flash lamp discharged. The light output of the flash lamp was monitored using an integrating circuit connected to a fast PIN photodiode, coupled to the flashlamp by a perspex lightpipe. The integrated intensity was displayed on a digital panel meter. The integrating circuit was triggered by the signal from the PIN diode.

The overall timing diagram for the hardware can be shown as below;

```
←  _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ 250 samples for AR-11 _ _ →
I                                                                    I
I ← _ _ _ _ _25 _ _ _ _ _ →                                          I
I    AR-11 samples                                                   I
I                                                                    I
I                                                                    I
I        _ _250_samples_for_610B _ _ _                               I
I      I                         II           I                      I
I      I                         II           I                      I
I      I  25 610B                II           I                      I
I      I _samples_               II           I                      I
I      ←  _ _ _ _ _ →            II           I                      I
───────────────────────────────────────────────────────────────────

Master     610B        Flash         610B        AR-11
trigger    starts      discharges    stops       stops
AR-11                  PIN
starts                 integrates
                       intensity
```
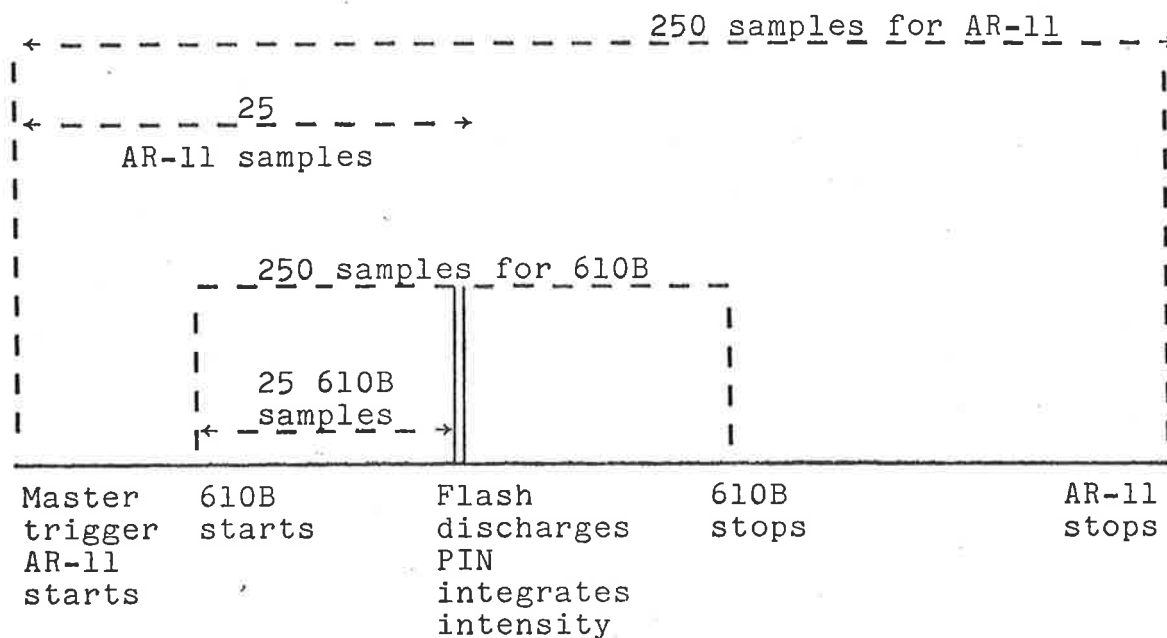
(b) <u>Cells</u>

Generally 2 cm path length cylindrical quartz cells were used, connected to the apparatus shown in plates 2 and 3, although for temperature dependence studies a 50 mm quartz jacketted cell was used. The cell filling device was used to change solutions under an inert atmosphere. Initially $W(N_2)_2(dppe)_2$ (*ca.* 10 mg) was placed in bulb A and the apparatus (without the ballast) connected to the thf, benzene, or toluene still and evacuated. After 30 minutes the Young taps were closed and solvent introduced into bulb A and the complex dissolved. The ballast was connected to maintain N_2 pressure and the solution was run into the cell by opening Young tap 1. When that aliquot of solution was to be changed, Young tap 1 was closed, no. 2 opened and the liquid poured into the (evacuated) bulb B. The cell was then refilled by closing tap 2,

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PLATE 2 The cell filler for the flash
         photolysis experiments.

Key 1. Ballast
    2. Bulb A
    3. Bulb B
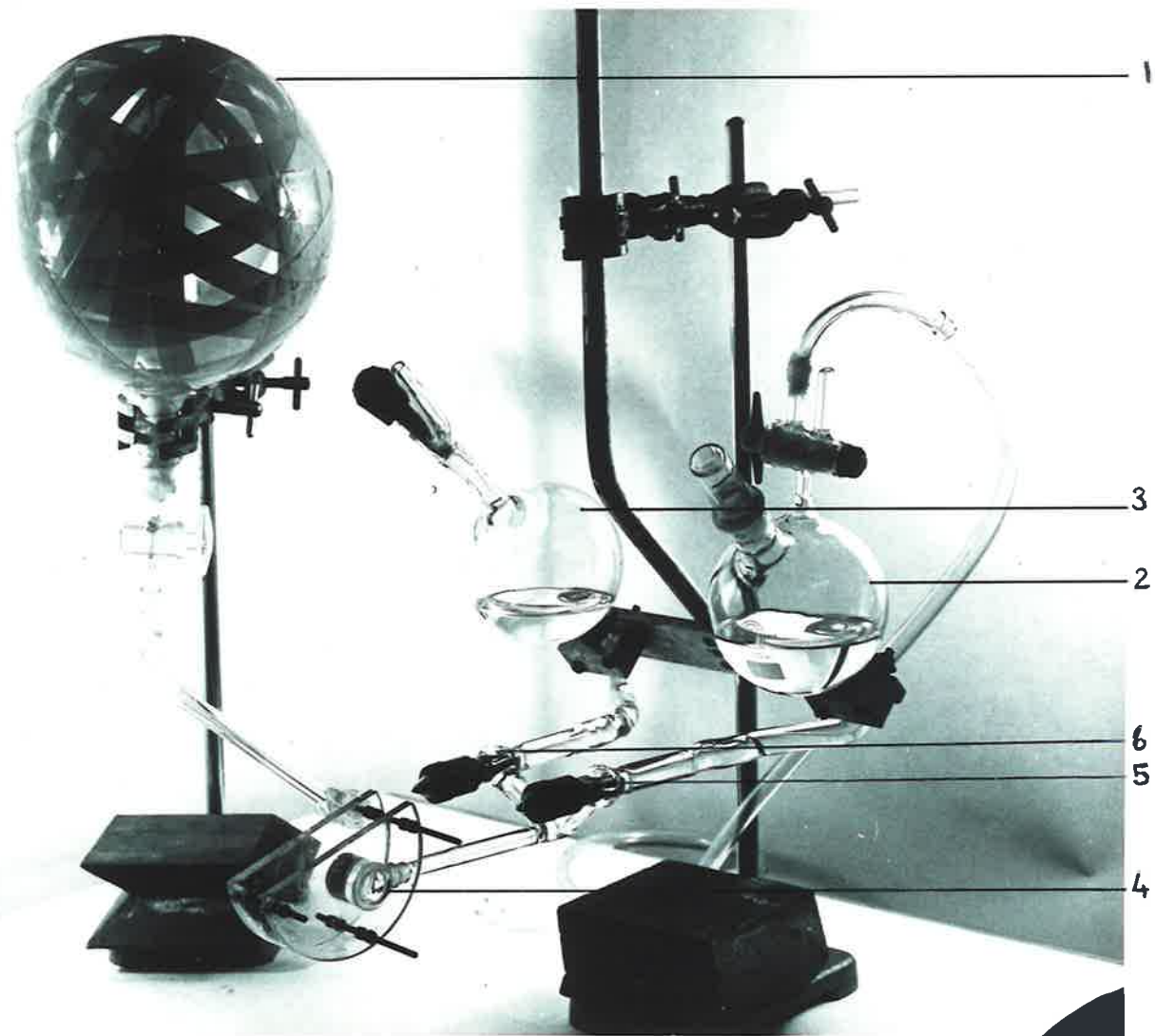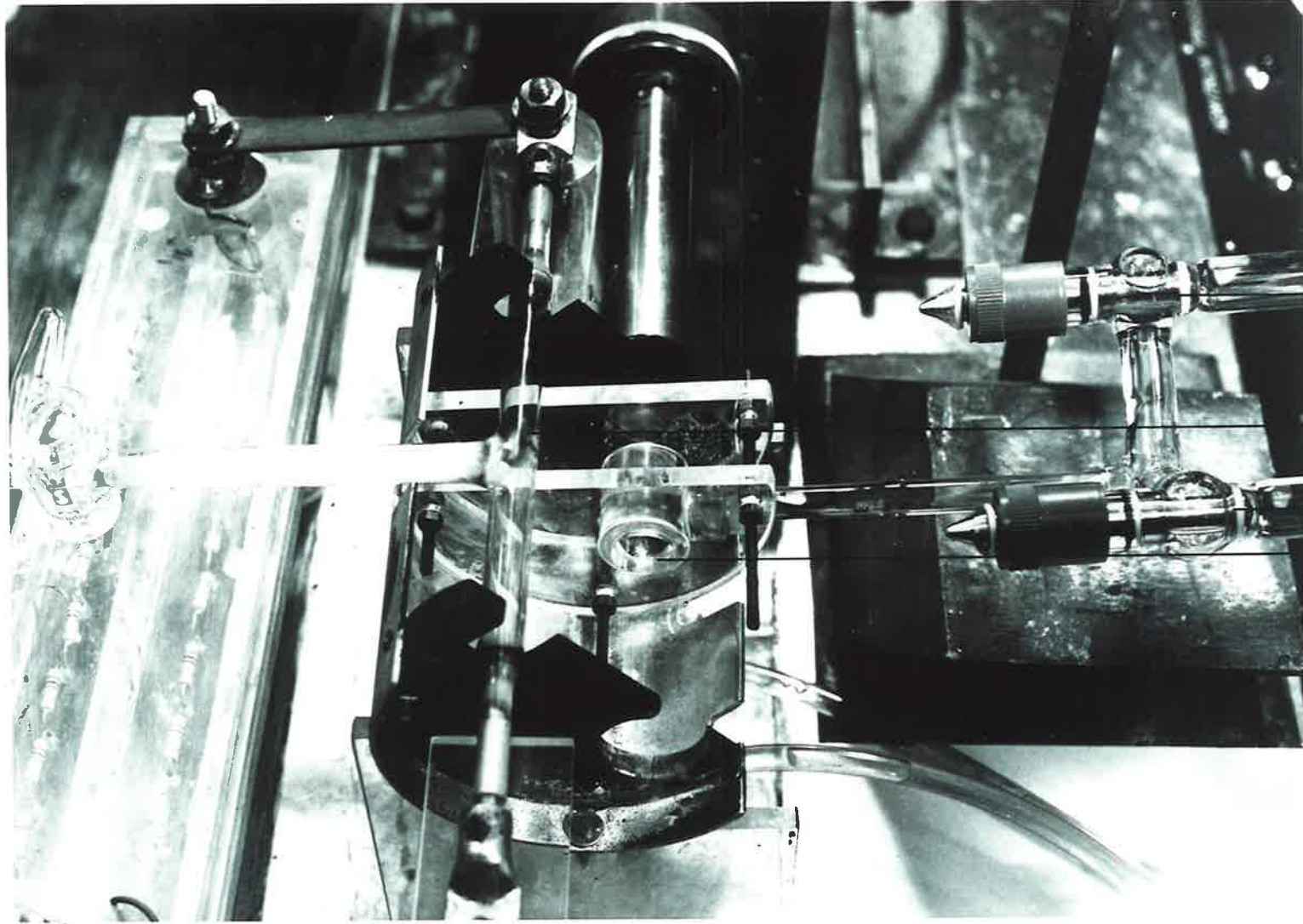   4. Cell
    5. Young Tap 1
    6. Young Tap 2

PLATE 3   Flash photolysis apparatus showing the
positions of the cell and flash lamp.

Key 1. Flash lamp

2. Cell

3. Young taps - cell was
filled and emptied
via these taps.

and reopening tap 1. The ballast had a total volume of over 2 litres, so that even when 200 cm^3 of solution had been used $P_{[N_2]}$ would not drop below .9 atmosphere. As the relaxation process involved N_2 as a reactant this precaution was necessary to minimise changes in observed rate during a run, due to changes in $[N_2]_{solv}$.

(c) Software

. Once the data had been acquired, using either the AR-11 or 610B, it was processed using programme KDATA (Thornton and Laurence). Parameters fed in to this programme were V0, the initial transmittance, V0 reference point, (the data point, any one of 250, which corresponded to that transmittance value), the time per sample and the volts full scale (or in the case of the AR-11, the gain). The data could be digitally smoothed and alternative kinetic treatments selected, first or second order, and optical densities calculated at various times. The final kinetic function and least squares line and parameters were displayed on the visual display unit. Data could be stored on floppy disc and read in from disc and treated at a later date if desired. A summary of the data sources used and kinetic results was printed on the line printer. Data could also be plotted on an X - Y digital recorder using programme PLOT (Laurence and Thomas) in order to provide hard copy of the actual transmittance changes observed.

3.3.2 Flash Photolysis Results

In preliminary experiments using N_2 saturated thf
solution two processes were observed after the flash,
one with $t_{\frac{1}{2}}$ in milliseconds, the other with $t_{\frac{1}{2}}$ in seconds.
Accordingly the two analog to digital converters were run
at different rates in order to maximise the amount of
information obtained from one flash.

In general, on flashing a solution of the complex
an immediate decrease in absorbance was observed at 297 nm,
this was then followed by a multistep process of recovery
of absorbance. The various reactants and solvents studied
are described below.

(i) N_2 saturated thf

Immediately (within the time scale of the apparatus
used) upon irradiation the absorbance at 297 nm decreased,
and then recovered by a two step process to within 95% of
the original value. The initial decrease in absorbance
suggested that the quantum yield of the primary
photochemical process had a minimum value of 0.7. This
value assumes $\varepsilon^{297} = 0$ for the product formed on
irradiating the dinitrogen complex, assuming a value of
$\varepsilon^{297} = 5 \times 10^3$ mol^{-1} cm^{-1} leads to a quantum yield of .9
to 1. While no accurate value of the flux of the output
from the flashlamp was known, it is possible to determine
approximate values of ϕ if it is assumed that all

Flash Photolysis

Flash photolysis of $W(N_2)_2(dppe)_2$ was carried out using
approximately 9 mg of $W(N_2)_2(dppe)_2$ in 200 cm^3 of solvent,
that is, upon 4.5×10^{-5} molar solutions.

absorbance declines dramatically upon irradiation. If, on the other hand, relaxation back to the ground state occurred very rapidly (in less than ten micro seconds) then a molecule which followed this path could absorb a second (or third or more) quantum of light. In this latter case estimates of quantum yield cannot be made. This would appear to be a probable scenario, given the steady state irradiation quantum yield maximum of 0.4.

The recovery of absorbance occurred in two distinct steps, both of which were fitted to first order kinetic parameters. For the first process $k_1^{25} = 3.15 \pm .05 \times 10^2$ sec^{-1} and for the second process $k_2^{25} = 1.88 \pm .05$ sec^{-1}, at 1 atmosphere of N_2 above the solvent. It was observed that if the pressure of N_2 in the cell filling device was decreased the rate also decreased marginally. However, no rate dependence on N_2 pressure was determined. Repeated irradiation (ca. 5-10 times) of the solution led to a permanent decrease in absorbance, which was attributed to reaction of the intermediate produced with photochemically generated peroxides derived from thf. This was particularly noticeable when the irradiating light had a spectrum rich in ultraviolet.

The initial change in absorbance and the two recovery processes are shown in figure 3.3.2. A difference spectrum (figure 3.3.3) was obtained for points A and B by measuring the change in absorbance at various wavelengths upon irradiation. A spectrum of the products of (a) irradiation and (b) irradiation followed by the rapid process were calculated assuming quantum yield was equal to one. A single isosbestic point was observed at 285 nm,
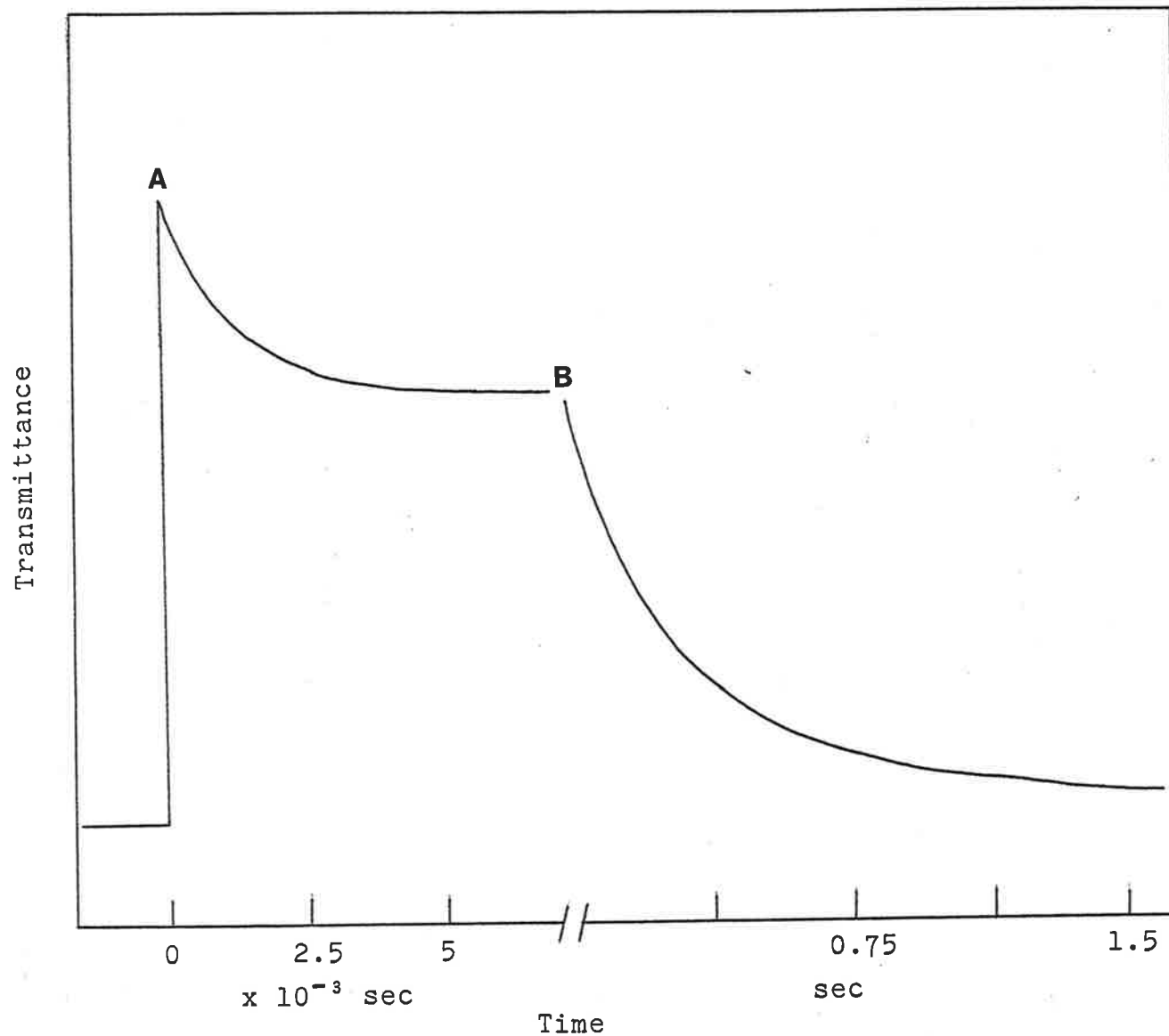
FIGURE 3.3.2 Processes observed following flash photolysis of W(N₂)₂(dppe)₂ in thf solution. Note the change of scale in the x axis.

FIGURE 3.3.2b   The changes in transmittance of a
solution of $W(N_2)_2(dppe)_2$ observed
following flash photolysis. Fast
process in N_2 saturated thf.

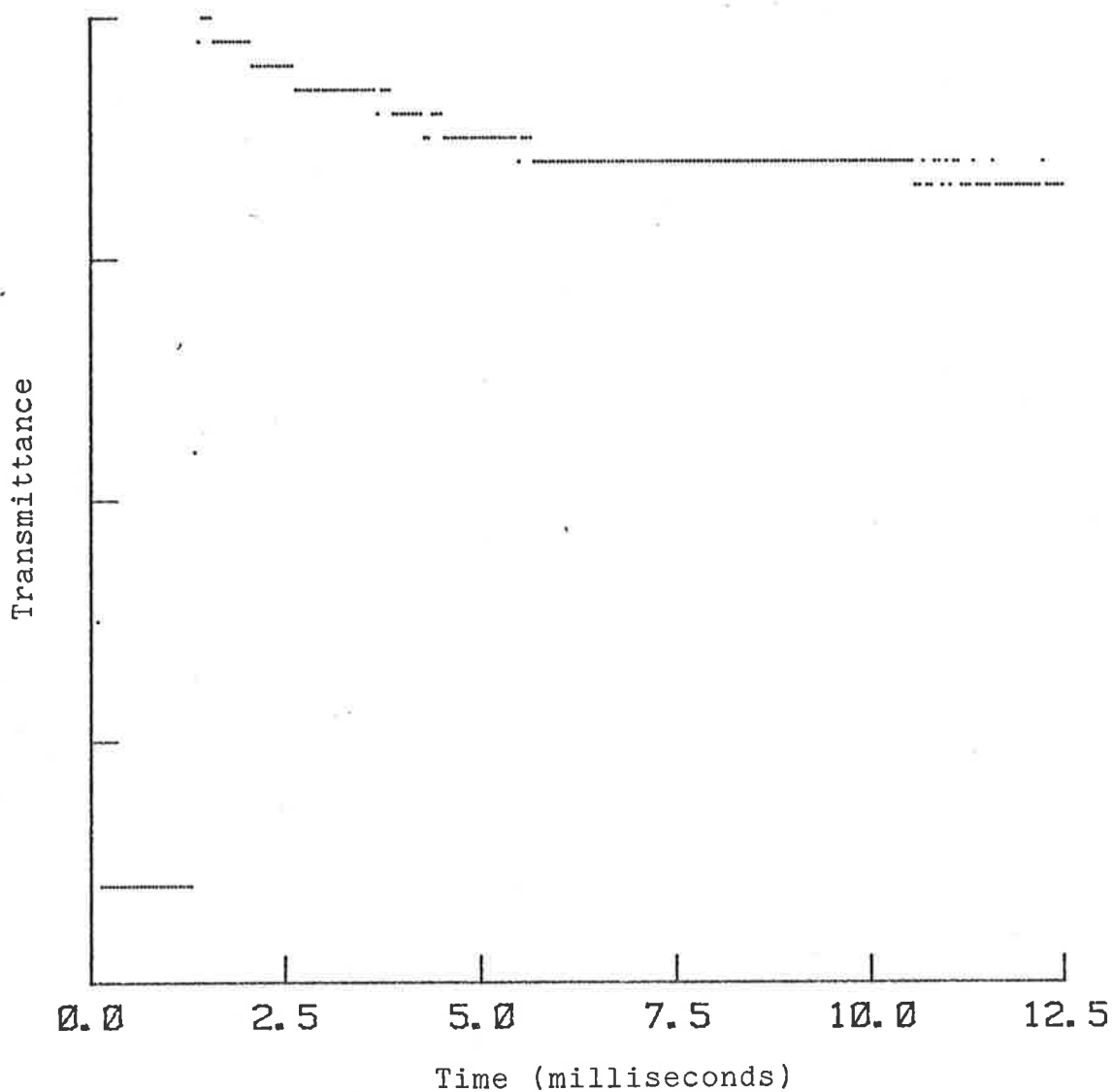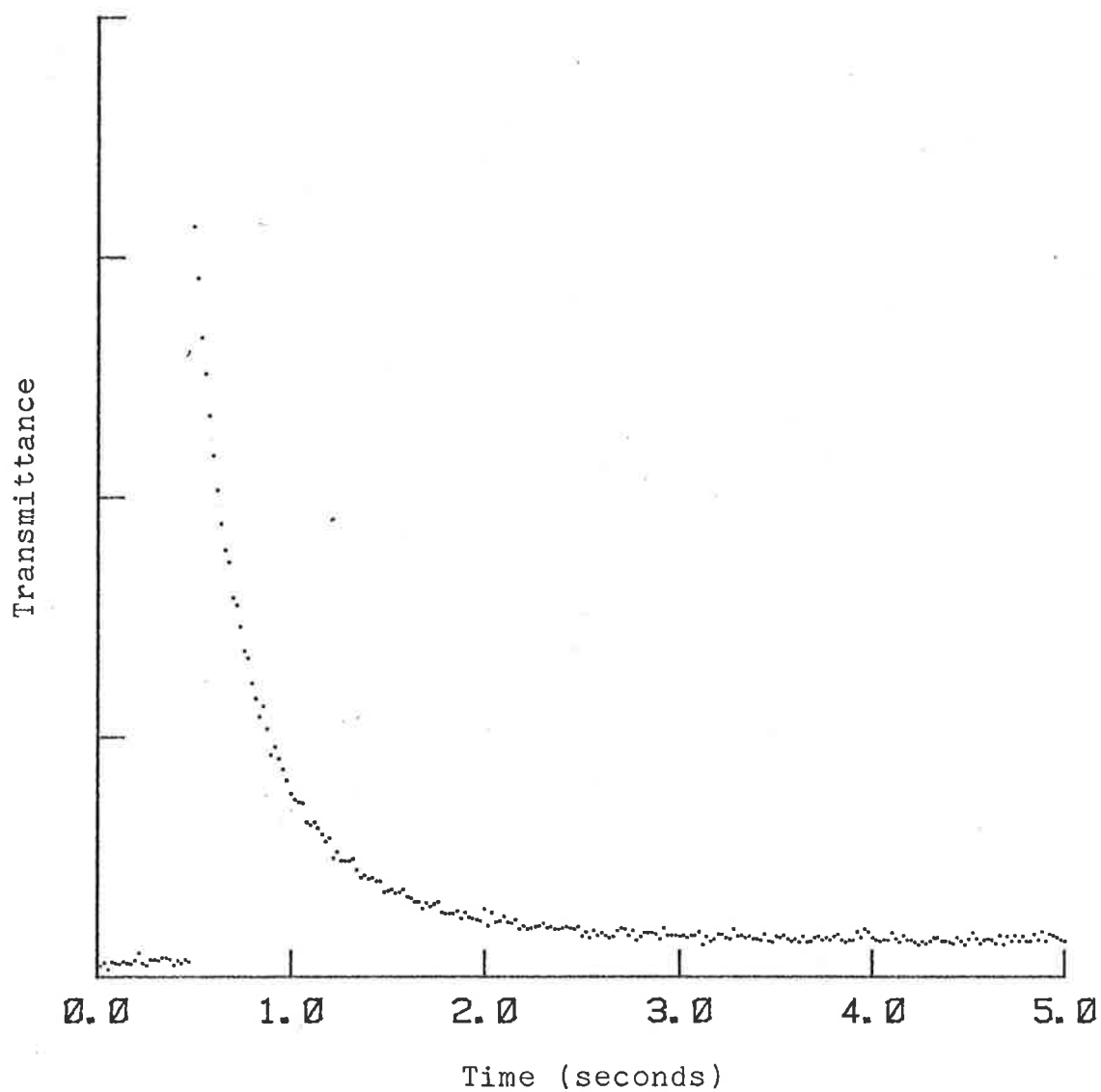FIGURE 3.3.2c The changes in transmittance of a
solution of $W(N_2)_2(dppe)_2$ observed
following flash photolysis. Slow
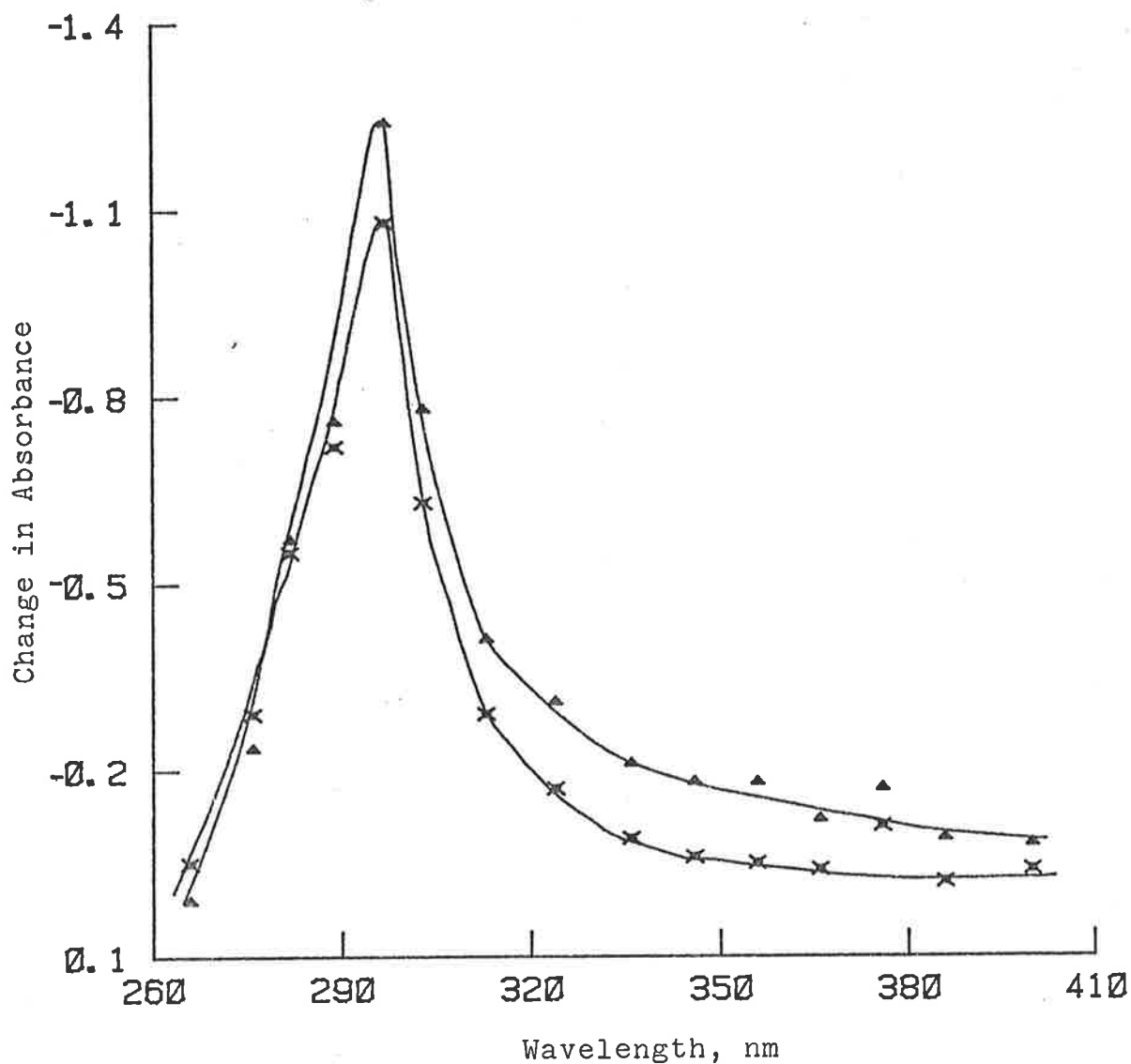process in N_2 saturated thf.

FIGURE 3.3.3 Difference spectra measured.

Δ Immediately following the flash
   discharge.

X After the first (fast) process upon
   flash photolysis of a dinitrogen
   saturated thf solution of
   $trans$-$W(N_2)_2(dppe)_2$ (4×10^{-5} molar).

suggesting that two species were involved in the fast and slow processes. The major change in absorbance upon irradiation was observed at 297 nm, which corresponded to the wavelength of the absorption assigned to W $(d\pi) \rightarrow N_2(\pi^*)$ transition.

The xenon flashlamp had a spectrum rich in ultra violet radiation, which bore little resemblance to the spectrum of the lamp used for steady state irradiation. In order to relate the results of the flash photolysis experiments to the steady state illuminations, flash photolysis experiments were also carried out with a perspex filter between the flash lamp and the spectrophotometric cell containing a thf solution of $W(N_2)_2(dppe)_2$. The perspex filter effectively eliminated light with a wavelength of 360 nm or less. The difference spectrum (figure 3.3.4) obtained was consistent with that observed without the filter in place, except that the absolute magnitude of the absorbance changes was smaller due to the decreased flux impinging upon the cell contents. The observed rates for the two steps were $3.32 \pm .14 \times 10^2$ sec^{-1} and $1.3 \pm .23$ sec^{-1}'. The difference between these results and those observed without the filter present was not statistically significant.

Because of the presence of one moiety of N_2 in the diazenido product, initially it was believed that the mechanism involved the labilisation of only one dinitrogen ligand. The two step process observed in the flash photolysis experiment was thought to involve a geometric change, followed by recovery of the labilised dinitrogen ligand to yield $W(N_2)_2(dppe)_2$.
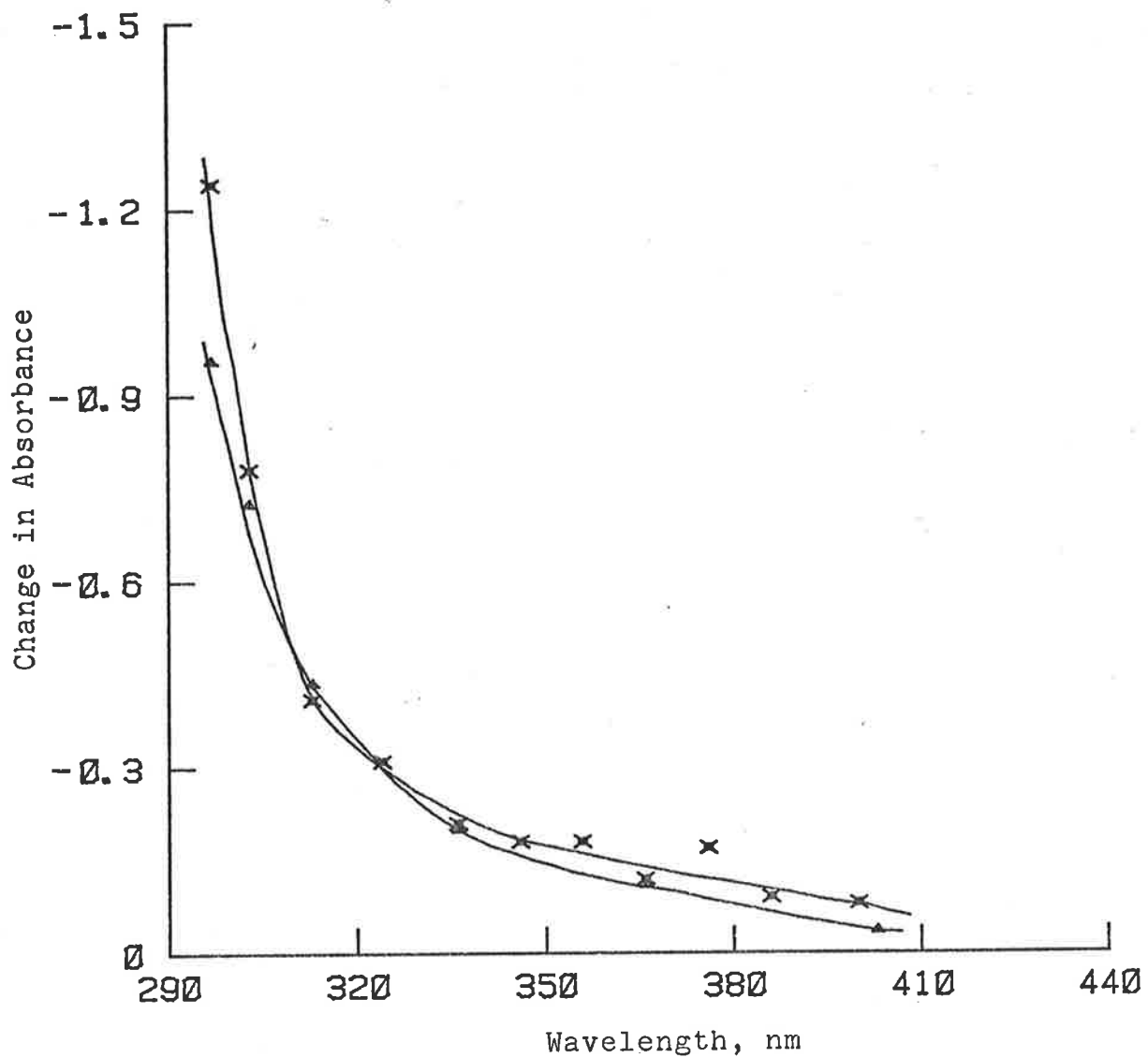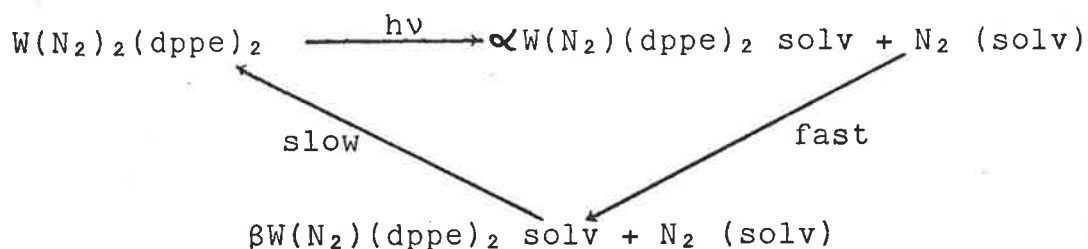
FIGURE 3.3.4   Difference spectra obtained immediately after flashing $W(N_2)_2(dppe)_2$ in thf.

Δ   With perspex filter in place.

X   Without perspex filter.

Dinitrogen saturated solvent

Such a mechanism would be depicted thus:

$$W(N_2)_2(dppe)_2 \xrightarrow{\quad h\nu \quad} \alpha W(N_2)(dppe)_2 \text{ solv} + N_2 \text{ (solv)}$$

slow   fast

$$\beta W(N_2)(dppe)_2 \text{ solv} + N_2 \text{ (solv)}$$

In an attempt to confirm this hypothesis by the technique of "flash labelling" it was actually discounted, and a double exchange mechanism suggested. Other preparative and labelling techniques, also suggested that two dinitrogen ligands were exchanged following the absorption of one quantum of light by $W(N_2)_2(dppe)_2$.

(ii) Flash labelling

It had been previously suggested that the photochemically induced reactions of $W(N_2)_2(dppe)_2$ and $Mo(N_2)_2(dppe)_2$ with alkyl halides proceed via the labilisation of one dinitrogen ligand, followed by substitution of RX at the vacant coordination site. This would seem to be a plausible mechanism, given that the reaction with RX results in the formation of the coordinated group -N-N-R. The labelling of $W(N_2)_2(dppe)_2$ with $^{15}N_2$, which results in the production of isotopomers $(^{15}N_2)W(^{14}N_2)(dppe)_2$ and $(^{15}N_2)W(^{15}N_2)(dppe)_2$ could be accounted for by one labilisation of the metal complex resulting in the $^{15}N_2W^{14}N_2$ group, and two consecutive labilisations (or more) resulting in the exchange of both N_2 groups for $^{15}N_2$ dissolved in the solvent. If this postulated scheme was correct, the two step recovery process observed in the flash photolysis experiments using
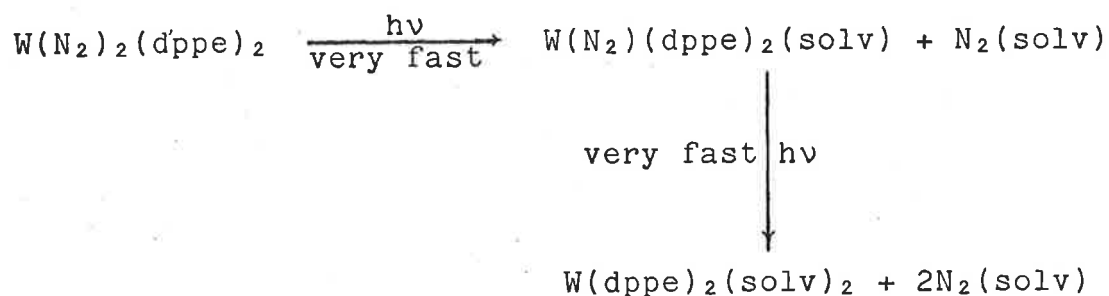
N_2 saturated solvents could be accounted for by a geometric change plus recovery of the dinitrogen ligand, as discussed above.

If the reaction step involving labilisation of one dinitrogen ligand postulated by Chatt et al was wrong in the case of light activated reactions, and in fact absorption of light caused labilisation of both ligands, one dinitrogen ligand would need to be recovered before reaction with RX occurred, to result in the grouping -N-N-R. In this latter case the production of isotopomers in the $^{15}N_2$ labelling experiment could be explained on a statistical basis, that is the expected product ratio would be based on the ratio a^2; 2ab, b^2. (a = $[^{14}N_2]_{solv}$; b = $[^{15}N_2]_{solv}$). The concentration ratio in the vicinity of a tungsten centre which had been labilised recently would be slightly higher in $[^{14}N_2]$, assuming unlabelled complex was used as starting material, due to diffusion of N_2 in the solvent. A qualitative test for labilisation of two ligands was developed using the flash photolysis apparatus. It was believed that if flash photolysis could labilise enough complex to yield sufficient isotopomer to be observed by infra red spectroscopy it would be possible to look for the presence of doubly labelled dinitrogen complex. Since ^{15}N - ^{15}N is only present in atmospheric nitrogen as .16%, the quantity of ^{15}N - ^{15}N - W - ^{15}N - ^{15}N isotopomer produced by labilisation of one dinitrogen ligand under an atmosphere of $^{15}N_2$ would be negligible (.16% of total labelled complex). If two dinitrogen ligands were labilised simultaneously the ratio a^2 : 2ab : b^2 could not be expected to be observed due to

changes in the local concentration of $^{14}N_2$ (in the solvent),
however, a reasonable proportion of $^{15}N - ^{15}N - W - ^{15}N - ^{15}N$
should be formed. Since the output of the flash lamp was
found to last 1×10^{-5} seconds, neither of the post flash
recovery processes would have occurred. The output of the
flash photolysis equipment operating at 15 kV was measured
in the region 300 - 500 nm, by irradiating a solution of
$[K_3Fe(ox)_3]$ in an airtight pyrex cell which was to be used
for the labelling experiment. It was found that 10^{-5} moles
of Fe^{2+} were produced; if a quantum yield of 1 is assumed
10^{-5} Einsteins were absorbed by the solution of $K_3Fe(ox)_3$.
Since $\varepsilon^{1945}_{,} cm^{-1} = 2.5 \times 10^3 mol^{-1} cm^{-1}$ for $W(N_2)_2(dppe)_2$
in thf and an infra red solution cell with a path length of
.8 mm had been found to be suitable for measuring the
intensity of $\nu(N-N)$, it was believed that a labelling
experiment using one intense flash of light would be
possible. Accordingly 10 mg of $W(N_2)_2(dppe)_2$ was dissolved
in $ca.$ 50 cm^3 of dry thf distilled under argon. This
solution was connected to a vacuum line equipped with a
toepler pump, and the argon atmosphere removed, and the
solvent degassed. An atmosphere of $^{15}N_2$ (81% $^{15}N - ^{15}N$,
10% $^{14}N - ^{14}N$, 9% $^{15}N - ^{14}N$) was introduced into the cell.
The solvent was initially collected under argon so that
the ratio of $^{15}N_2$ to $^{14}N_2$ in the solution would be a maximum.
This solution of $W(N_2)_2(dppe)_2$ under an atmosphere of $^{15}N_2$
was placed in the flash photolysis apparatus and irradiated
by discharge of 15 kV through the flash lamp. The
atmosphere of $^{15}N_2$ was then removed and the solvent
reduced in volume in $vacuo$ to $ca.$ 5 cm^3. The solution of
$W(N_2)_2(dppe)_2$ was handled in the dark from the point in

time when $^{15}N_2$ was introduced until the $^{15}N_2$ atmosphere was removed and the solvent reduced in volume. A solution infra red was run and the remaining solution taken to dryness on finely ground KBr. This KBr was then used to prepare a disc suitable for infra red spectroscopy, and a spectrum run in the region 2200 to 1700 cm^{-1}. (figure 3.3.5) It was quite clear from this spectrum that both isotopomers $^{15}N - ^{15}N - W - ^{14}N - ^{14}N$ and $^{15}N - ^{15}N - W - ^{15}N - ^{15}N$ were present. This would be impossible if only one dinitrogen ligand was labilised initially, unless the following reaction scheme occurred.

$$W(N_2)_2(dppe)_2 \xrightarrow[\text{very fast}]{h\nu} W(N_2)(dppe)_2(solv) + N_2(solv)$$

$$\text{very fast} \Big| h\nu$$

$$W(dppe)_2(solv)_2 + 2N_2(solv)$$

Given the very high flux of light produced by the xenon discharge lamp this mechanism was believed to be possible, but not probable. Later preparative experiments using a far lower flux suggested that double exchange occurred under those conditions, which discounted this mechanism.

Accordingly it was concluded that excitation of $W(N_2)_2(dppe)_2$ by visible light led to loss of both dinitrogen ligands, followed by the consecutive uptake of two dinitrogen groups from the solvent.*

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* The assumption has been made throughout this discussion that a six coordinate 18 electron complex normally existed, and so intermediates in solution have been assumed to be solvated. Some discussion on the validity of this assumption is presented in section 3.3.3.
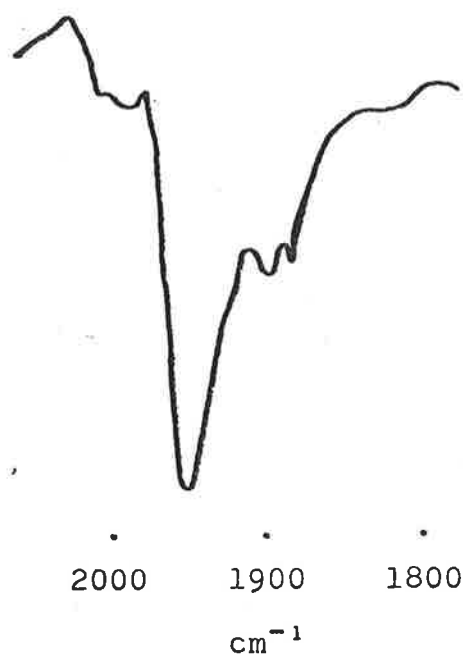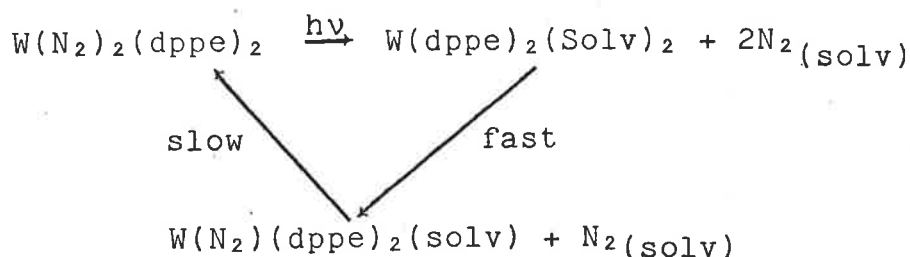
2000   1900   1800

cm^{-1}

FIGURE 3.3.5   Infrared spectrum of KBr
disc of "flash labelled"
$W(N_2)_2(dppe)_2$.

The mechanism below was postulated to account for this observation:

$$W(N_2)_2(dppe)_2 \xrightarrow{h\nu} W(dppe)_2(Solv)_2 + 2N_{2(solv)}$$

slow   fast

$$W(N_2)(dppe)_2(solv) + N_{2(solv)}$$

(iii) N_2 Saturated Benzene

Flash photolysis of dinitrogen saturated benzene solutions of $W(N_2)_2(dppe)_2$ revealed a two step process similar to that discussed above, but with $k_1 = 3.6 \pm .6 \times 10^2$ sec^{-1}, and $k_2 = 2.4 \pm .2$ sec^{-1}. (Ambient *ca.* 25°C).

(iv) N_2 Saturated Toluene

Processes observed following flash photolysis of toluene solutions of $W(N_2)_2(dppe)_2$ were similar to those observed in benzene or thf, with $k_1^{25} = 2.55 \pm .05 \times 10^2$ sec^{-1}, and $k_2^{25} = 2.1 \pm .1$ sec^{-1}.

(v) CO Saturated thf

A two step recovery process similar to that observed in N_2 saturated thf or benzene was observed when a CO saturated thf solution of $W(N_2)_2(dppe)_2$ was irradiated. The initial change in absorbance upon irradiation was identical to that observed for N_2 saturated thf solution. However, when the two recovery processes were complete the absorbance of the solution was consistently lower than the starting material at 297 nm. The difference spectrum of the product between 297 and 403 nm was consistent with the formation of *trans*-$W(CO)_2(dppe)_2$.

FIGURE 3.3.5d Flash photolysis of $W(N_2)(dppe)_2$ in benzene solution. Slow process.

Dinitrogen saturated solvent

FIGURE 3.3.5e Flash photolysis of $W(N_2)_2(dppe)_2$ in benzene solution. Fast process.

Dinitrogen saturated solvent

FIGURE 3.3.5f   Flash photolysis of $W(N_2)_2(dppe)_2$ in toluene solution. Slow process.

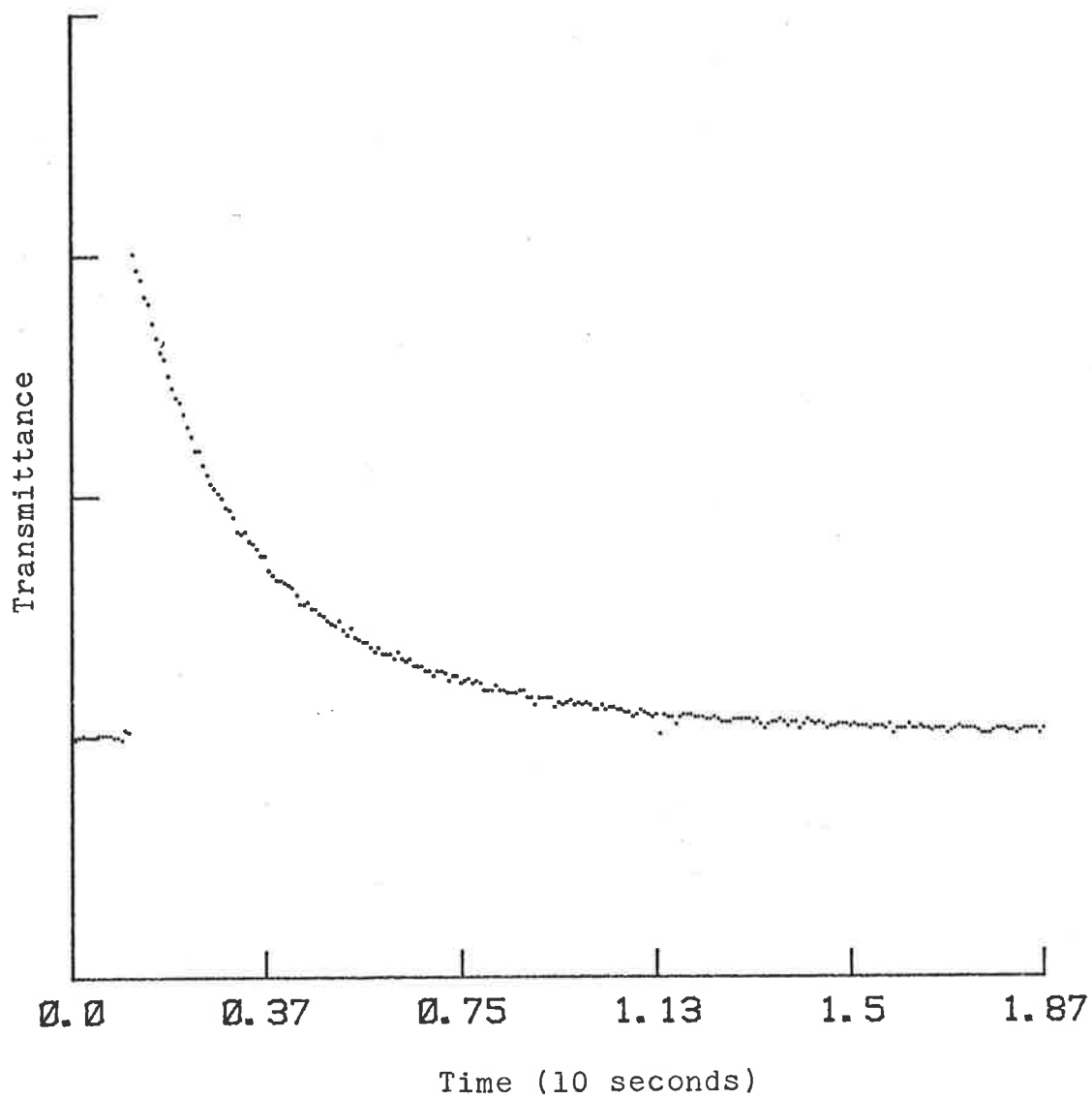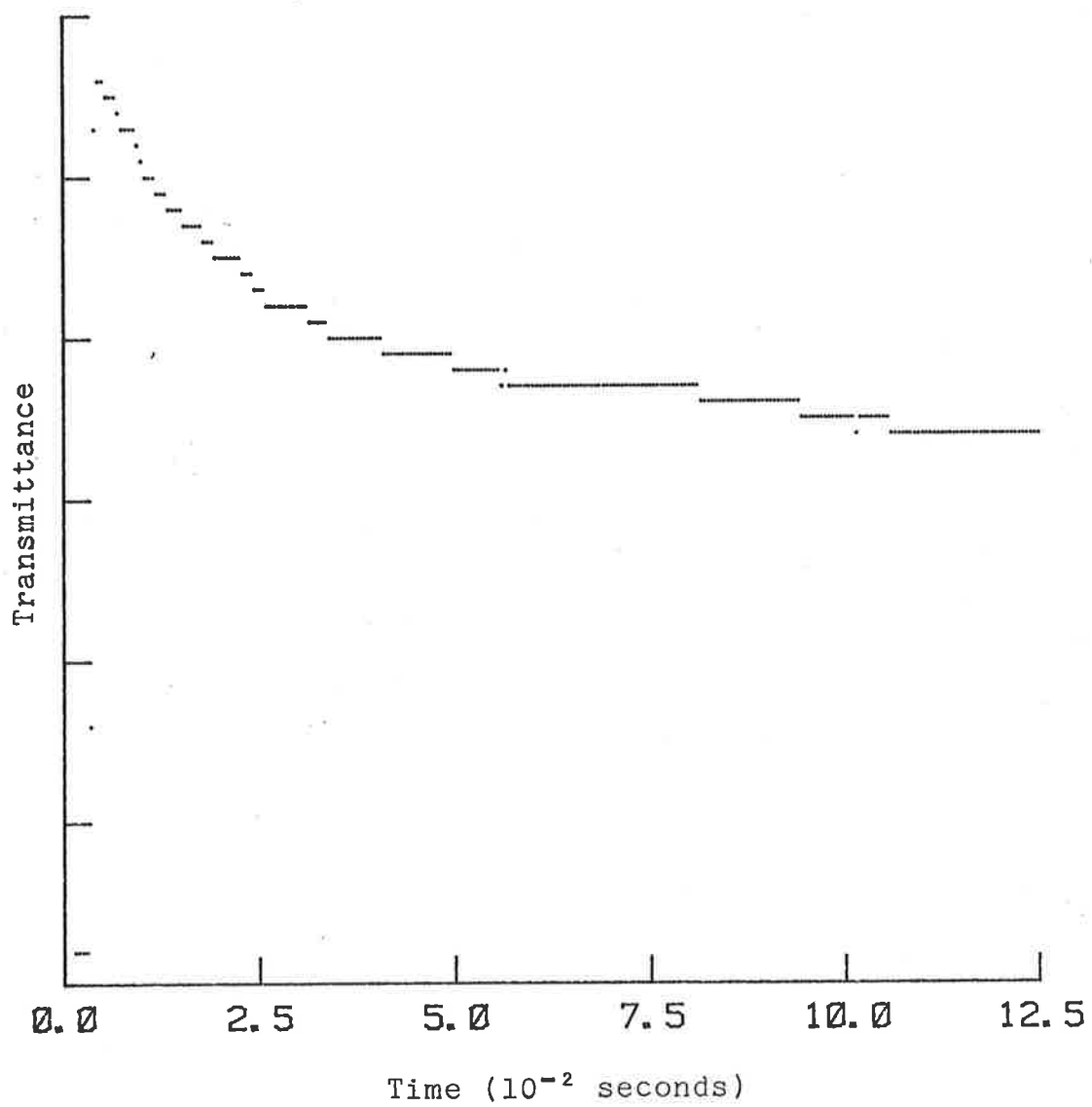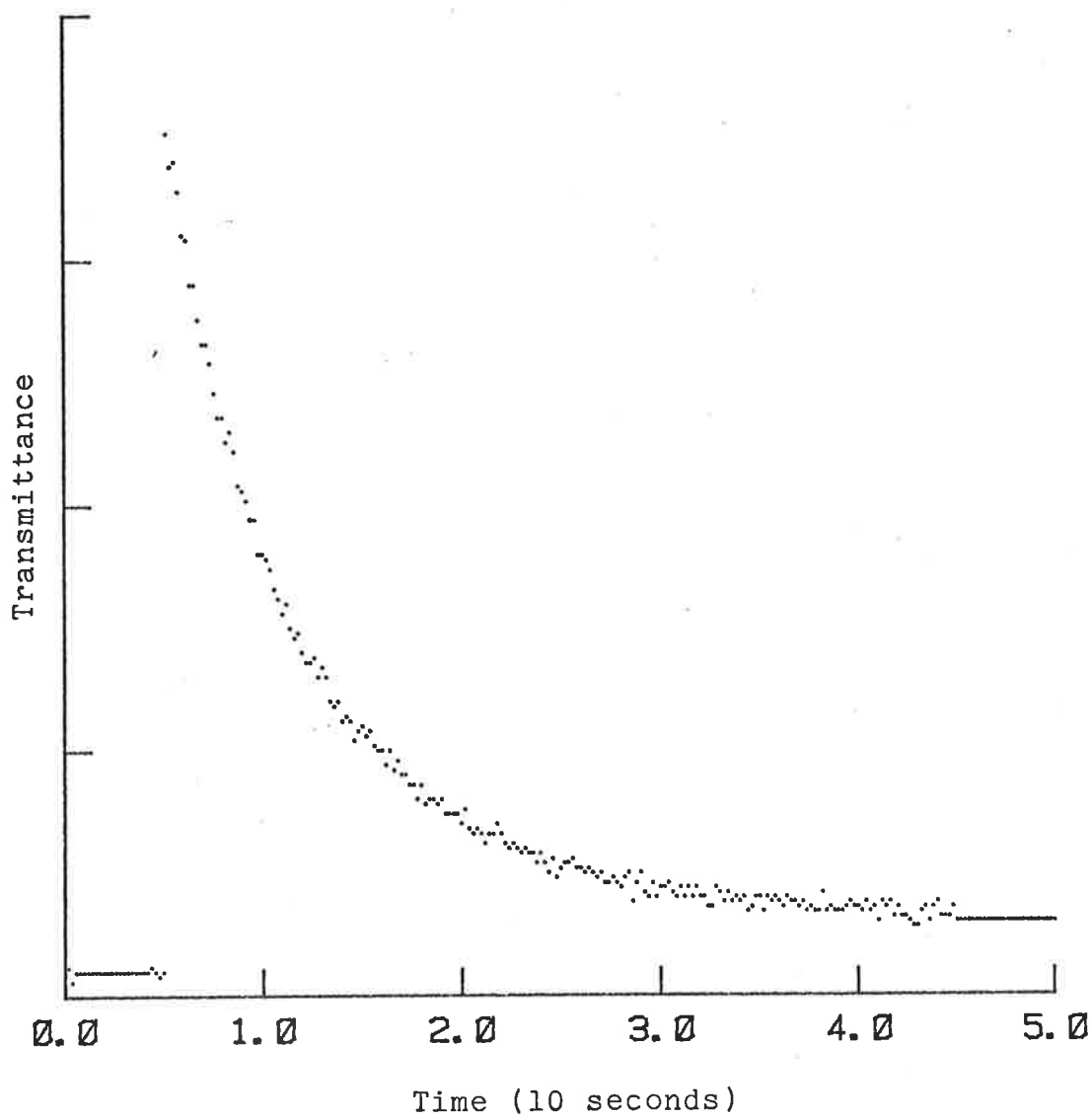Dinitrogen saturated solvent
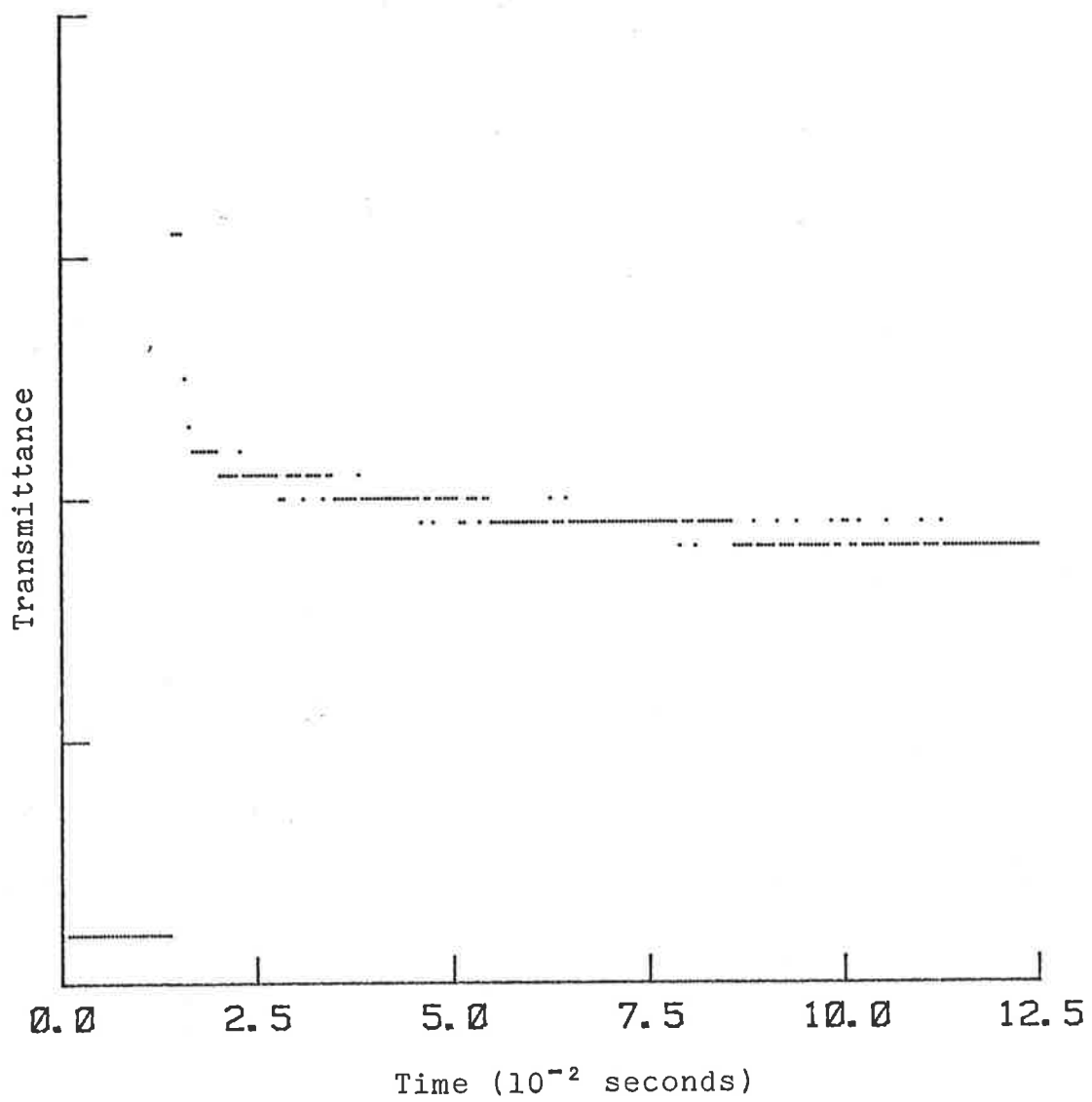
FIGURE 3.3.5g Flash photolysis of $W(N_2)_2(dppe)_2$ in
toluene solution. Fast process.
Dinitrogen saturated solvent
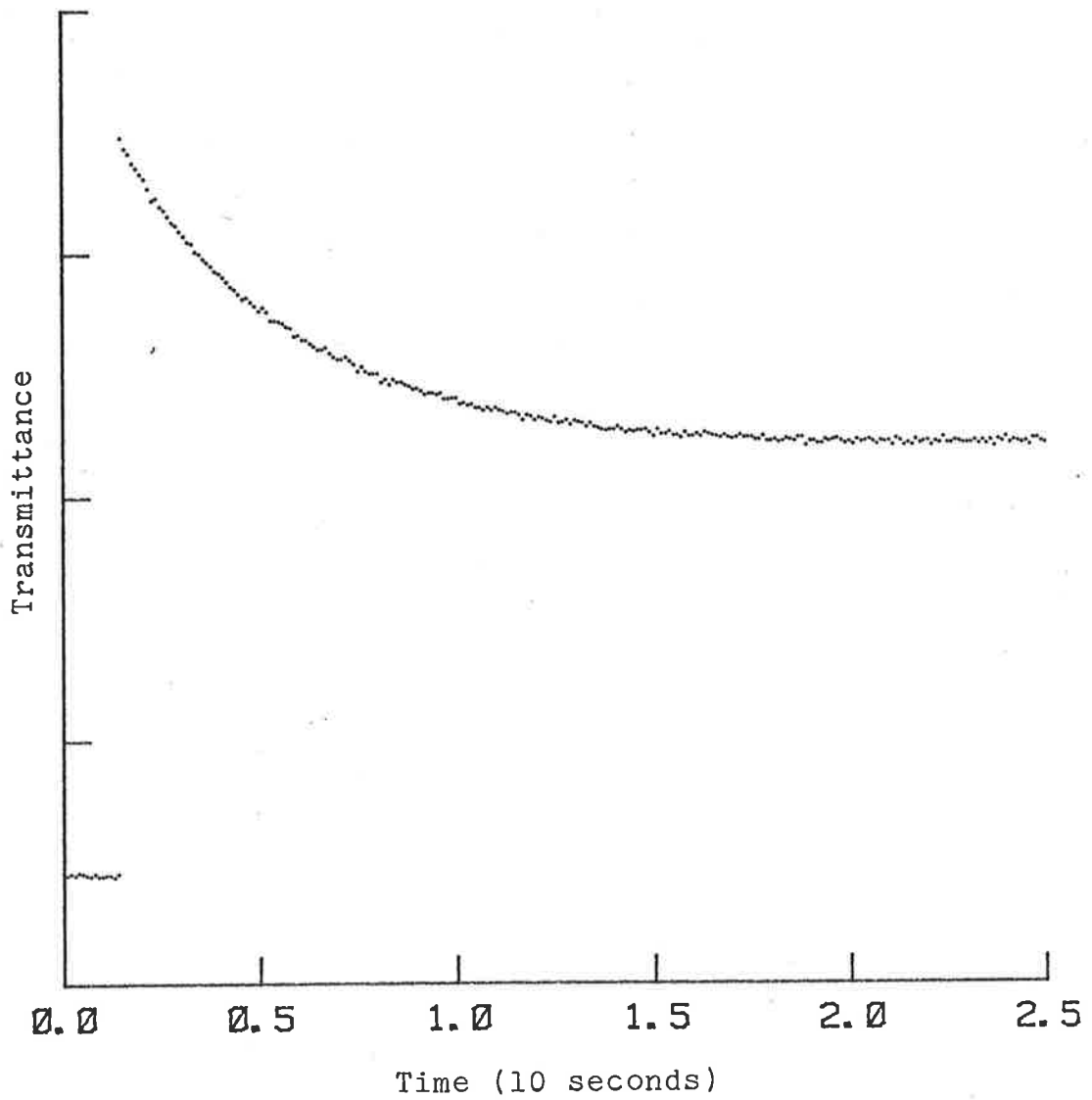
FIGURE 3.3.5h   Flash photolysis of $W(N_2)_2(dppe)_2$ in CO saturated benzene. Slow process.
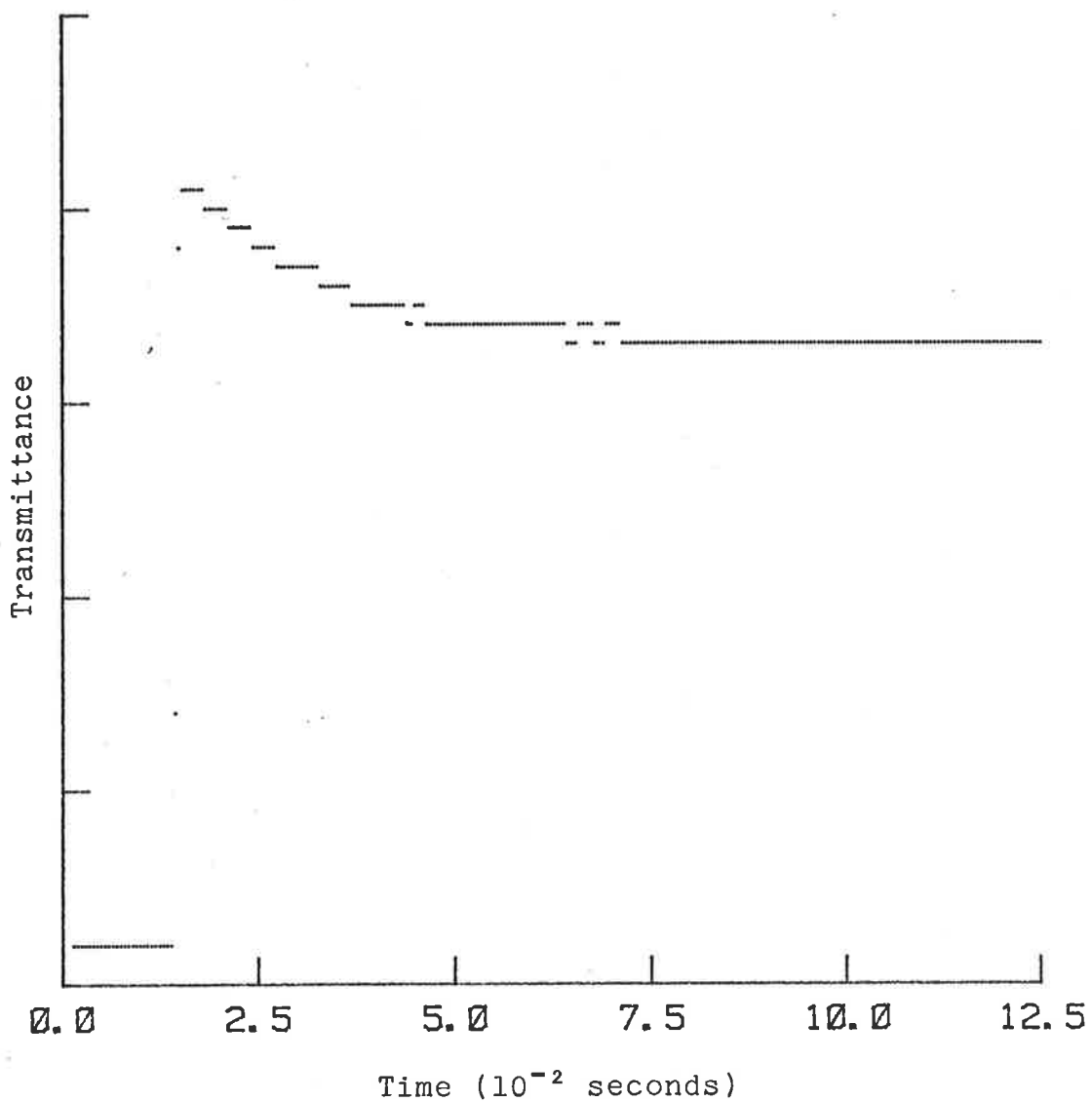
FIGURE 3.3.5i   Flash photolysis of $W(N_2)_2(dppe)_2$ in CO saturated benzene. Fast process.

This data is consistent with the reaction scheme:

$$2CO + W(N_2)_2(dppe)_2 \longrightarrow W(dppe)_2(solv)_2 + 2CO + 2N_2$$

k_1 | fast

$$W(CO)(solv)(dppe)_2 + 2N_2 + CO$$

k_2 | slow

$$trans\text{-}W(CO)_2(dppe)_2 + 2N_2(solv)$$
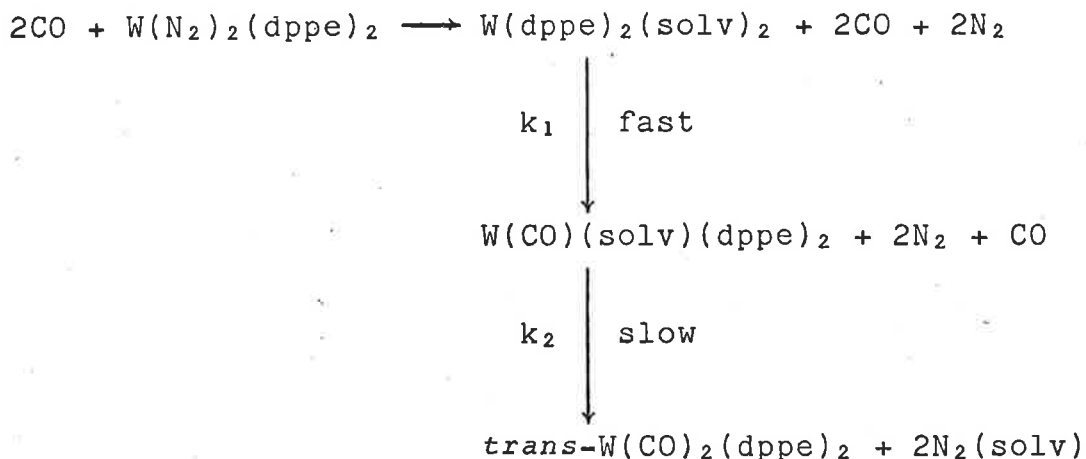
First order kinetic parameters for the two steps were found to be $k_1 = 5.1 \pm .7 \times 10^2$ sec^{-1}, and $k_2 = 2.5 \pm .4$ sec^{-1}.[*]

(vi) Argon Saturated thf or Toluene

An initial bleaching of absorbance at 297 nm observed in N_2 saturated thf or toluene was observed in argon saturated thf. No recovery of absorbance was observed after the initial bleaching. This observation was consistent with the mechanism described above. If all the $W(N_2)_2(dppe)_2$ had been labilised the maximum N_2 concentration in the solvent would have been 8×10^{-5} M, compared to $ca.$ 7×10^{-3} M in N_2 saturated thf.[**] Since the two back reactions were probably second order, it would be expected that at such low concentrations of N_2 the back reaction would be slow, but should actually occur, to return the system to the original photostationary state. However, it had previously been observed that on the

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[*] Ambient temperature $ca.$ 25°C.

[**] The determination of the solutility of dinitrogen in thf is described in chapter 4.

preparative scale, irradiation of solutions of the
dinitrogen complex under Argon led to a permanent loss of
$\nu(N-N)$. No dinitrogen could be incorporated into the
product of such an irradiation by bubbling N_2 through the
solution after the irradiation was complete. (Section
2.2.2). This observation led to the conclusion that the
reactive intermediate formed by irradiation was not
stable, even in thoroughly dried and oxygen free thf.
This was ascribed to competition for the reactive
intermediate by other species, such as traces of inhibitor
distilled over with thf, or peroxides formed by the action
of light on thf.

(vii) N_2 Saturated thf solution containing alkyl bromide

Dinitrogen saturated solutions of $W(N_2)_2(dppe)_2$ in
thf containing RBr (.04 M. R = 1-Butyl, tert-Butyl, ethyl)
revealed a four step process upon flash photolysis.
(Figure 3.3.6).

(1) An immediate decrease in absorbance at 297 nm,
identical in intensity to that observed in N_2
saturated thf.

(2) The first rapid recovery of absorbance with
$k \doteq 4.5 \times 10^2 \ sec^{-1}$. This appeared to be identical
to that observed in N_2 saturated thf.

(3) The slow recovery process was observed to begin with
$k \doteq 3. \ sec^{-1}$, however, before it was complete a fourth
process commenced.

(4) A slight decrease in absorbance at 297 nm was
observed, which was neither first nor second order
in kinetics.
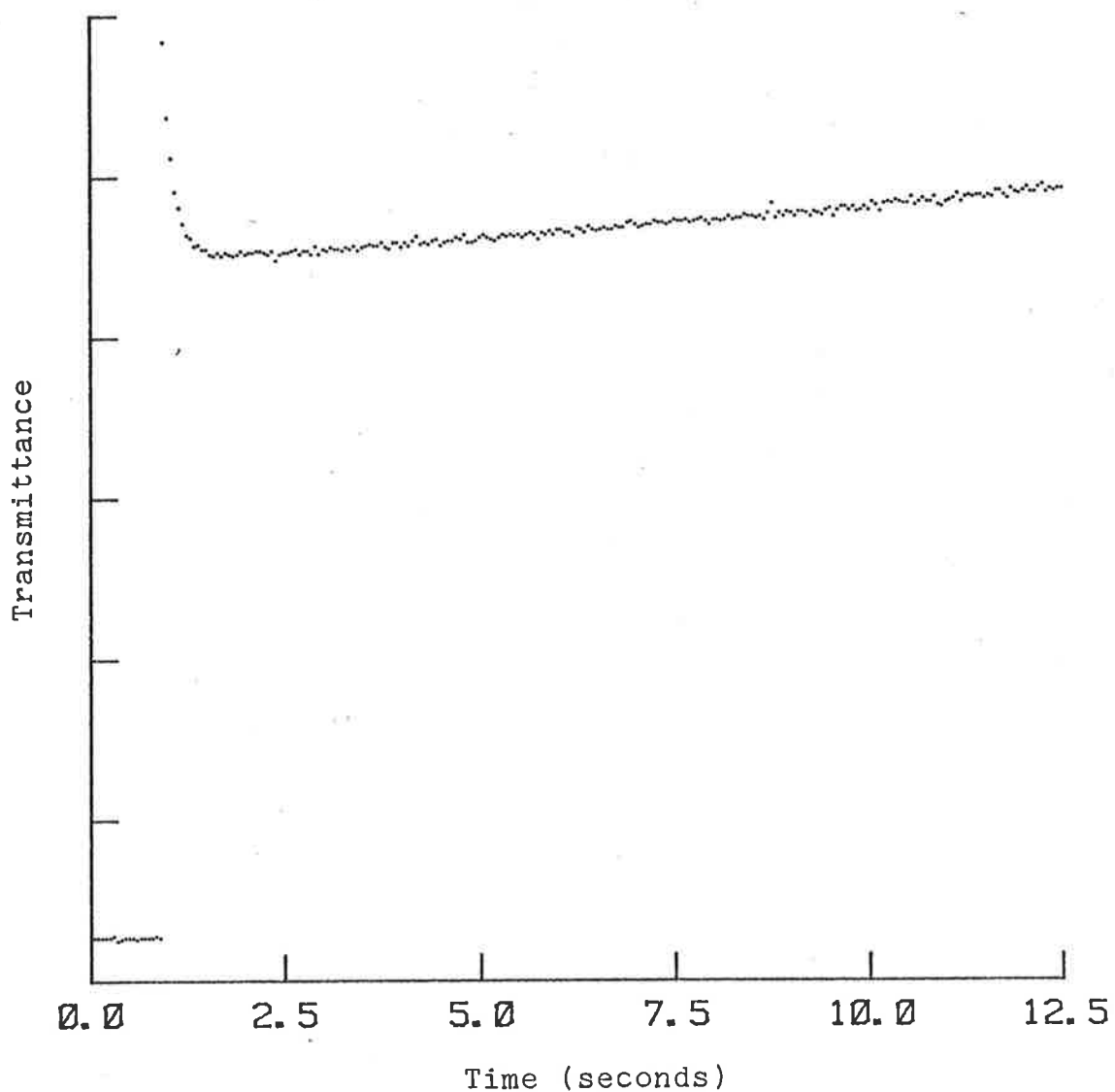
FIGURE 3.3.6a1   Slow process following flash photolysis
of $W(N_2)_2(dppe)_2$ in dinitrogen saturated
benzene solution containing
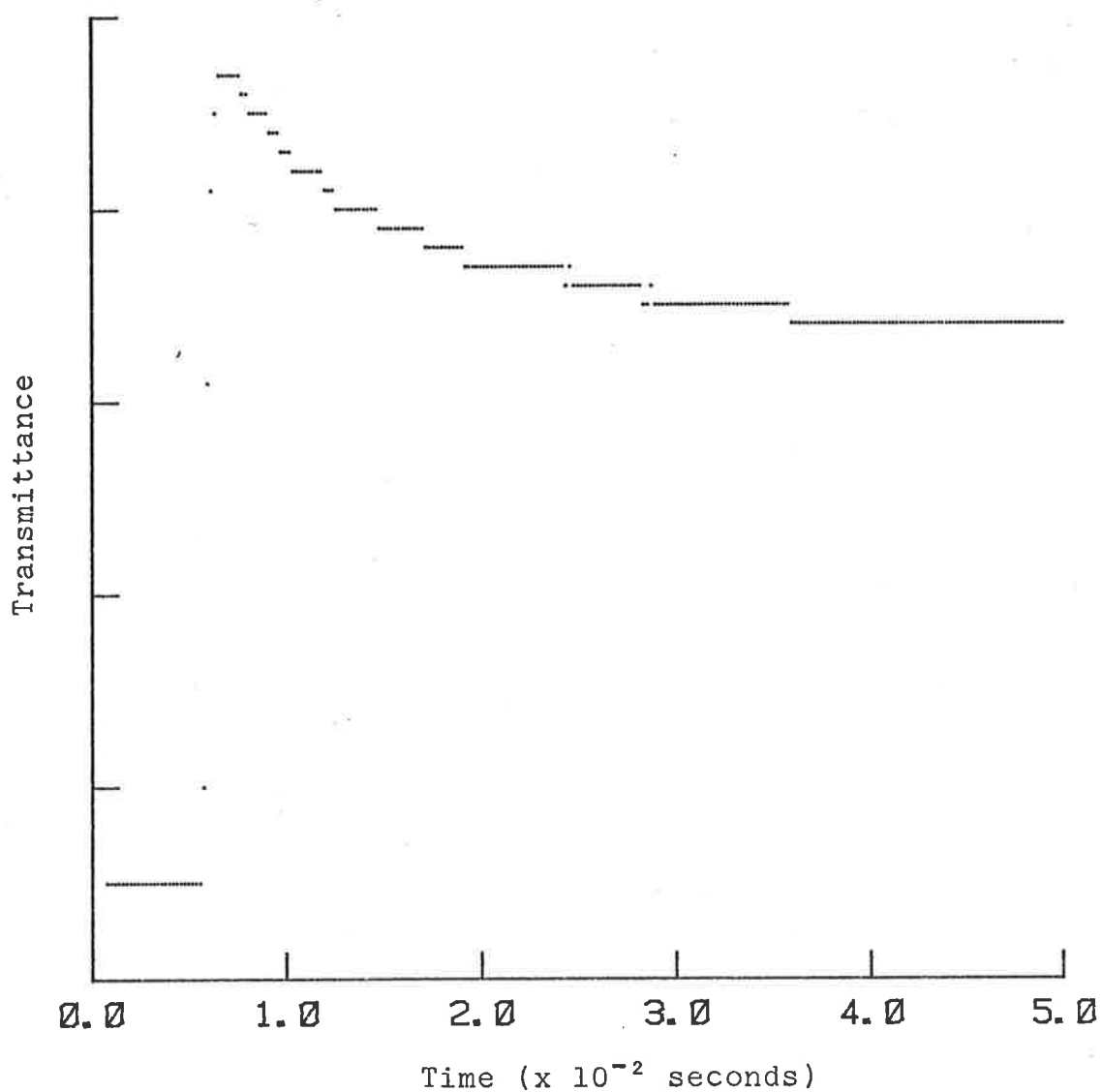
1-bromobutane

FIGURE 3.3.6a2   Fast process following flash photolysis
of $W(N_2)_2(dppe)_2$ in dinitrogen
saturated benzene solution containing
1-bromobutane
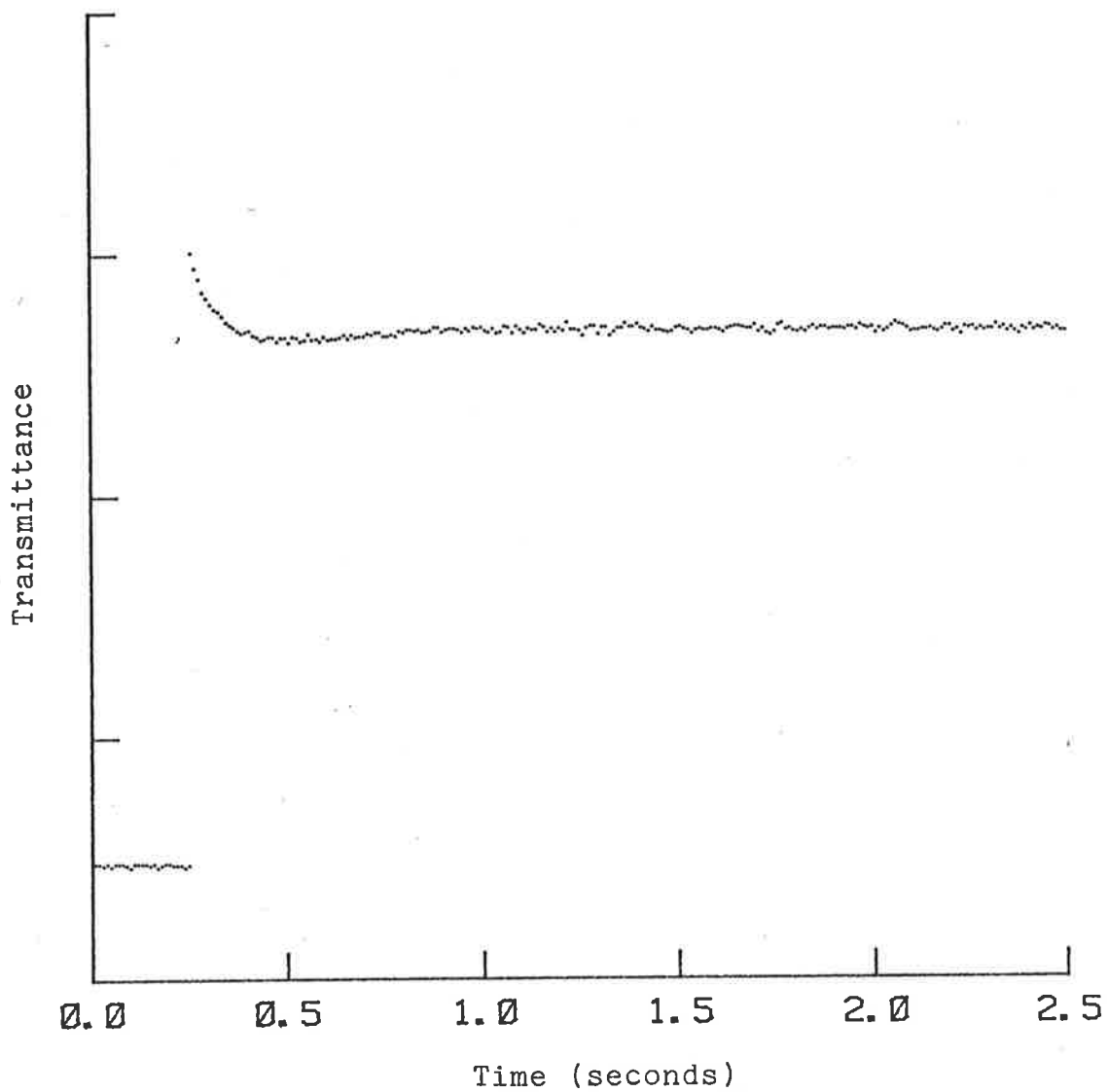
FIGURE 3.3.6b1 Slow process following flash photolysis of $W(N_2)_2(dppe)_2$ in dinitrogen saturated benzene solution containing Ethylbromide.
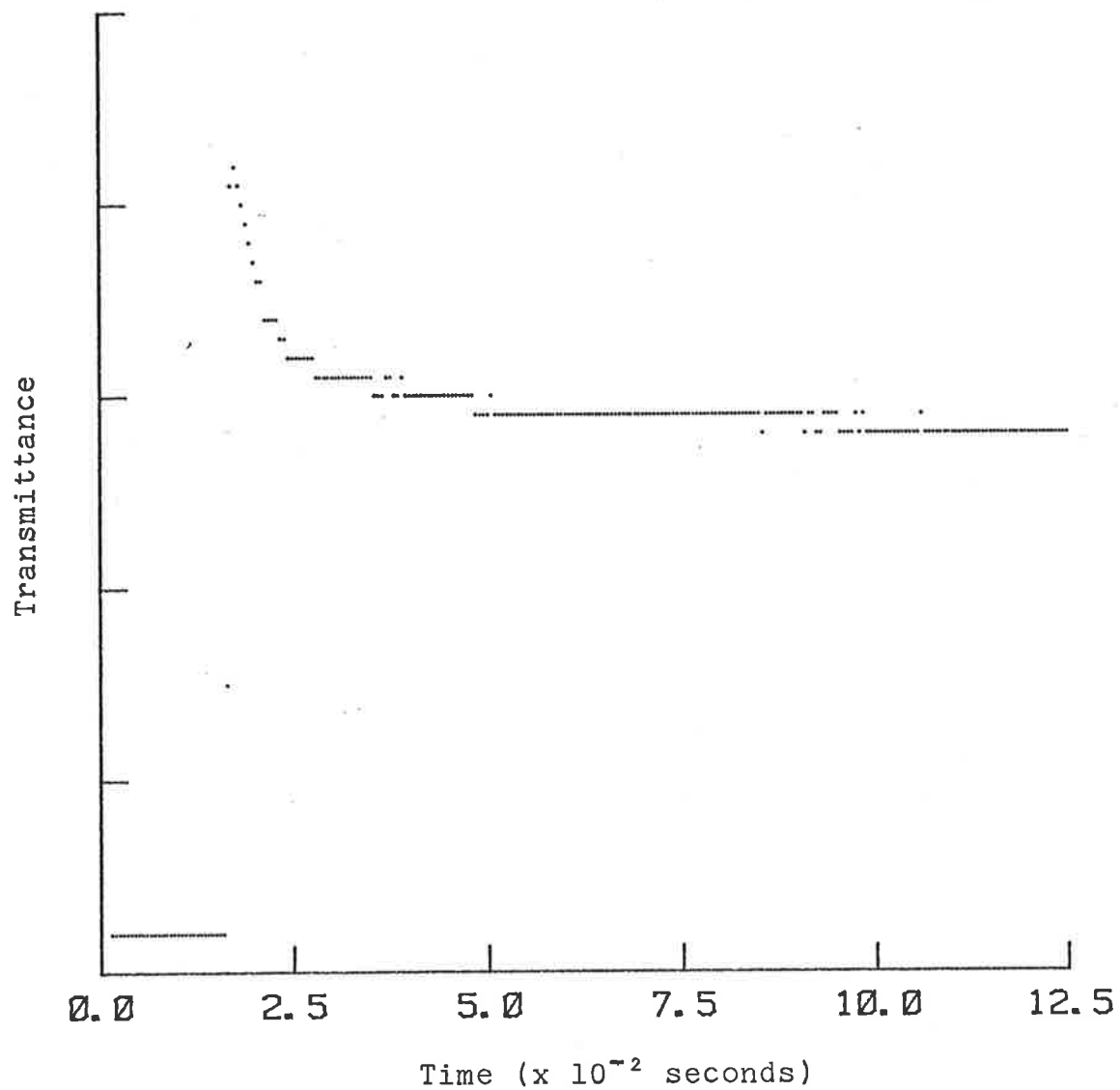
FIGURE 3.3.6b2   Fast process following flash photolysis
of $W(N_2)_2(dppe)_2$ in dinitrogen
saturated benzene solution containing
Ethylbromide.

This fourth step was interpreted as signifying competition for the species $W(N_2)(dppe)_2(solv)$ by N_2 to yield $W(N_2)_2(dppe)_2$ and RBr to yield $W(N_2)(RBr)(dppe)_2$. Therefore the reactive intermediate for the alkyl halide reaction was seen to be the second intermediate observed, i.e. $W(N_2)(dppe)_2(solv)$, not $W(dppe)_2(solv)_2$. However, $W(dppe)_2(solv)_2$ is formed first by a concomitant loss of both dinitrogen ligands, followed by recovery of one dinitrogen to yield the active intermediate thus:

$$W(N_2)_2(dppe)_2 \xrightarrow{\ h\nu\ } W(dppe)_2(solv)_2$$

$$W(N_2)(dppe)_2(solv)$$

$$W(RBr)(N_2)(dppe)_2 + N_2$$

with k_2, N_2 on the diagonal recovery path and k_1, N_2 on the downward path, and RBr on the lower step.
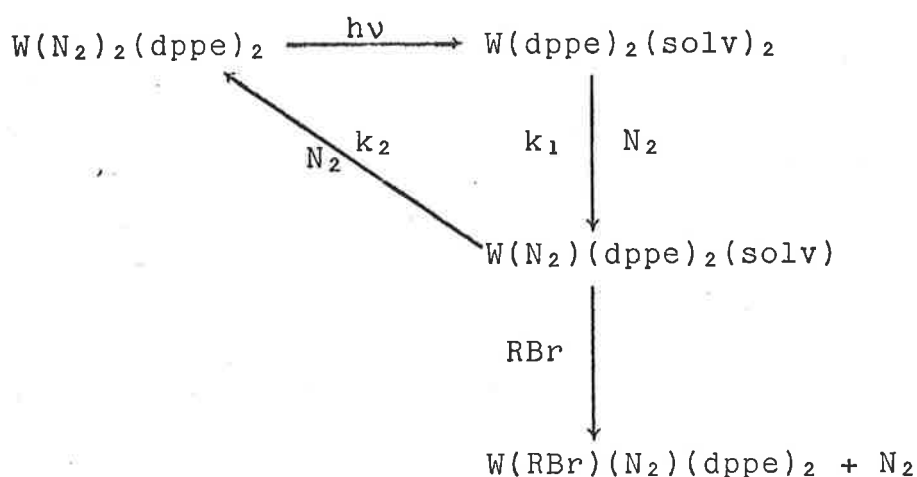
3.3.3 Temperature Dependence of Rates

The rates of the two recovery processes were determined as a function of temperature in N_2 saturated toluene and thf using a 50 mm quartz jacketted cell connected to the same cell filler as was described previously. A water/ethanol mixture was circulated through the outer compartment of the cell using a Haak "FK" thermostatted bath/pump. The temperature of the cell was measured by an accurately calibrated thermistor which was in contact with the outer jacket of the cell and insulated from the surroundings. A flow of dry N_2 was maintained over the surface of the cell at low temperature to minimise condensation and frosting.

Since the rates observed were for a thermal process of relaxation back to the photostationary state (rather than for a photochemical step) a plot of $\log(k)$ versus $1/T$ gave $Ea/2.303R$, where Ea is the activation energy (or ΔH^{*}) and R the gas constant (figure 3.3.7). The Gibbs free energy of activation at any temperature is given by

$$\Delta G^{\#} = -RT\ln(k) + RT\ln(\frac{kT}{h}).$$

Once a least squares line had been fitted to the experimentally observed values of $\log(k)$ versus $1/T$ the slope gave Ea ($\Delta H^{\#} = Ea - .59$), and the intercept and slope allowed a consistent value of k^{25} to be determined. The enthalpy of activation ΔH^{*}_{298} was determined by use of the equation $\Delta H^{*} = Ea - .59 kcal\ mol^{-1}$. Since $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$, $\Delta S^{\#}$ could then be calculated. The activation parameters determined in toluene and thf solutions are given in table 3.3.1.

The negative values for $\Delta S^{\#}$ of around 18 J mol^{-1} K^{-1}, suggested that an associative or I_D mechanism was involved in the recovery process. The values of $\Delta H^{\#}$ which were all around 10 kJ mol^{-1} were indicative of a dissociative or an I_D reaction mechanism.

Two factors weighed against the theory that an associative mechanism was involved.

(1) The recovery processes observed following flash photolysis under a dinitrogen atmosphere had essentially the same rates as did the recovery processes in CO saturated solvent.

(2) Ashwood[7] had observed that the rate of the recovery processes observed in the Mo(N$_2$)$_2$(dppe)$_2$ system
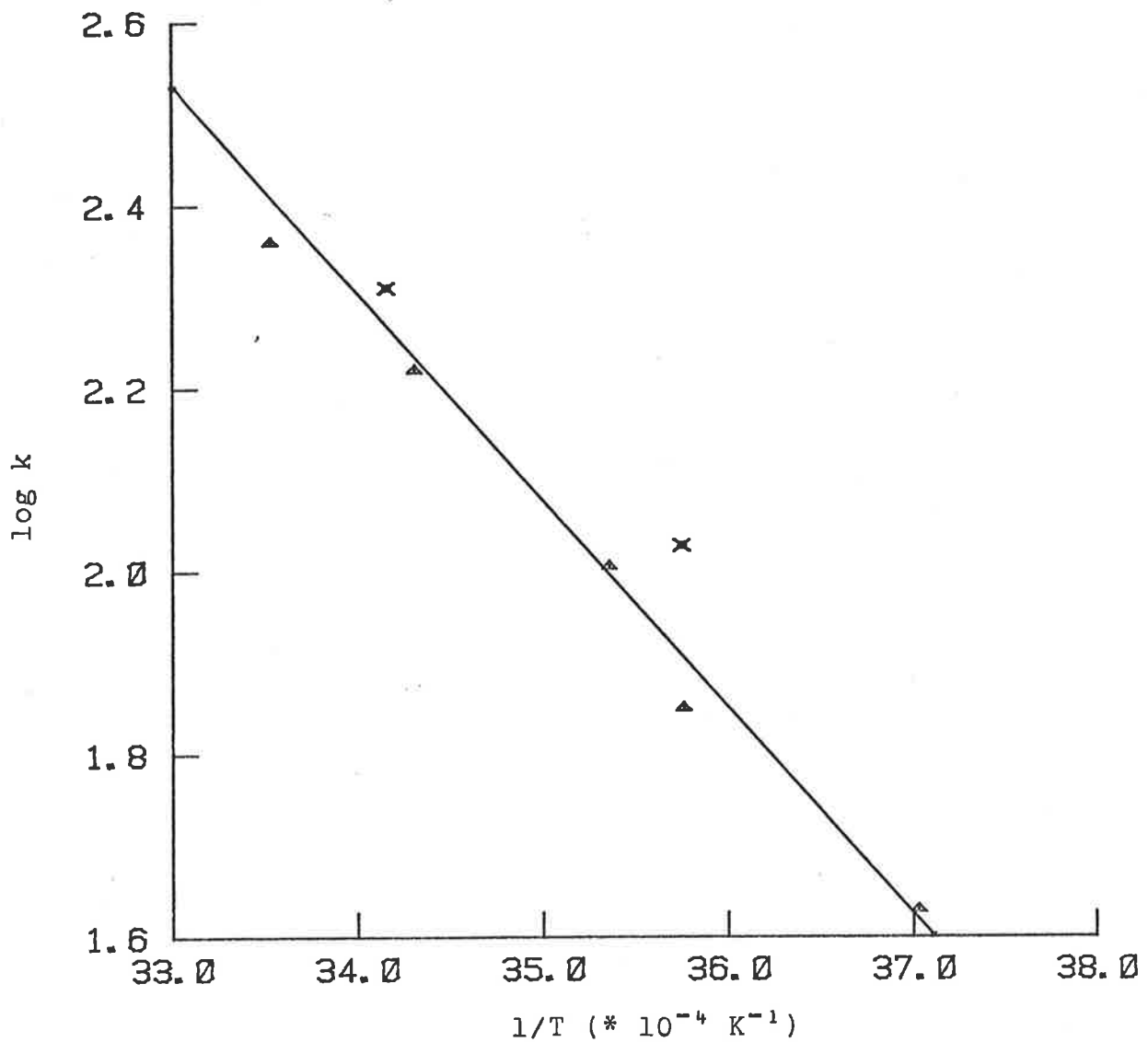
FIGURE 3.3.7a   Plot of log k versus 1/T for relaxation
process observed following flash photolysis
of $W(N_2)_2(dppe)_2$. The slope gives
$E_a/2.303R$. Fast process.

Δ Toluene solution (Dinitrogen saturated)

X   Thf solution
                    (Dinitrogen saturated)
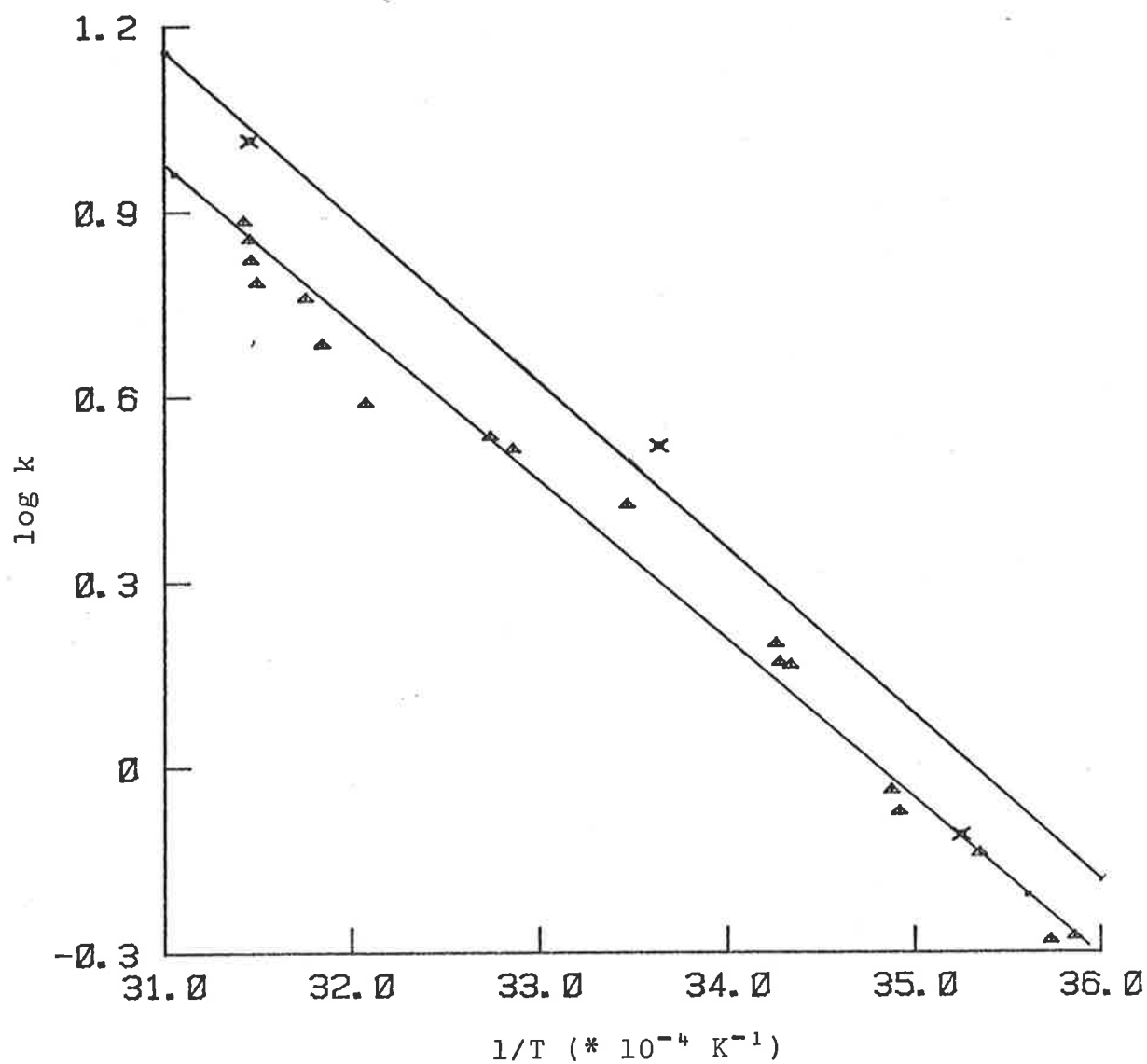
FIGURE 3.3.7b   Plot of log k versus 1/T for relaxation
process observed following flash photolysis
of $W(N_2)_2(dppe)_2$.   The slope gives
$E_a/2.303R$.   Slow process.

Δ   Toluene solution (Dinitrogen saturated)

X   Thf solution
(Dinitrogen saturated)

Table 3.3.1

| | Toluene | | Thf | |
	Fast	Slow	Fast	Slow
E_a kcal mol^{-1}	10.4	11.3	9.3	12.2
kJ mol^{-1}	43.4	47.1	38.9	51.2
k^{25} sec^{-1}	2.55 x 10^2	2.09	3.12 x 10^2	1.88
$\Delta G^{\#}$ kcal mol^{-1}	14.1	17.1	14.0	17.1
kJ mol^{-1}	62.9	71.6	58.7	71.4
$\Delta H^{\#}$ kcal mol^{-1}	9.8	10.7	8.7	11.6
kJ mol^{-1}	40.9	44.6	36.4	48.7
$\Delta S^{\#}$ cal mol^{-1} K^{-1}	-17.6	-21.6	-17.9	-18.2
J mol^{-1} K^{-1}	-73.6	-90.4	-74.8	-76.

(2) (Continued)

did not appear to be markedly dependent upon $[N_2]_{solv}$. A similar observation was made in this work pertaining to the effect of $p[N_2]$ upon reaction rates for $W(N_2)_2(dppe)_2$.

The negative values of $\Delta S^{\#}$ seemed to indicate that the rate of the reaction was not controlled by a dissociative step, however, this simplistic view is not necessarily correct.

If $\Delta S^{\#}$ was equal to zero, and Ea as observed, values of k_1 and k_2 for $W(N_2)_2(dppe)_2$ would lie in the range $10^4 - 10^5$ sec^{-1}. The fact that the rates observed were much slower than this indicated that the reaction rates were limited by entropy, that is, an ordered transition state was necessary for the reactions to proceed. This suggested that there was a geometric condition which needed to be fulfilled before the reaction could occur. This possibly meant that an incoming ligand needed to be oriented in a certain way relative to the metal centre or that the solvent moiety which was lost from the coordination sphere may have only been able to escape from the sterically hindering dppe ligands in a certain direction or orientation.

The values of Ea ($\approx$ 50 kJ mol^{-1}) indicated that the solvent moiety was not tightly bound to the metal centre, if the solvated intermediate existed. An alternative hypothesis is that solvent was not coordinated to the metal centre, and that the intermediates observed were four and five coordinate, 14 and 16 electron, complexes.

This appeared to be unlikely, but the similarity of observed rates and activation parameters[*] in thf, benzene and toluene, suggested that the intermediate was not a solvated moiety, or that the solvent did not play an important part in the rate determining step, or that thf and toluene bound in similar ways to the metal centre.

In an attempt to determine whether a radical change of solvent would induce a change in the observed rate, it was found that $W(N_2)_2(dppe)_2$ in thf/dmso (1:3)[**] underwent the changes in absorbance illustrated in figure 3.3.8. The initial rapid decrease in absorbance was followed by a step which resulted in a further decline of absorbance, with a rate of $ca.$ .06 mol^{-1} sec^{-1}. This process would not have been observed unless for some reasons N_2 could not recombine with the active intermediate. If the intermediate was a four coordinate species then the reaction should have occurred resulting in the normally observed recovery processes. The proportion which reacted with dmso in this case should have been equal to $k_3/(k_1 + k_3) = 3.8\%$.

$$W(solv)_2(dppe)_2 \xrightarrow[k_3]{dmso} W(dmso)(solv)(dppe)_2 \quad (?)$$
$$k_1 \downarrow N_2 \qquad\qquad\qquad \downarrow$$
$$W(N_2)(dppe)(solv) \qquad W(dmso)_2(dppe)_2$$
$$k_2 \downarrow N_2$$
$$W(N_2)_2(dppe)_2$$

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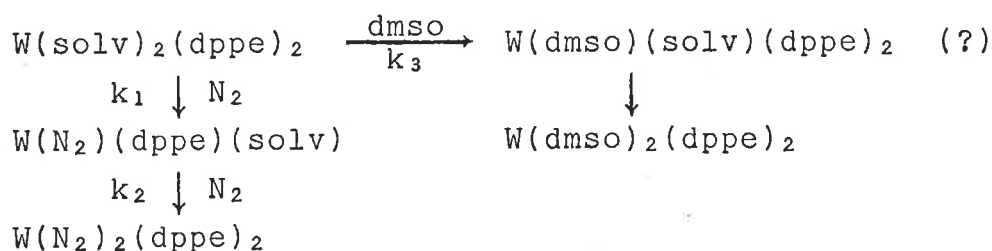
[*] For thf and toluene.

[**] $W(N_2)_2(dppe)_2$ is not soluble to any appreciable extent in dmso alone.
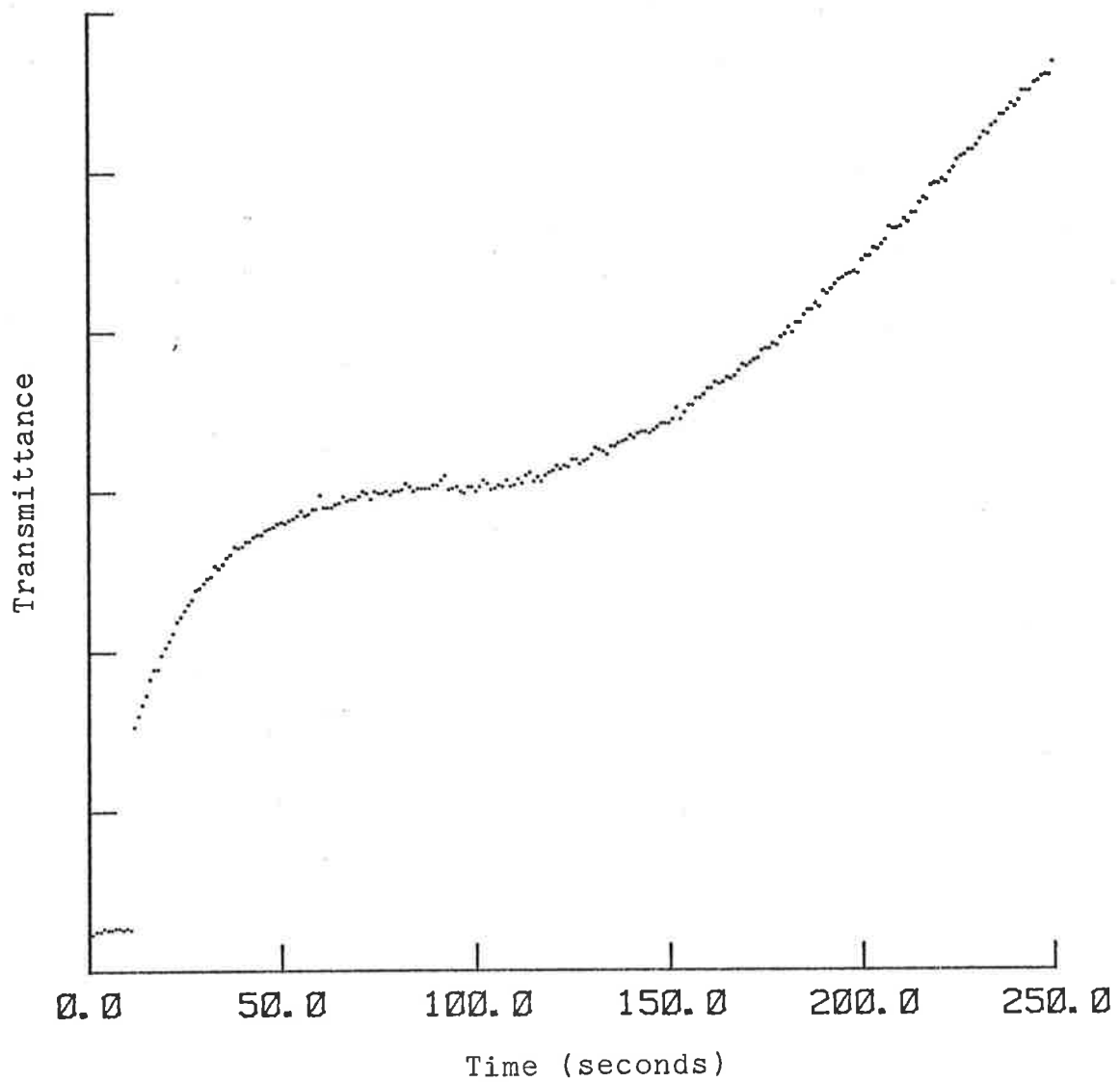
FIGURE 3.3.8 Processes following flash photolysis of a solution of $W(N_2)_2(dppe)_2$ in dmso/thf.

However, if a reasonable proportion of the
initially formed intermediate contained coordinated dmso
it is probable that the reaction path followed from that
point onwards would differ greatly from that followed in
thf or toluene, due to the highly coordinating nature of
dmso.

The conclusion reached from this experiment was that
in all probability the active intermediate was solvated,
and that in dmso/thf solution dmso is coordinated to the
metal centre. In the presence of thf, benzene or toluene,
the solvent was then lost by an Id type mechanism, where
there is a concomitant loss of solvent and gain of N_2 (or
any other incoming group.) See figure 3.3.9.

3.3.4   Probable Reaction Mechanism

The conclusions drawn from the flash photolysis
experiments described above were:

(1) Visible light irradiation labilised two dinitrogen
    ligands.

(2) The intermediate formed was a six coordinate solvated
    species.

(3) The ligands were recovered from dinitrogen saturated
    solution in two distinct steps, which each involved
    an I_D mechanism.

(4) Alkyl halides reacted with the species
    $W(N_2)(solv)(dppe)_2$ in competition with N_2.

Figure 3.3.9

$$M(N_2)_2(dppe)_2 \quad - - - - - - - \overset{h\nu}{- - - - - -} \to \quad M(dppe)_2(solv)_2 + 2N_2$$

$$+ N_2 \qquad - N_2 \qquad\qquad\qquad + solv \quad | \quad - solv \text{ (slow)}$$

$$M(dppe)_2(solv) + solv$$

$$RXM(N_2)(dppe)_2 \quad \overset{RX}{\underset{-RX}{\rightleftharpoons}} \quad M(N_2)(dppe)_2 \qquad - N_2 \quad | \quad + N_2 \text{ (fast)}$$

$$- solv \qquad + solv$$

$$M(N_2)(dppe)_2(solv)$$
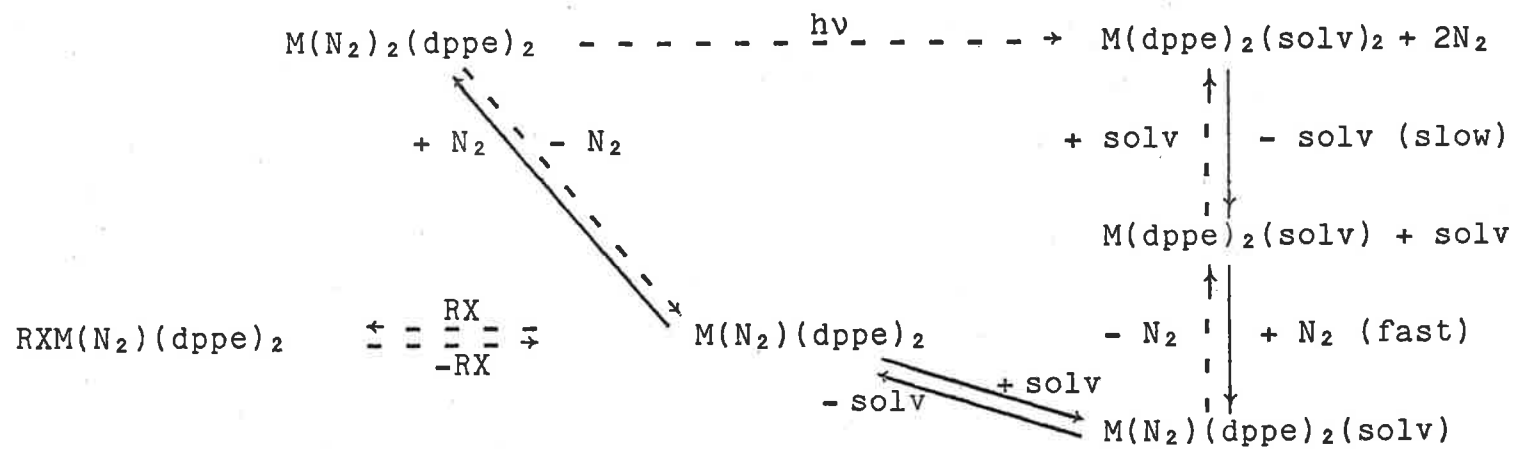
3.4.1 $^{15}N_2$ exchange mechanism

The hypothesis that $W(N_2)_2(dppe)_2$, when excited by light released two dinitrogen ligands simultaneously, and then (in N_2 saturated solvent) regained these ligands in two consecutive steps was central to the interpretation placed upon the above results. Therefore, it was seen to be imperative that this hypothesis was tested in some critical way. Three techniques were utilized; "flash labelling" (discussed above), preparation of a product *in vacuo*, and the kinetics of $(^{15}N_2)W(^{14}N_2)$ formation in relation to $(^{14}N_2)W(^{14}N_2)$ when a solution of $W(^{15}N_2)_2(dppe)_2$ was irradiated under an atmosphere of $^{14}N_2$.

(1) Flash labelling

As has been discussed above, the discovery that the isotopomer $(^{15}N_2)W(^{15}N_2)(dppe)_2$ could be detected after flash photolysis (by one flash) of $W(N_2)_2(dppe)_2$ under $^{15}N_2$ led to the hypothesis that two ligands were exchanged upon one excitation.

(2) Preparative techniques

As has been discussed above, when some alkyl halide was present during flash photolysis, the initial rapid process, attributed to the reaction

$$W(solv)_2(dppe)_2 + N_2 \longrightarrow W(N_2)(solv)(dppe)_2$$

was unchanged, while the second slower process was disrupted. However, in argon saturated thf neither fast nor slow process was observed. In other words, N_2 appeared to be essential for the recovery processes. Since the intermediate $W(N_2)(solv)(dppe)_2$ was believed to be the active species

towards attack by RX, it would appear that for the
reaction

$$W(N_2)_2(dppe)_2 + RBr \longrightarrow BrW(N_2R)(dppe)_2$$

the percentage yield should decrease significantly if the
formation of the intermediate $WN_2(solv)(dppe)_2$ was
retarded by a low concentration of N_2. Obviously, under
the reaction conditions used some N_2 would be present,
produced by the photolysis of $W(N_2)_2(dppe)_2$. Dinitrogen
is present in thf (under 1 atmosphere of dinitrogen gas)
at a concentration of ca. .007 M.[*] If (as was the
procedure) .4 g of $W(N_2)_2(dppe)_2$ was photolysed in 100 cm^3
of thf (.4 moles in .1 litre) a final N_2 concentration of
.01 M would be attained unless some dinitrogen left the
solvent, into the vessel containing the reaction mixture.

This was taken into account in planning the
preparative experiment, and thus the following procedure
was adopted. $W(N_2)_2(dppe)_2$ (374 mg) was placed in a
500 ml flask with a magnetic stirrer, the flask was
attached to the thf solvent still and evacuated for
ca. 30 minutes. Thf (ca. 100 cm^3, Argon saturated) was
added, followed by .5 cm^3 of 2,2-bromomethylpropane
(t-butyl bromide). The resulting mixture was stirred
under Argon in the dark to affect dissolution of the
dinitrogen complex. The flask was then evacuated, shaken
to partially degas the thf (of Argon) and reevacuated.
The flask was then exposed to light (100 W mirror backed
flood lamp) for 2½ hours. During this time the flask
was evacuated every thirty minutes. At the end of
2½ hours the solution was a straw colour, characteristic

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[*] See Chapter 4 for measurement of N_2 solubility in thf.

of the hydrazido (2-) complex. Yield .13 g, 29%. This was a considerable reduction of percentage yield when compared to the reaction carried out under a dinitrogen atmosphere, (*ca.* 70%).

A similar experiment was carried out on a far smaller scale, by using ^{1}H n.m.r. to monitor progress of the photochemical reaction of $W(N_2)_2(dppe)_2$ with 1-bromobutane   under N_2 or vacuum. Two sealed n.m.r. tubes were prepared, each containing *ca.* 3 mg of complex and *ca.* 1 ml of C_6D_6 which contained 1.5 µ litre of 1-bromobutane . An initial spectrum was recorded, and then spectra taken after irradiation by visible light had proceeded for some time. (Both tubes were exposed to diffuse light for the same time.) The solution in the tube sealed under N_2 turned a light yellow colour characteristic of $BrW(N_2Bu)(dppe)_2$, while the tube sealed under vacuum became a redder/orange, characteristic of $WBr_2(dppe)_2$. The final n.m.r. spectra were appreciably different. (Figure 3.4.1)

Furthermore, the n.m.r. tube sealed under vacuum rapidly became contaminated with paramagnetic impurities. This behaviour was observed in two independent experimental runs.

It was felt that these results were in accordance with the mechanism hypothesised.

(3) Kinetics of labelling

Two possible mechanisms involved in dinitrogen ligand exchange are:

(A) $W(N_2)_2(dppe)_2 \xrightarrow[\;\;\longleftarrow\;\;]{h\nu} W(N_2)(dppe)_2 + N_2$
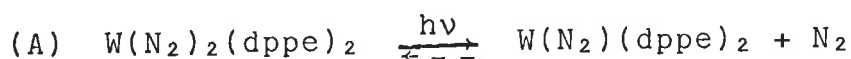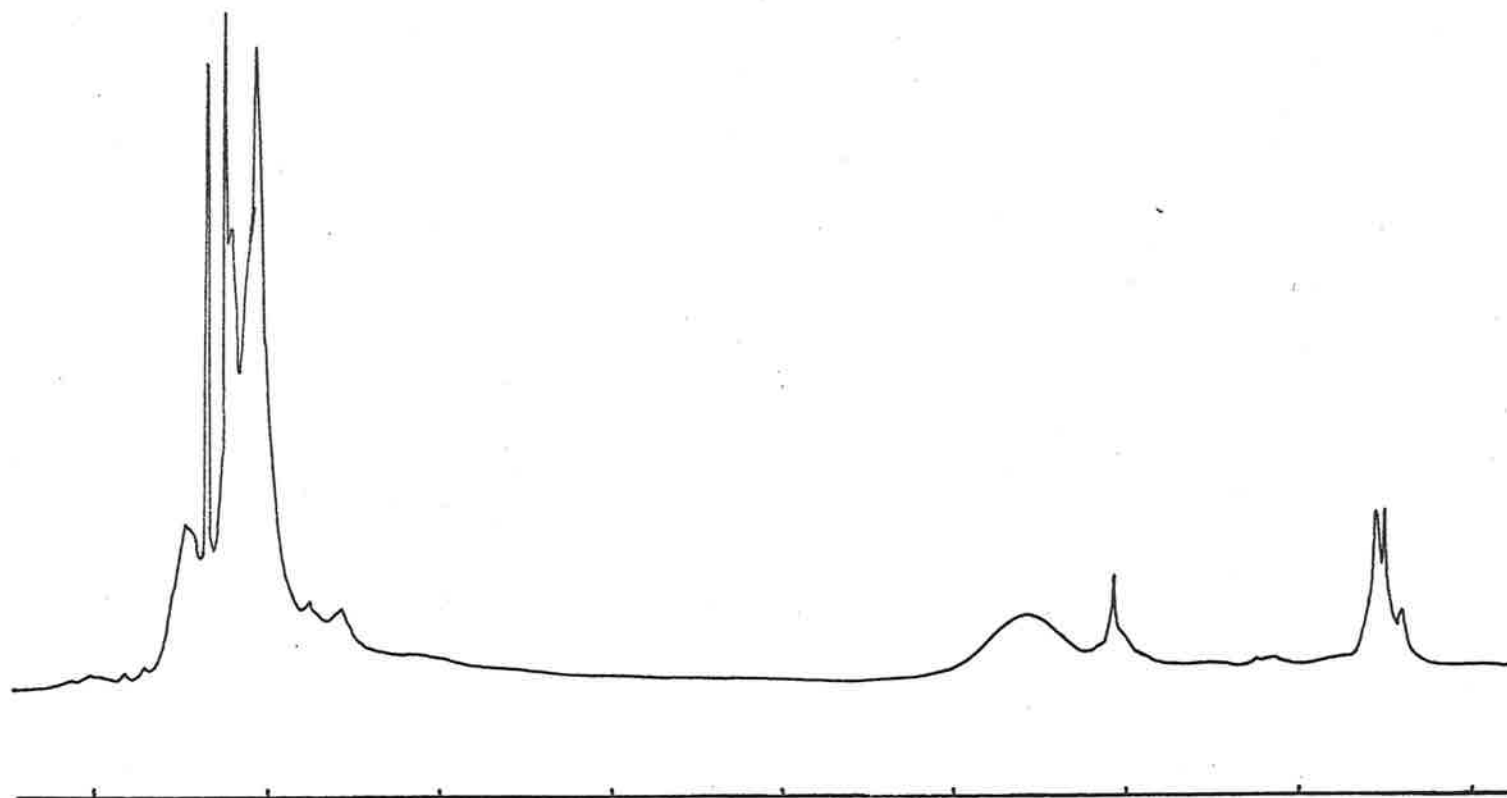
FIGURE 3.4.1a ^{1}H nmr spectrum of product of reaction of $W(N_2)_2(dppe)_2$ with nBuBr under N_2.
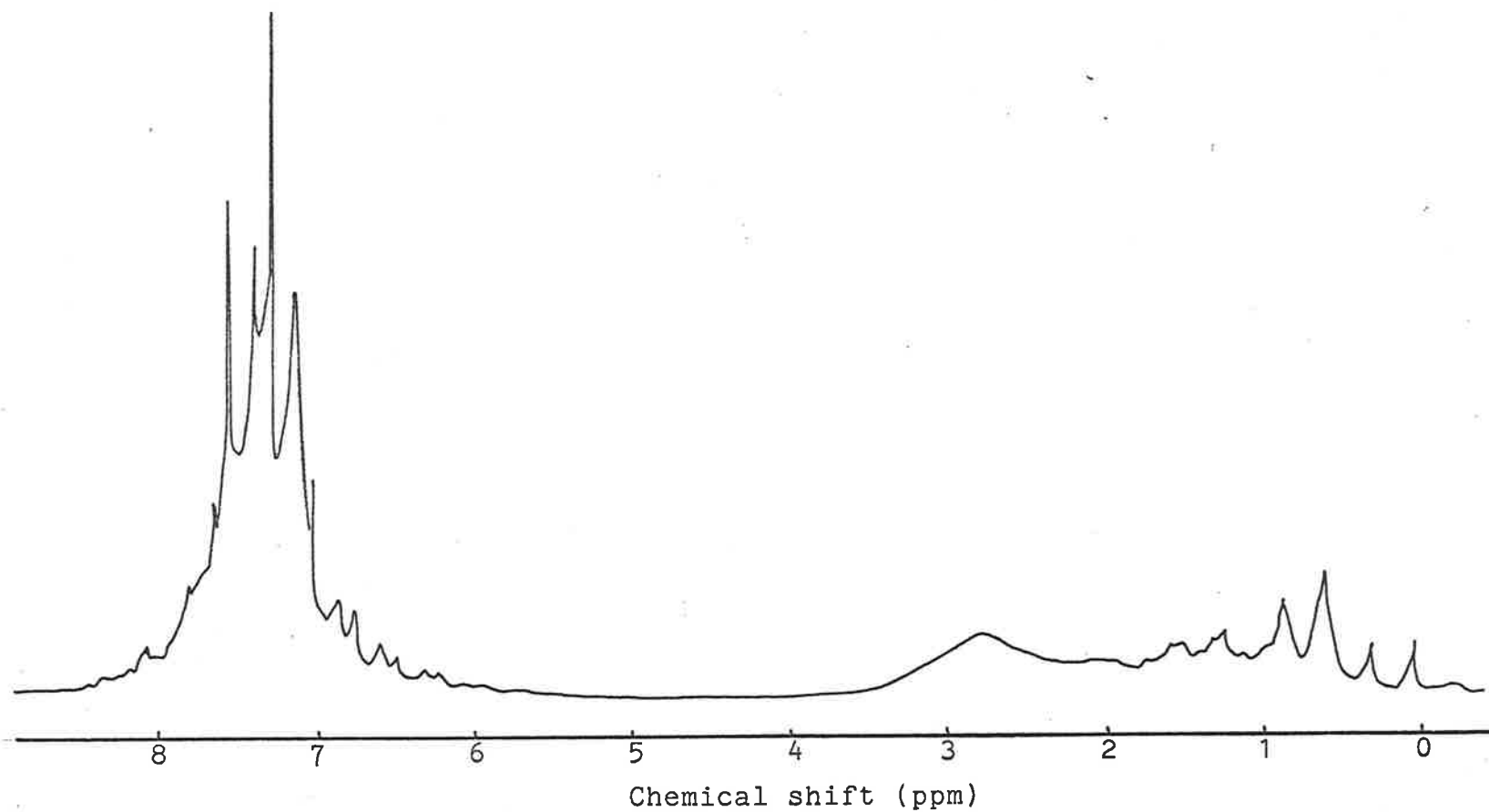
FIGURE 3.4.1b ^{1}H nmr spectrum of product of reaction of $W(N_2)_2(dppe)_2$ with n-BuBr under vacuum.

and

(B) $W(N_2)_2(dppe)_2 \xrightleftharpoons{h\nu} W(dppe)_2 + 2N_2$.
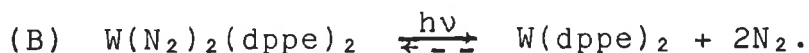
If isotopic substitution reactions are carried out, by using $^{15}N_2$ (or $^{14}N_2$ with $^{15}N_2$ labelled complex) these two mechanisms give rise to different *relative* rates of, formation of singly and doubly labelled isotopomers.

This effect is most noticeable if a high concentration of the substituting species is maintained during the course of the reaction. Accordingly, an experiment was carried out in the following way.

A sample of $W(^{15}N_2)_2(dppe)_2$ was prepared by, irradiating and exposing a solution of $W(N_2)_2(dppe)_2$ to a fresh aliquot of $^{15}N_2$ three times. The final atmosphere used was approximately 98% $^{15}N{-}^{15}N$.

This procedure produced predominantly $W(^{15}N{-}^{15}N)_2(dppe)_2$. The solution of this isotopomer was then exposed to an atmosphere of $^{14}N_2$ under controlled illumination. The $^{14}N_2$ (dry, high purity, oxygen free) was bubbled through the solution. Aliquots were periodically withdrawn and the infra red spectrum of the solution determined as a function of time.

A plot of $[W(^{15}N_2)(^{14}N_2)(dppe)_2]$ (figure 3.4.2) and $[W(^{14}N_2)_2(dppe)_2]$ against time showed no induction period for $[W(^{14}N_2)_2(dppe)_2]$, and also showed a rapid increase in $[W(^{14}N_2)_2(dppe)_2]$ with no great increase in $[W(^{15}N_2)(^{14}N_2)(dppe)_2]$.

If mechanism A (above) was correct, any $W(^{14}N_2)_2(dppe)_2$ would have been formed by a two step reaction, e.g.

$$^{14}N_2 + W(^{15}N_2)_2 \xrightarrow{h\nu} W(^{15}N_2)(^{14}N_2) + {}^{15}N_2$$

$$^{14}N_2 + W(^{15}N_2) \xrightarrow{h\nu} W(^{14}N_2)_2 + {}^{15}N_2$$
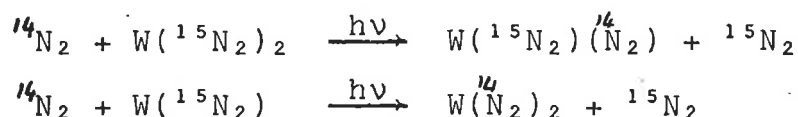
FIGURE 3.4.2   Infrared spectra showing reaction
              between $^{14}N_2$ gas and $W(^{15}N_2)_2(dppe)_2$
              in thf solution. The peak at 1876
              cm^{-1} corresponds to $W(^{15}N_2)_2(dppe)_2$,
              that at *ca*. 1900 cm^{-1} to
              $W(^{15}N_2)(^{14}N_2)(dppe)_2$ and the peak
              at 1940 cm^{-1} to $W(^{14}N_2)_2(dppe)_2$.

              Note that the formation of
              $W(^{14}N_2)_2(dppe)_2$ does not appear to
              require $W(^{15}N_2)(^{14}N_2)(dppe)_2$
              formation first.

Figure axes: Absorbance ($\times 10^{-1}$) versus Wavenumber (cm^{-1}), with spectra at t = 0 minutes, t = 13 minutes, t = 18 minutes, t = 53 minutes, and t = 80 minutes.
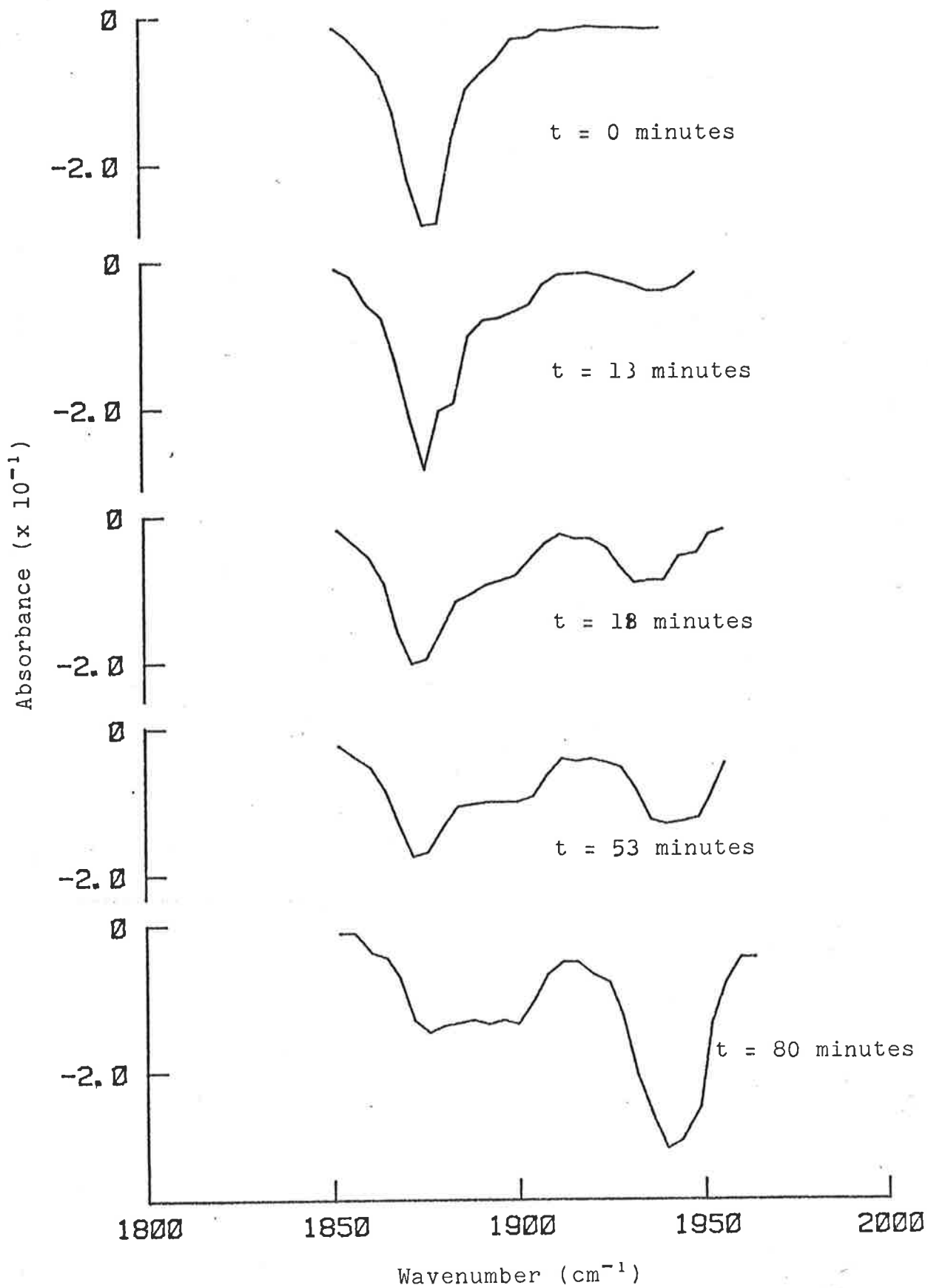
If mechanism B was correct $W(^{14}N_2)_2(dppe)_2$ could be formed directly from $W(dppe)_2$ and $^{14}N_2$ in the solvent, e.g.

$$W(^{15}N_2)_2 + 2^{14}N_2 \xrightarrow{h\nu} W(^{14}N_2)_2 + {}^{15}N_2.$$
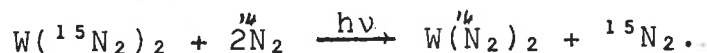
These mechanisms result in different rates of formation of $W(N_2)_2(dppe)_2$:

For mechanism A $\qquad \dfrac{d[W(^{14}N_2)_2(dppe)_2]}{dt} \propto \phi^2[W(^{15}N_2)_2]^2$

while for mechanism B $\qquad$ rate $\propto \phi[W(^{15}N_2)_2]$

Since ϕ at constant temperature, pressure and wavelength is a constant the rate for A reduces to that for a simple second order reaction, the rate for B reduces to that for a first order reaction.*

A plot of experimentally observed $\log([W(^{14}N_2)_2]^{final} - [W(^{14}N_2)]^t)$ versus t was found to be linear, (figure 3.4.3). Thus the formation of $W(^{14}N_2)_2(dppe)_2$ from $W(^{15}N_2)_2(dppe)_2$ in $^{14}N_2$ saturated thf was observed to be a first order reaction, which supports hypothesised mechanism B.

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* It has been noted above that light catalysed reactions are normally zero order in substrate, rate relying purely on ϕI_{abs}. However, I_{abs} may depend upon concentration. In the circumstance where $A \to B \to C$ and A, B and C have sensibly identical spectra at the irradiating wavelengths

$$I^A_{abs} \propto I_o \, \frac{\varepsilon_A C_A}{\Sigma \varepsilon_i C_i}$$

or, since $\varepsilon_A = \varepsilon_B = \varepsilon_C$ $\qquad I^A_{abs} \propto I_o \, \dfrac{C_A}{C_A + C_B + C_C}$

Now $C_A + C_B + C_C$ = constant, $\therefore \; I^A_{abs} \propto C_A$
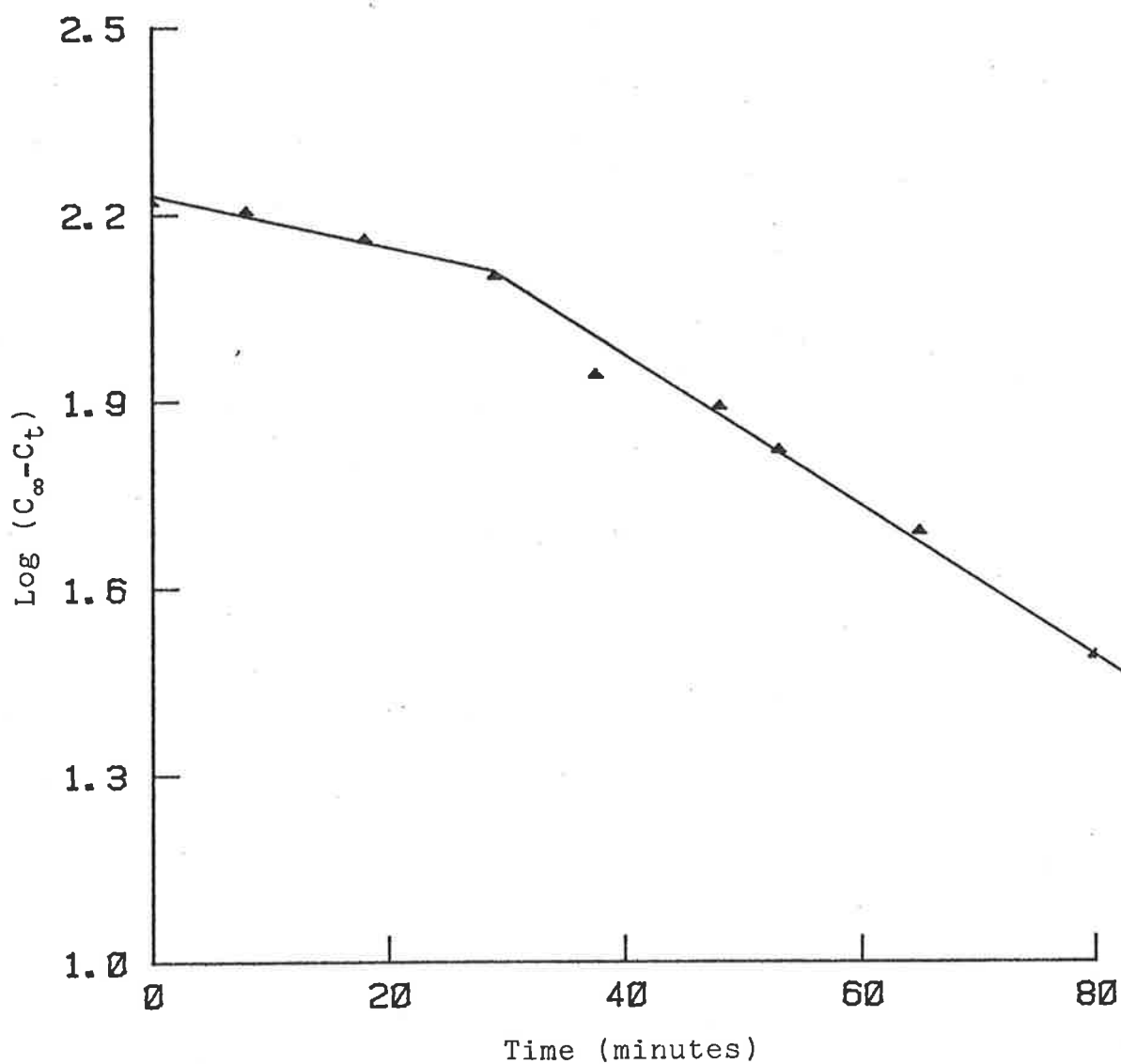
FIGURE 3.4.3 Plot of log ($[W(N_2)_2]_\infty - [W(N_2)_2]_t$ for the formation of $W(N_2)_2(dppe)_2$ from $W(^{15}N_2)_2(dppe)_2$ under $^{14}N_2$.

Note: Intensity of the light source was increased by a factor of *ca*. 2 at 30 minutes.

3.5 Emission studies:

While flash photolysis results showed what happened
to $W(N_2)_2(dppe)_2$ in solution when irradiated by light in
the time domain from 10 microseconds after the flash to
seconds after the flash, little could be determined
concerning the properties of the initially formed excited
state. In an attempt to investigate the time domain
5 nanoseconds to 10 microseconds after irradiation, laser
excited emission studies were undertaken on frozen benzene
solutions of $W(N_2)_2(dppe)_2$. The laser used (pulsed
nitrogen laser, Lambda Physik M100A) had a pulse width of
2ns, timing jitter reduced the resolution to 5ns.
Emission from the frozen solution was studied using a
Bausch and Lomb high intensity monochromator and
photomultiplier electronics monitored by a gated
integrator (Princeton Applied Research Type 163), as
described by Thornton and Laurence.[6]

Some emission was detected at 600 ± 20 nm with
a lifetime of *ca.* 80 nanoseconds, however this could also
be obtained from a frozen solution of dppe in benzene.
No other emission could be found.

3.6 Conclusion

The combination of isotopic labelling experiments
and flash photolysis clearly established that the following
mechanism occurs upon irradiation of benzene, toluene or
thf solutions by visible light.

$$W(N_2)_2(dppe)_2 \xrightarrow[-2N_2]{h\nu} W(dppe)_2(solv)_2$$
$$\downarrow +N_2$$
$$W(N_2)(dppe)_2 solv$$
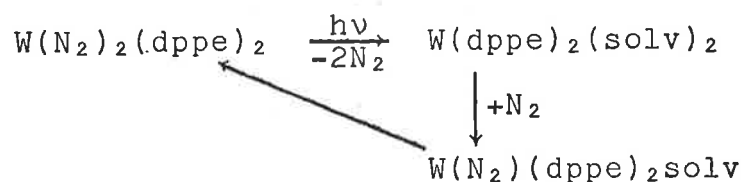
It was also shown that $W(N_2)(dppe)_2solv$ was the reactive species in the light catalysed reaction between $W(N_2)_2(dppe)_2$ and alkyl halides.

Quantum yield determination for the reaction with alkyl halides suggested that the limiting quantum yield for the reaction in general was *ca.* .4 to .45.

The results of this project have been parallel to results obtained by Ashwood and Laurence in the $Mo(N_2)_2(dppe)_2$ system, with the exception that $Mo(N_2)_2(dppe)_2$ undergoes a thermal reaction *in addition* to the light catalysed reactions. Activation parameters for the recovery process observed in the molybdenum system were comparable to those observed in this project.

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CHAPTER 4

4.0 Materials and methods

4.1.1 Syntheses

(a) Tungsten Hexachloride

WCl_6 was obtained from Merck or B.D.H., or else was produced by the method of Lefler and Penque.[1] In the latter case tungsten metal was heated to reflux in thionyl chloride for 4 hours, filtered off under N_2, washed with CCl_4, and dried *in vacuo*. The tungsten was then transferred to the silica reaction tube of the apparatus described by Leffler and Penque.[1] The tungsten was heated to *ca.* 400°C and a current of dry dinitrogen passed over the metal. This was followed after 30 minutes by a stream of chlorine/N_2 mixture. The temperature of the tube furnace around the reaction tube was increased to *ca.* 500°C. Solid WCl_6 condensed in the cyclone at the end of the reaction tube and was collected in a flask below.

Analysis

Titration for Cl^- found 53 . 24% theoretical for WCl_6 is 53.63% WCl_6 produced in this way was purer than commercially obtained WCl_6 which was found to contain considerable quantities of oxychloride.

(b) 1,2 bis diphenyl phosphino ethane

Dppe was either produced by the method of Chatt and Hart[2] or obtained from Strem Chemical Corporation.

(c) Tungsten(IV)bis(triphenylphosphine)tetrachloride

The preparation of $WCl_4(P\phi_3)_2$ was based on that reported by Chatt et al,[3] 16 g of WCl_6 (50   mmol), 22 g $P\phi_3$ (84 m mole), and 20 g of zinc "wool" ~~was~~ were placed in a schlenck flask which was connected to the CH_2Cl_2 solvent still and evacuated for 20 to 30 minutes. Dry, freshly distilled dichloromethane was added and a stream of dinitrogen passed through the flask while it was shaken for 10 minutes. The orange/yellow precipitate which formed was collected in a schlenck filter ~~stick~~, and washed with a small volume of CH_2Cl_2, and dried *in vacuo*. Yield *ca.* 18 g, 21   mmol   53%.

(d) Tungsten(IV)(1,2,bisdiphenylphosphinoethane)tetrachloride

The preparation of WCl_4dppe was also based on that reported by Chatt et al,[3] 18 g of $WCl_4(P\phi_3)_2$ and 8.5 9 of dppe were placed in a 250 cm^3 flask with a magnetic bar stirrer, the flask attached to the toluene solvent still and evacuated for *ca.* 20 to 30 minutes. Dry, dinitrogen saturated toluene (100 cm^3) was added followed by a dinitrogen atmosphere. The suspension of $WCl_4(P\phi_3)_2$ was heated at *ca.* 75°C with vigorous stirring for *ca.* 2 hours during which time it turned green. The green product was collected on a schlenck filter ~~stick~~, washed with dry hexane (dried over CaH_2) and dried *in vacuo*. Yield *ca.* 15 g,   20.6   mmol , 96%.

(e) Tungsten(O)bis(dinitrogen)bis(1,2,bisdiphenylphosphino-ethane)

The preparation of $W(N_2)_2(dppe)_2$ which was based on that reported by Chatt et al[3], required the use of carefully dried apparatus and gases. In the procedure used 15 g WCl_4 dppe, 8.5 g dppe, 25 g Mg turnings and a magnetic bar stirrer were placed in a 2 litre three necked flask, which was attached to the thf solvent still and evacuated for 20 to 30 minutes. At the end of that time thf (ca. 500 cm^3') was introduced into the flask followed by a dinitrogen atmosphere. A flow of dinitrogen was maintained over the mixture while it was stirred vigorously for 3 to 15 hours. A coil condenser was fitted to minimise solvent loss during this time. If necessary a crystal of iodine was added to start the reduction. The green coloured suspension turned dark red/brown within a few minutes once the reduction had started, and the suspension became quite warm.

The solution was filtered and orange crystals of the product obtained by reducing the volume to ca. 50% *in vacuo*. The complex was recrystallised by temperature gradient from thf, generally 3 to 4 times.

The UV/visible spectrum of the product was used as a general measure of purity. <u>Analysis</u>: Theoretical 5.4% N, 4.66% H, 60.2% C. Found: 5.3% N, 4.7% H, 59.7% C.

(f) *trans*-$W(CO)_2(dppe)_2$

The novel complex *trans*-$W(CO)_2(dppe)_2$ was produced in the following way. $W(N_2)_2(dppe)_2$ (.5 g) was placed in a 250 cm^3 flask, with a magnetic stirrer, and

attached to the thf solvent still. The flask was
evacuated (*ca.* 30 minutes) and thf (60 cm^3) introduced
The reaction mixture was cooled to 0°C in an ice water
bath. An atmosphere of CO (Matheson-CIG, dried over
CaCl$_2$ followed by P$_2$O$_5$) was introduced into the reaction
vessel and the solution stirred vigorously. The reaction
mixture was irradiated by using a 100 W tungsten filament
mirror backed lamp for 3 hours, and then the solution was
reduced to *ca.* 15 cm^3 *in vacuo*. The temperature of the
solution was maintained at 0°C during the entire course
of the reaction. A yellow microcrystalline substance was
produced on leaving the solution at *ca.* 0° for 4-5 hours.
The product was collected under a dinitrogen atmosphere
in a schlenck filter stick, and dried *in vacuo*.
Yield .43 g, 86%. The complex was characterised as being
the *trans* by the use of infra red spectroscopy, and was
analysed for elemental composition as the *cis* isomer.

(g) *cis*-W(CO)$_2$(dppe)$_2$

The *cis* isomer of the carbonyl complex was produced
either from the *trans* isomer or from the dinitrogen complex.
In the latter case W(N$_2$)$_2$(dppe)$_2$ (.5 g, .5 mmol) was placed
in a 250 ml flask with a magnetic bar stirrer and attached
to the thf solvent still. The flask was evacuated for
ca. 30 minutes, and then thf (*ca.* 60 cm^3) introduced
followed by a dinitrogen atmosphere. The atmosphere of N$_2$
was replaced by CO(Matheson-CIG, dried over CaCl$_2$ then P$_2$O$_5$)
and the solution stirred vigorously. The reaction mixture
was irradiated using a 100 W tungsten mirror backed lamp
for 3 hours, and then stirred at 30°C for 1 hour. The
solvent was then reduced to 15 cm3 *in vacuo*, and the product

crystallised on standing in a refrigerator for 4-5 hours. The pale yellow microcrystalline product was collected using a schlenck filter stick under a dinitrogen atmosphere and dried *in vacuo*. Yield .4 g, 80%. The isomeric purity was checked by use of infra red spectroscopy.

Elemental analysis: Theoretical: 62.56% C, 0.0% N, 4.67% H

Found: 64.24% C, 0.01% N, 5.06% H

(h) WH₄(dppe)₂

The hydride complex was produced by direct reaction of H_2 and the dinitrogen complex. *Ca.* .4 g of $W(N_2)_2(dppe)_2$ and a magnetic bar stirrer were placed in a 250 cm^3 flask, which was attached to the thf solvent still and evacuated for *ca.* 30 minutes. Thf (40 cm^3) was introduced into the flask followed by a dinitrogen atmosphere. The atmosphere was then flushed away by a stream of H_2 (dried over $CaCl_2$, P_2O_5 and molecular sieves), and the solution was stirred vigorously. The reaction mixture was thermostatted at 35°C in a water bath and irradiated using two tungsten filament 100 W lamps for 3 hours. During the course of the reaction the solution turned pale yellow. At the end of this time the solution was reduced in volume *in vacuo* and the yellow microcrystalline product collected in a schlenck filter stick under a dinitrogen atmosphere. The product was washed with hexane and dried *in vacuo*. Yield, .32 g, 79%.

Analysis: Theoretical: 0% N, 5.33% H, 63.5% C

Found: 0% N, 5.22% H, 62.4% C

4.1.2 Gases

(a) Isotopically labelled dinitrogen

Dry oxygen free $^{15}N_2$ was prepared from $^{15}NH_4Cl$ using the method of Glasscock.[4]

Fresh NaOBr was prepared in solution by reacting 200 g NaOH in 300 cm3 .H_2O with 60 cm3 Br_2, while maintaining the temperature between -5°C and 0°C. After the bromine was slowly added the solution was then stirred for 1 hour at *ca.* -5°C. A 40 cm^3 aliquot of this stock NaOBr was reacted with a solution of 250 mg $^{15}NH_4Cl$. The solutions were placed in two flasks on a vacuum line, arranged so that the contents could be mixed by rotating the ground glass joints. The solution of $^{15}NH_4Cl$ was acidified with dilute H_2SO_4. A grain of KI was also added to minimise oxygen generation.

The solutions were degassed using four freeze/pump/thaw cycles and then carefully mixed and stirred with a magnetic "flea". The vacuum line had a gas burrette attached which allowed the progress of the reaction to be monitored. One hour after mixing had taken place the solution was frozen, and permanent gases removed to a separate vessel using a toepler pump. The reaction vessels were removed from the vacuum line and replaced with two vessels containing pyrogallic acid and an argon saturated solution of sodium hydroxide. The vessels were degassed by four freeze/pump/thaw cycles and the contents mixed. The atmosphere produced earlier was introduced and the alkaline pyrogallol solution stirred vigorously. After 2 hours the solution was frozen and the remaining

permanent gases returned to the storage vessel which had previously been pumped out (to less than .001 Torr).

(b) Dinitrogen

Dry, high purity dinitrogen was used as supplied by Commercial and Industrial Gases.

(c) Argon

Argon (high purity grade) was used as supplied by Commercial and Industrial Gases.

(d) Carbon Monoxide

Carbon monoxide was supplied by Matheson-CIG.

(e) Nitrous oxide

Nitrous oxide (BP) was supplied by Commercial and Industrial Gases. It was further purified by freezing and subliming under vacuum after drying with P_2O_5.

4.1.3 Solvents

All solvents used were dried and distilled under dinitrogen prior to use.

Thf was distilled twice, once from calcium hydride and then from sodium benzophenone.

Toluene was distilled from sodium benzophenone.

Benzene was distilled from calcium hydride.

Dichloromethane was distilled from P_2O_5.

DMSO was distilled from molecular sieves which had previously been baked out at *ca.* 150°C *in vacuo*.

Small quantities of solvents such as thf or benzene were distilled when required *in vacuo* from $LiAlH_4$.

Methanol was distilled from a solution of magnesium methoxide.

4.2 Spectral measurements

4.2.1 Infra red spectroscopy

Infra red spectra were recorded using a Perkin-Elmer model 457 grating spectrophotometer (4000-250 cm^{-1}). Nujol mulls between KBr or NaCl plates, KBr discs and solutions in demountable KBr solution cells were used.

4.2.2 Ultraviolet/Visible spectroscopy

Routine spectra were récorded on a Varian 635 dual beam spectrophotometer.

Accurate measurements were carried out using Zeiss QR-50 dual beam spectrophotometer.

4.2.3 Nuclear Magnetic Resonance Spectroscopy

Four nmr spectrometers were used:

(a) A Varian T-60 spectrometer was used for 60 MHz continuous wave ^1H spectra.

(b) A Bruker HX-90 spectrometer was used to obtain 36.435 MHz ^{31}P spectra, 22.63 MHz ^{13}C spectra and 90 MHz ^1H spectra (all as pulse fourier transform spectra).

(c) A Bruker HX-270 spectrometer was used to obtain 270 MHz ^1H spectra and 67.89 ^{13}C spectra.

(d) A Bruker WP-80 spectrometer was used to measure the spectra of solutions undergoing reaction in sealed tubes (section 3.4.1).

4.2.4 Mass Spectroscopy

(a)   Mass spectra of gaseous complexes were obtained using two   spectrometer·s.

(i) An Hitachi Perkin-Elmer RMU7D double focus mass
    ε spectrometer   was used for samples of a
    reasonable size (10 cm^3 at STP).

(ii) A MS10   spectrometer   with a very small gas
    inlet train was used for small samples (1 cm^3 at STP).

(b)   Mass spectra of non gaseous materials were obtained using an AEI MS30.

4.3.1 Microanalyses

Microanalysis for C, H, N, O and P were carried out by the Australian Analytical Service, Melbourne.

4.3.2 Weights

Quantities greater than approximately 20 mg were weighed on a Mettler five decimal place balance. A Cahn Model 10 electrobalance was used for samples weighing less than 20 mg.

4.4.1 Solubility of N_2 in thf

At times an estimate of the solubility of N_2 in thf was needed, in order to compare concentrations of reactants. It was found that while values for the solubility of N_2 in benzene were reported in the literature, no value could be found for N_2 in thf.

The technique described by Clevere and Battino[5] was used to measure the solubility of N_2 in thf. The apparatus

illustrated in figure 4.4.1 was used, connected via a gas burette to a vacuum line. Bulb A was filled with degassed thf (distilled under argon and then degassed by freeze, pump, thaw cycles), and the left hand side of the apparatus filled with thf saturated nitrogen at 1 atmosphere total pressure. A slight excess of liquid thf was added to ensure that the nitrogen was saturated with thf vapor.

Tap 1 was then opened to allow the degassed thf to flow into bulb B, and tap 2 was opened to allow nitrogen to flow into bulb A. Each bulb contained a magnetic "flea" stirrer, which was used to agitate the thf. The pressure was maintained at 1 atmosphere by manipulating the gas burette mercury reservoir, and the change in gas volume noted. It was found that a volume of 130 cm^3 of thf would dissolve approximately 21 cm^3 of dinitrogen gas at 1 atmosphere total pressure, at 25°C. (pN_2 was less than 1 atmosphere due to the vapor pressure of thf.)

This gives a value of .16 cm^3 N_2 gas/1 cm^3 thf liquid, or, in 1 litre of thf 160 cm^3 of N_2. This gives the value of $[N_2] = 7.1 \times 10^{-3}$ molar in thf at 25°C under an atmosphere of thf vapor and nitrogen with a total pressure of 1 atmosphere.

Stopper

To rough
vacuum

Bulk degassed
thf

To gas
burette

Tap 3. Used to
fill bulb A with
degassed thf.

Tap 2

Bulb B

Bulb A

Tap 1

"Flea"
stirrer

"Flea"
stirrer
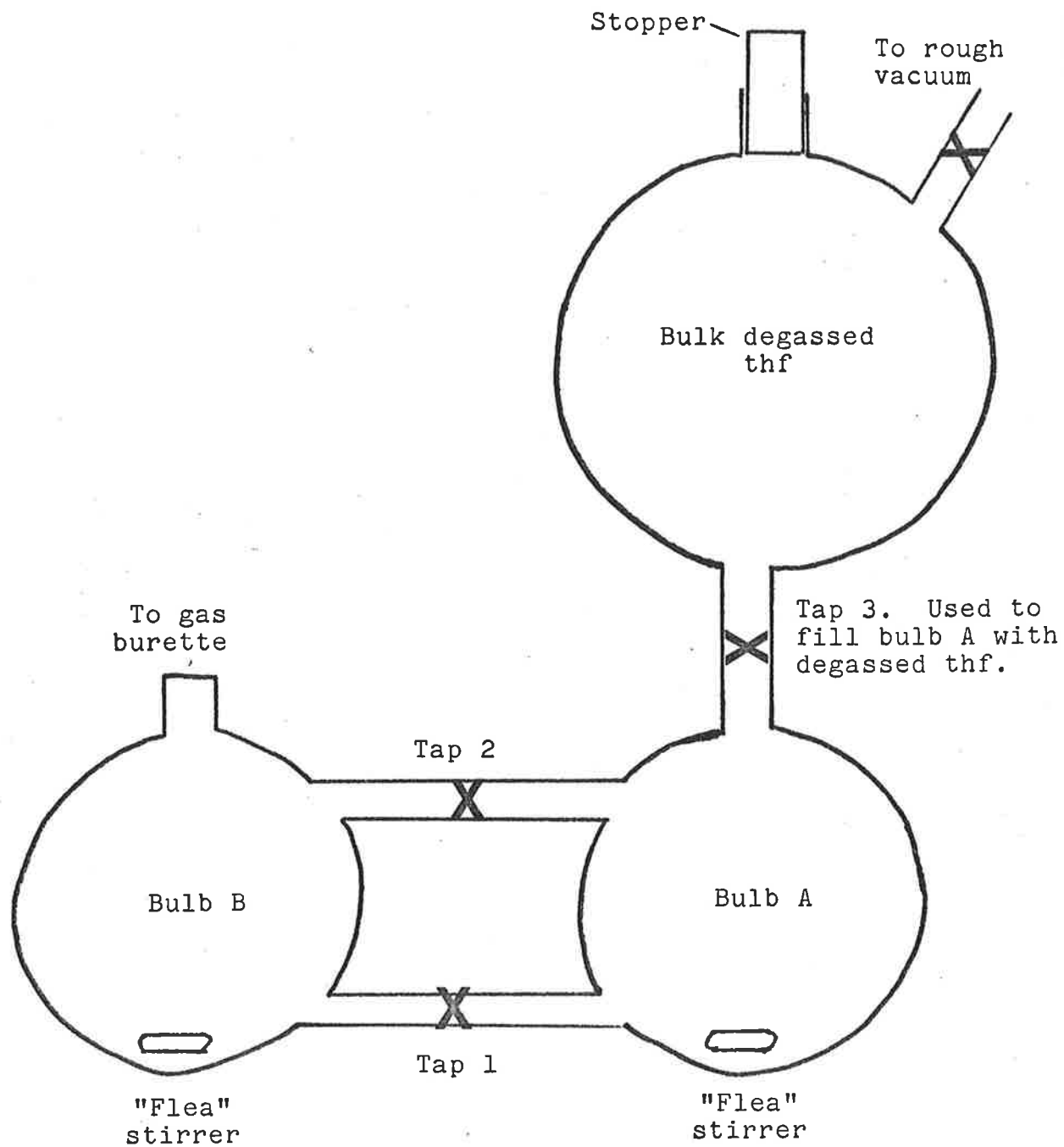
FIGURE 4.4.1   Apparatus used to measure solubility of
N_2 in thf.

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APPENDIX A

Crystal and molecular structure of $W(H_4)(dppe)_2$

Two crystals of the putative $W(H_4)(dppe)_2$ were selected which had sharp extinctions under the crossed polars of a polarised light microscope. These were mounted with the axes of rotation parallel to a^* and b^* respectively, and used for precession photographs.

Cell parameters found were:

$$a^* = .051 \text{ Å}^{-1}$$
$$b^* = .098 \text{ Å}^{-1}$$
$$c^* = .039 \text{ Å}^{-1}$$
$$\alpha^* = \psi^* = 90.0°$$
$$\beta^* = 87.92°$$

The following conditions for reflection were observed:

h0l	h+l=2n	h=2n
h1l	h+l=2n	
0kl	l=2n	
1kl	l=2n+1	
hk0	h=2n	
hkl	h=2n+1	

These conditions can be summarised as:

$$h + l = 2n \text{ for all hkl}$$
$$h = 2n \quad \text{ for h0l,}$$

and are consistent with the monoclinic space group B_a or $B_{2/a}$. (With a suitable change in nomenclature of axes and directions this space group can also be viewed as P_c or P_n. (See figure A.1).

FIGURE A.1   Unit cell of B_a viewed as P_c or P_n also.
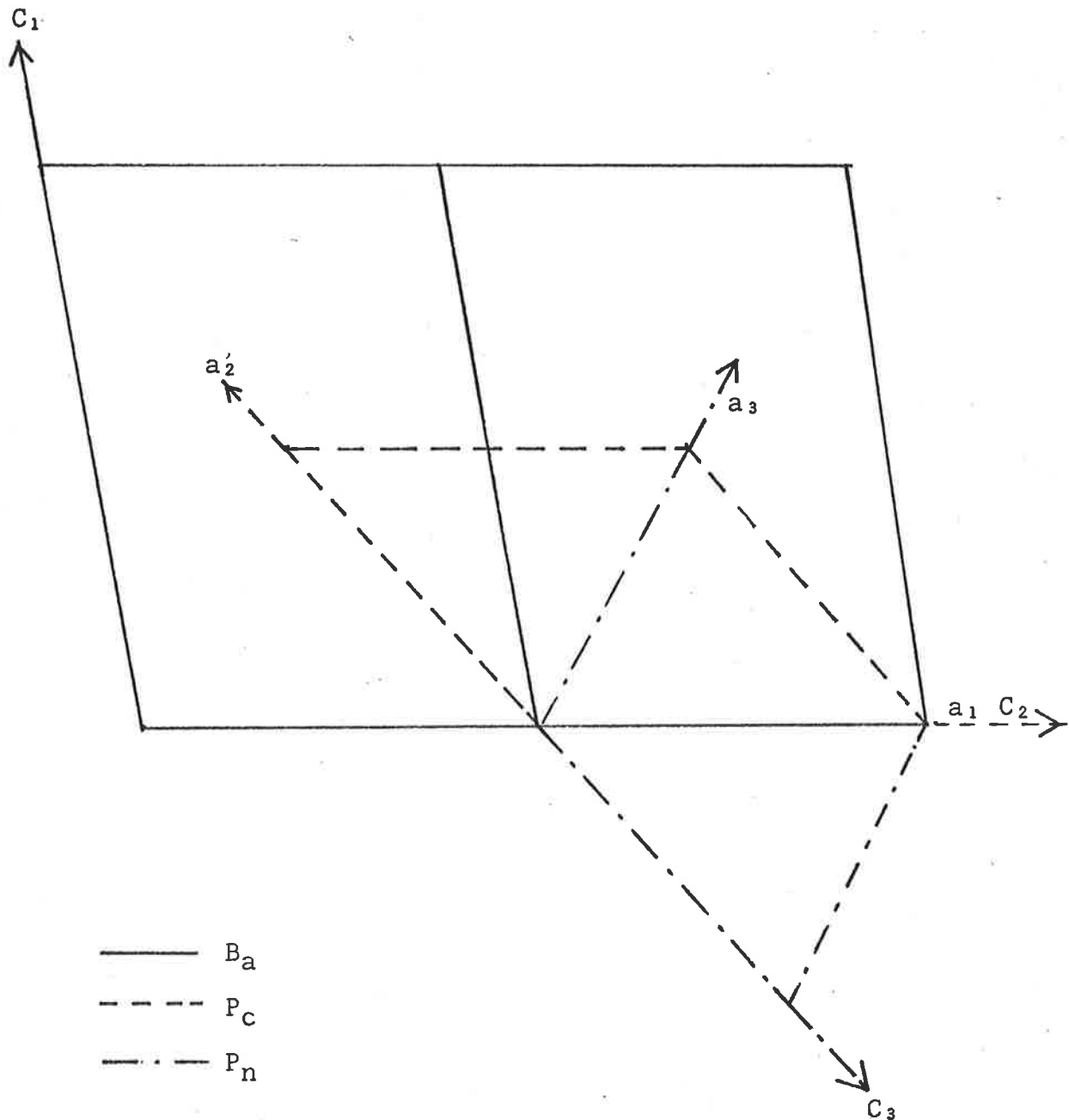
B_a has axes a_1 and c_1 in this plane.

P_c has axes a_2 and c_2 in this plane.

P_n has axes a_3 and c_3 in this plane.

b is perpendicular to the plane and is the same for
   all 3 cells.

The crystal used for precession work which was mounted parallel to b* was transferred to a STOE two circle diffractometer and the lattice parameters refined. This process gave: a = 19.43 Å, b = 10.223 Å, c = 25.456 Å, β = 92.08°, V = 505.6 A³.

Seven levels of data were collected (h0l to h6l) using two crystals, as severe decomposition (ca. 10% per level) occurred during data collection. Levels 0 and 1 were collected using crystal 1 and levels 2 through 6 using crystal 2. Both crystals were mounted parallel to b*. Data from the two crystals was normalised by observing the reflection 002 before and after the recording of each level. Data was collected using the scan/prescan technique, and 2786 reflections were measured. The data (in the form of paper tape) was then read into a CDC 6400 computer for processing. Program AUPTP was used to read the paper tapes and to check for background imbalances due to misalignment or twinning of the crystal. AUPTP also checked the variation in standard reflection intensity during each level. Program AULAC was then used to scale each layer, no absorption corrections were applied and individual reflections were not corrected at this stage to account for crystal decomposition. The scale factors applied are listed below.

h0l	11.905
h1l	13.930
h2l	1.000
h3l	1.062
h4l	1.362
h5l	1.40
h6l	1.49

A Patterson synthesis was created using program FORDAPB and the tungsten atom located from the intense W-W vector of ±0.5x, .2934y, 0.0z.

Since in B_a equivalent positions are x y z, $x+\frac{1}{2}$ $\bar{y}$ z, x $\bar{y}$ $z+\frac{1}{2}$ and $x+\frac{1}{2}$ y $z+\frac{1}{2}$ the y coordinate for W was set to .1467. P-W vectors were located with:

1. Δ^x = .1175 $\qquad \Delta^y$ = 0.0 $\qquad \Delta^z$ = 0.03928
2. Δ_x = -.0574 $\qquad \Delta_y$ = 0.0 $\qquad \Delta_z$ = 0.0834

These two phosphorous atoms and the central tungsten were input to program FOURFLS which refined the coordinates of these atoms. A difference map was then calculated, using FORDAPB. Successive cycles of FOURFLS and FORDAPB enabled one tungsten, four phosphorous and fifty two carbon atoms to be located. However, temperature factors of many of the atoms were not within a reasonable range, and although the basic form of the dppe ligands around the central metal atom was quite apparent, some sections of the phenyl rings could not be found, or else contained anomalous bond lengths or angles. This was probably due in part to the decomposition of the complex during data collection, and in part to disorder within the lattice. This disorder would be expected since the molecule has a spherical shape, with no outstanding differences between different orientations. At the end of this stage of refinement R_w = 0.1048.

Since some of the phenyl rings would not refine it was decided to use program SHELX which allowed the insertion of rigid groups such as phenyl rings and the refinement of such groups as one entity. At the same

time the indexing of the reflections was changed to space group P_C. Positions in the space group B_a were transformed into positions in P_C by using the matrix

$$[x_2 y_2 z_2] = [x_1 y_1 z_1] \begin{bmatrix} 2 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Similarly the reflections were reindexed using:

$$[h_2 k_2 l_2] = [h_1 k_1 l_1] \begin{bmatrix} 0.5 & 0 & 0 \\ 0.0 & 1 & 0 \\ -0.5 & 0 & 1 \end{bmatrix}$$

The output of program AUPTP (indexed as for B_a) was read into a program which converted the indexes using the above matrix operation, and also corrected the intensities for interlayer and intralayer changes in intensity due to decomposition of the crystal, and changing the crystal. For P_C the new cell parameters became a = 16.29, b = 10.223, c = 25.456; β = 143.416.

SHELX was then used to read the output from the reindexing program in order to generate a Patterson synthesis. The strongest peak (other than unit cell translations) was observed at x = 0, y = .271, z = .5. Since P has equivalent positions x,y,z and x,$\bar{y}$,z+$\frac{1}{2}$ the tungsten atom was allocated coordinates x = 0.5, y = .1355, z = .25. A difference map was then generated and the four phosphorus atoms located with the same coordinates as previously determined. A further difference map allowed the bridging carbon atoms of the

dppe to be located, as well as parts of some phenyl rings. These rings were found to have sensibly the same coordinates as previously found using FOURFLS and FORDAPB. Accordingly the coordinates of the complete rings found previously were used, and these rings refined as rigid groups. A molecule of solvent of crystallisation (benzene) was found in the lattice by SHELX.

Further refinement allowed seven phenyl rings to be located, but the temperature factors of the atoms would not refine to a reasonable value, and the r factor could not be refined to any better than $R_W = .136$. Accordingly, it was assumed that the combination of crystal decomposition, and lattice disorder had resulted in poor reflection data quality. The refinement of the structure was left at this stage and no protons were assigned positions.

Notwithstanding the poor R factor, it was possible to determine two things about the structure:

(a) The metal centre was only ligated by phosphorus from dppe and other atoms which were lighter than carbon.

(b) The general shape of the ligating phosphines was similar to that observed by Guggenberger for $Mo(H_4)(CH_3(C_6H_6)_2P)_4$.[1]
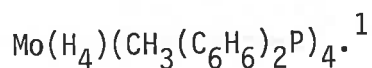
From these two observations it was possible to come to the conclusion that the complex being studied was almost certainly $W(H_4)(dppe)_2$ and not some species generated by photochemical labilisation of the phosphine ligand.

References

1. L.J. Guggenberger, *Inorganic Chemistry*, <u>12</u>(10), 1973, p. 2295-2304.

APPENDIX B

When a molecule containing an element with more than one naturally occurring element (with a non trivial natural abundance) is subjected to mass spectral analysis, the isotopic composition must be taken into account in predicting the m/e values expected.

Thus carbon containing compounds must be treated in this way, since ^{12}C has an abundance of 98.89% and ^{13}C an abundance of 1.11%. In a molecule containing a number of carbon atoms it becomes necessary to use the formula

$$C_m^n = \frac{m!}{(m-n)!n!} * p^n * q^{m-n}$$

to determine C_m^n, the probability of having $n.^{13}C$ atoms amongst m carbon atoms. (Where p is the natural abundance of ^{13}C and q the abundance of ^{12}C.)

Tungsten also has more than one isotope, since all complexes studied had only one metal atom the probabilities are given by the natural abundance. Thus in looking at the mass spectrum of a tungsten complex with approximately 50 carbon atoms the combined effect of tungsten and carbon isotopes had to be taken into account. How this was achieved is illustrated below.

Taking $W(dppe)_2(PBu_2H)H_2$

or W C_{60} H_{69} P_5

W has isotopes[1]

	182	26.41%
	183	14.4%
	184	30.64%
	186	28.41%

C has isotopes   12   98.89%

                      13   1.11%

H has isotopes   1   99.985%

                      2   .015%

For this case (where exceptionally high resolution mass spectroscopy was not used) the contribution of ^2H to the mass spectrum is not significant.

Given 60 carbon atoms, the carbon contribution to the mass spectrum can be shown thus:

60 ^{12}C atoms: $\quad C_{60}^{0} = \dfrac{60!}{(60-0)!0!} * .011^0 * .9889^{60}$

$$= .512 \quad mass = 720.$$

59 ^{12}C atoms, 1 ^{13}C atom:

$$C_{60}^{1} = \dfrac{60!}{59!1!} * .011^1 * .9889^{59}$$

$$= .345 \quad mass = 721.$$

58 ^{12}C atoms, 2 ^{13}C atoms:

$$C_{60}^{2} = \dfrac{60!}{58!2!} * .011^2 * .9889^{58}$$

$$= .114 \quad mass = 722.$$

57 ^{12}C atoms, 3 ^{13}C atoms:

$$C_{60}^{3} = \dfrac{60!}{57!3!} * .011^3 * .9889^{57}$$

$$= .025 \quad mass = 723.$$

When this effect is combined with the isotopes of tungsten, the following table can be drawn up:

^{182}W 26.41%			^{183}W 14.4%			^{184}W 30.64%			^{186}W 28.4%			TOTAL	
Num. ^{12}C	Prob.	O/all Prob.	Num. ^{12}C	Prob.	O/all Prob.	Num. ^{12}C	Prob.	O/all Prob.	Num. ^{12}C	Prob.	O/all Prob.	Mass	Prob.
60	.512	13.5										1126	13.5
59	.345	9.1	60	.512	7.4							1127	16.5
58	.114	3.	59	.345	5.	60	.512	15.7				1128	23.7
57	.025	.7	58	.114	1.6	59	.345	10.6				1129	12.9
			57	.025	.4	58	.114	3.5	60	.512	14.5	1130	18.4
						57	.025	.8	59	.345	9.8	1131	10.6
									58	.114	3.2	1132	3.2
									57	.025	.7	1133	.7

The "total mass" column takes all contributing atoms into account, the probability column reflects the effect of both $^{12}C/^{13}C$ and $^{182}W/^{183}W/^{184}W/^{186}W$.

This isotopic splitting pattern causes a characteristic "fingerprint" of 1 tungsten/50-60 carbon atom molecules.

References

1. Chemical Rubber Company Handbook of Chemistry and Physics, 54th Edition, 1973-1974. Edited by R.C. Weast, p. B250-B251 and p. B441-B444.

APPENDIX C

In the discussion it was commented that the very low value for the quantum yield determined by Archer[1] for the reaction

$$Mo(^{14}N_2)_2(dppe)_2 + {}^{15}N_2 \longrightarrow Mo(^{15}N_2)(^{14}N_2)(dppe)_2 + {}^{14}N_2$$
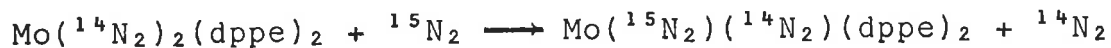
was discussed as an experimental artifact. The following description and analyses of some of the experiments which Archer carried out explain why this is believed to be so.

Archer took a 20.0 cm^3 aliquot of 5×10^{-3} M $Mo(N_2)_2(dppe)_2$ (1×10^{-4} moles) in toluene or thf and exposed it to a volume of $^{15}N_2$ containing 1×10^{-3} moles of gas, that is, a 5 fold excess of $^{15}N_2$. (This ratio arose because each $Mo(N_2)_2$ moiety had two $^{15}N_2$ groups.) The aliquot was then either (a) irradiated at some wavelength or (b) left in the dark.

At the end of some time interval (apparently usually 3600 seconds) the atmosphere was removed and the ratio $^{15}N_2/^{14}N_2$ determined, and quantum yields calculated.

Ashwood[2], Chatt[3] and Carter[4] have studied the thermal reaction of $Mo(N_2)_2(dppe)_2$ and have each obtained rate constants of comparable magnitude to the rate measured by the other. If one uses $k = 1.45 \times 10^{-4}$ sec^{-1} for the reaction

$$Mo(N_2)_2(dppe)_2 + X \longrightarrow Mo(N_2)X(dppe)_2 \quad [1]$$
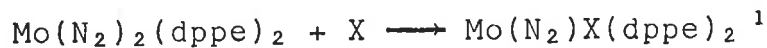
then in 3600 seconds, in a solution which was initially 5×10^{-3} M in $Mo(N_2)_2(dppe)_2$ one would expect *ca.* 2×10^{-4} M to have reacted. In doing so, 4×10^{-5} moles of $^{14}N_2$ should be produced. This gives a $^{15}N_2/^{14}N_2$ ratio of 40:1.

If one assumes that the $Mo(N_2)_2(dppe)_2$ which reacts can react with either $^{15}N_2$ or $^{14}N_2$, at a rate proportional to this *final* concentration[*] of $^{15}N_2$ or $^{14}N_2$, then *ca*. 90% should exchange with $^{15}N_2$ and 10% with $^{14}N_2$. This means that the solution should be 1.8×10^{-3} M in $Mo(^{15}N_2)(^{14}N_2)(dppe)_2$ if one assumes single dinitrogen ligand exchange. In turn, this will give rise to $1.8 \times 10^{-3} \times \frac{1}{50}$ moles $= 3.6 \times 10^{-5}$ moles of $^{14}N_2$ gas and there will be 9.64×10^{-4} moles of $^{15}N_2$. The final ratio $^{15}N_2gas/^{14}N_2gas \doteqdot 27$.

Archer found that in the dark the final isotopic ratio $^{15}N_2gas/^{14}N_2gas = 132$ in the dark. Now since all assumptions made have decreased the probability of isotope exchange in the dark the ratio of $^{15}N_2gas/^{14}N_2gas$ should be lower than calculated above, *unless* diffusion of gas across the gas/liquid interface was a limiting factor. Similarly, values of quantum yields of $^{15}N_2$ plus $Mo(N_2)_2(dppe)_2$ are considerably lower than quantum yields found by Ashwood[1] for a reaction involving an initial dissociative step,

$$Mo(N_2)_2(dppe)_2(solv) \xrightarrow{hv} Mo(N_2)(dppe)_2(solv) + N_2(solv).$$
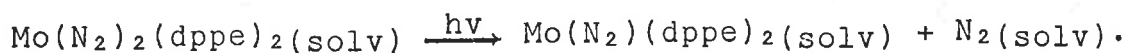
These low values found by Archer can only be explained by limitation of isotope exchanges by slow diffusion across the gas/liquid and liquid/gas interface.

Archer carried out experiments aimed at proving that diffusion of gas across the interfaces was not a rate controlling factor, these experiments are described on

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[*] This assumption results in *less* exchange than calculating possible ratios all the way through.

p. 51 of the thesis. In doing so, he states

"Since the rate of any photochemical reaction is equal
to the quantum yield multiplied by the concentration
of the reactant, this implies that the rate is one
half when the concentration is one half. Diffusion
limitations were not believed to be a problem."

The first statement in this quotation is not quite
correct, the rate of photochemical reaction $A \xrightarrow{h\nu} B$
is given by $\frac{-dA}{dt} = \phi I_{abs}$, where ϕ is quantum yield (which
is not a concentration dependent factor) and I_{abs} is the
intensity of the light absorbed.[5] I_{abs} can be altered by
the concentration, but not in a linear fashion;
$I_{abs} = I_0(1-10^{-l\epsilon c})$ when there is one absorbing substance
present. (ϵ = extinction coefficient, l the pathlength,
c the concentration of substance and I_0 the incident light
intensity.) In the situation where

$$Mo(N_2)_2(dppe)_2 + {}^{15}N_2 \longrightarrow Mo({}^{15}N_2)(N_2)(dppe)_2$$

the reaction appears to be first order when followed by
disappearance of $Mo(N_2)_2(dppe)_2$ as the light absorbed by
unlabelled complex diminishes as does the quantity present.
The initial rate is however, still given by $\frac{-dA}{dt} = I_{abs}\phi$.

Accordingly one can not accept that the experiment
supposed to prove that diffusion control was not a
limitation actually did so. From work carried out in this
project it would appear that rapid equilibration of
isotope ratios across a gas/liquid interface is difficult
to achieve, and in any labelling experiment different
rates may be measured by, for example, simply altering the

rate of stirring of the solution, or agitating the solution in some other way.

References

1. L.J. Archer, Ph.D. Thesis, University of Nebraska, Lincoln, Nebraska.

2. L.J. Archer and T.A. George, *Inorganica Chimica Acta*, 1980, <u>44</u>, L129-L132.

APPENDIX D

Flash Photolysis of a Tungsten-Dinitrogen Complex.

Flash Photolysis of a Tungsten–Dinitrogen Complex. An Intermediate in the Formation of Carbon–Nitrogen Bonds

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Reactions of coordinated dinitrogen to form nitrogen–carbon bonds have been observed for a number of complexes of the type $[M(N_2)_2(dppe)_2]$ (M = W, Mo, Re; dppe = 1,2-bis(diphenylphosphino)-ethane) [1]. The reactions take place with acyl halides (M = Re, Mo, W) or alkyl halides (M = Mo, W) and the reactions with the alkyl halides are catalyzed by visible light. The products are complexes of the type $[MX(N_2R)(dppe)_2]$ and $[MX(N_2HR)(dppe)_2]X$. The reactions have been assumed to involve a free radical mechanism [2] in which alkyl radicals are generated from the alkyl halide or from the solvent (a butanol chain is incorporated in the product when the solvent is tetrahydrofuran, thf) [3]. No dinitrogen is evolved in the absence of alkyl halides.

Photochemical reactions of this type may have considerable potential in the photochemical fixation of nitrogen and the present flash photolysis studies have been undertaken in order to define the mechanism of carbon–nitrogen bond formation more precisely. The reactions proceed through a photochemically generated intermediate from which both coordinated dinitrogen molecules have been lost.

Experimental

The $[W(N_2)_2(dppe)_2]$ complex was prepared by the method of Chatt, Heath and Richards [4] and characterised by an $\epsilon = 2.7 \times 10^4 \ M^{-1} \ cm^{-1}$ at 297 nm in thf. All operations with the complex and solutions were carried out in dry atmospheres and where necessary in completely sealed systems. Solvents were dried and distilled under N_2. Flash photolysis experiments were carried out using the standard techniques of this laboratory [5, 6] with the addition of an irradiation cell which allowed the solutions to be changed under controlled atmospheres.

Photolysis experiments with steady illumination were carried out with a tungsten (200 W) or a tungsten halogen lamp (100 W) as the light source, using interference filters to select the irradiation wavelength. In flash photolysis experiments identical results were obtained with or without a Perspex filter which eliminates wavelengths shorter than 300 nm. The concentration of the complex was determined by the intensity of the N–N infra-red stretch or by the absorbance at 297 nm in lower concentration solutions.

Results

Steady illumination of *ca.* $10^{-2} \ M$ solutions of the $[W(N_2)_2(dppe)_2]$ complex in dry thf saturated with nitrogen resulted in very little change (Table I). When the irradiation took place with the solution evacuated, or under argon, coordinated dinitrogen was lost rapidly. Irradiation of similar solutions saturated with CO or H_2 resulted in the production of the carbonyl, $[W(CO)_2(dppe)_2]$ and hydride, $[WH_4(dppe)_2]$ complexes respectively. In the presence of CH_3COCl or t-butyl bromide the organic group was incorporated at comparable rates. Previously [1] the reaction with CH_3COCl has been reported to require several hours at ambient conditions. The quantum yields for the reactions in Table I are somewhat uncertain but all lie between 0.3 and 0.7.

When the atmosphere above the thf solution of the complex was saturated with ^{15}N labelled dinitrogen $(^{15}N_2 \ 48\%; \ ^{14}N_2 \ 46\%; \ ^{14}N^{15}N \ 6\%)$ irradiation resulted in the incorporation of the $^{15}N_2$ in the complex. The $^{15}N_2$ labelling experiments gave products with solution infra-red spectra which showed dinitrogen stretch peaks at 1948, 1904, and 1885 cm^{-1}, which can be assigned to the isotopomers $W(dppe)_2(^{14}N_2)_2$, $W(dppe)_2(^{14}N_2)(^{15}N_2)$ and $W(dppe)_2(^{15}N_2)_2$ [7]. On prolonged irradiation the ratio of the three peaks was 2.0:1:1. No incorporation of the $^{15}N_2$ occurred in the dark, and the $^{15}N_2$ complex did not lose the label when kept under an atmosphere of $^{14}N_2$ in the dark. It is apparent that the dinitrogen exchange occurs by the same type of dynamic light-induced process which is responsible for the photo-reactions with CO and H_2.

Flash photolysis experiments showed that an intermediate is formed following photo-excitation of $[W(N_2)_2(dppe)_2]$. When solutions of the complex $(4 \times 10^{-5} \ M)$ in thf or benzene were flashed under dinitrogen or argon an immediate bleaching was observed. Solutions saturated with argon showed no further change. When the solutions contained dinitrogen, the bleached absorbance recovered to within 5% of the original value by a two-stage process. The change in transmittance with time at 297 nm is shown in Figure 1. The two stages of the recovery of the absorbance in N_2 saturated solutions were well separated in time (Figure 1) and the difference spectra at the end of the first recovery process, and

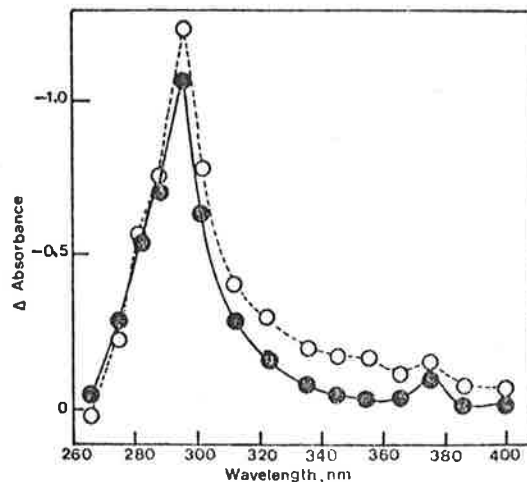TABLE I. Steady Illumination Photolysis Experiments, Visible Light.

Conditions	$[W(N_2)_2(dppe)_2]$, M[a]	Results
N_2 saturated	5×10^{-3}	*ca.* 5% decomposition, 6 hr
Ar saturated	2.5×10^{-3}	50% decomposition in 2 hr
Vacuum	2.5×10^{-3}	50% decomposition in 2 hr
CO saturated	2.5×10^{-3}	50% conversion to $[W(CO)_2(dppe)_2]$ in 45 min
H_2 saturated	1.6×10^{-3}	50% conversion to $[W(H_2)(dppe)_2]$ in 35 min
t-BuBr 0.05 M	2.9×10^{-3}	50% formation of $[WBr(N_2 t\text{-}Bu)(dppe)_2$ in 50 min
CH_3COCl 0.05 M[b]	2.5×10^{-3}	50% formation of $[WCl(NNCOCH_3)(dppe)_2]$ in 45 min
$^{15}N_2$ saturated	5×10^{-3}[c]	50% labelled $[W(N_2)_2(dppe)_2$ in 2 hr

[a]Reaction volume 150 ml thf.   [b]Negligible reaction in dark over comparable time period.   [c]Reaction volume 5 ml.
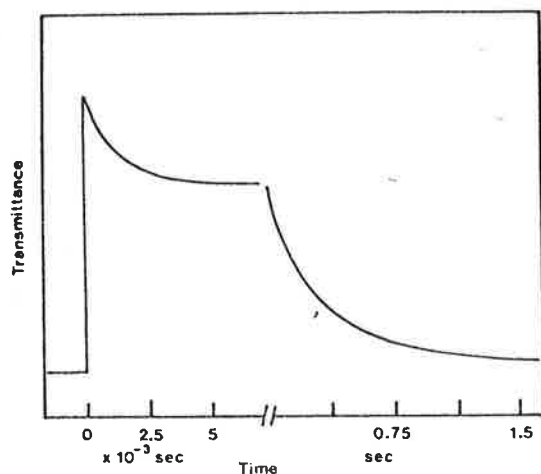
Figure 1. Changes in transmittance at 297 nm following flash photolysis of $[W(N_2)_2(dppe)_2]$, 4×10^{-5} M in thf saturated with N_2. Note change of scale on x-axis.

Figure 2. Difference spectra taken after flash photolysis of $[W(N_2)_2(dppe)_2]$ in thf saturated with N_2. O, immediately following the flash; X, 11.25 msec after the flash at the end of the first stage of the reactions shown in Fig. 1.

immediately after flashing are shown in Figure 2. By the conclusion of the second reaction almost all of the absorbance lost in the bleaching reaction was restored. The rate constants for the two processes of Figure 1 were first order, with rate constants of 3.9 $\pm$ 0.8 $\times 10^2$ sec^{-1} and 1.6 $\pm$ 0.3 sec^{-1} in thf saturated with N_2 at 25 °C. The quantum yield for the bleaching was the same for the solutions saturated with argon or dinitrogen, and the difference spectra taken immediately after the flash were the same.

When solutions saturated with CO were flashed, a bleaching, followed by a two stage recovery process was again observed, but the absorbance did not return to the original value, and at the completion of the reaction the product was the carbonyl complex $[W(CO)_2(dppe)_2]$. The rate constants for the formation of the carbonyl complex were very similar to those for the reaction of the bleached intermediate with dinitrogen and were 5.1 $\pm$ 0.4 $\times$ 10^2 sec^{-1} and 2.5 $\pm$ 0.4 sec^{-1}.

When N_2 saturated solutions of $[W(N_2)_2(dppe)_2]$ containing 2-bromobutane (0.04 M), which were prepared and handled in the dark, were flashed, the same

initial bleaching of the absorbance due to the dinitrogen complex was observed. The bleaching was followed by three identifiable reaction steps. An initial return towards the original absorbance was followed by a second, slower return which was competing with a third reaction which led to a permanent decrease in absorbance at 297 nm, where the final reaction product, $[WBr(N_2Bu)(dppe)_2]$ has a smaller absorbance than $[W(N_2)_2(dppe)_2]$. The initial reaction had the same rate constant as that for an N_2 saturated solution alone, 4.6 $\pm$ 0.8 $\times$ 10^2 sec^{-1}, and the second step was also similar to that in the absence of 2-bromobutane, with a rate constant of 3.9 $\pm$ 0.6 sec^{-1}. The third reaction which leads to a permanent change to form the product had a rate constant of 0.5 $\pm$ 0.1 sec^{-1}.

Similar results were obtained for solutions in benzene containing dinitrogen.
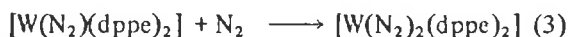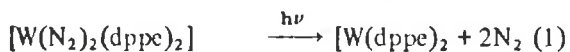
Flash photolysis of solutions of $[W(N_2)_2(dppe)_2]$ in thf saturated with $^{15}N_2$ ($^{15}N_2$ 81%; $^{14}N^{15}N$ 10%; $^{14}N_2$ 9%) showed that dinitrogen exchange occurred after a single flash. The infra-red spectrum of the

solutions after one flash showed the nitrogen stretch absorbances at 1945, 1905, and 1885 cm^{-1}. It is significant that, although only a fraction of the coordinated dinitrogen is exchanged, both isotopomers $W(dppe)_2(^{15}N_2)_2$ and $W(dppe)_2(^{14}N_2)(^{15}N_2)$ are present in the solution.

Discussion

The steady illumination experiments show that light labilizes the dinitrogen in the complex, decomposition occurring when the photolyses were carried out under argon or vacuum. The labilized complex from which dinitrogen has been lost is able to take up CO, H_2. The dinitrogen-labelling experiments prove that the intermediate (or the photo-excited state) has been labilized for dinitrogen exchange. The role which has been assigned previously to the alkyl halide in assisting in the evolution of N_2 [1] is therefore clearly, at least in part, that of competing with the N_2 for the labilized metal centre.

The flash photolysis experiments provide clear evidence for the nature of the initial photochemical process. The loss of absorbance due to $[W(N_2)_2(dppe)_2]$ is coincidental with the flash and is not due to the formation of an excited state but to the loss of dinitrogen from the complex [8]. As the recovery of the original absorption under nitrogen is a two stage reaction we conclude that both the dinitrogen molecules must be lost in the first stages of the photo-reaction, although whether simultaneously or consecutively cannot be decided without experiments using laser excitation at shorter time resolution. In the presence of dinitrogen the reactions are

$$[W(N_2)_2(dppe)_2] \xrightarrow{h\nu} [W(dppe)_2 + 2N_2] \quad (1)$$

$$[W(dppe)_2] + N_2 \longrightarrow [W(N_2)(dppe)_2] \quad (2)$$

$$[W(N_2)(dppe)_2] + N_2 \longrightarrow [W(N_2)_2(dppe)_2] \quad (3)$$

The role of the solvent (thf or benzene) has not so far been defined. The rates of the first and second reactions are almost the same for N_2 and CO, suggesting that the reactions are governed by the rates of solvent exchange at the sites originally occupied by the two dinitrogen molecules. The $^{15}N_2$ exchange experiments in which exchange is induced by flash photolysis confirm that both dinitrogen molecules are lost from the complex upon photo-excitation.

The reactions in the presence of N_2 and 2-bromobutane indicate that it is the complex with only *one* coordinated N_2 which reacts with 2-bromobutane (and by implication, with other alkyl halides)

$$[W(N_2)(dppe)_2] + RX \rightarrow [WX(N_2R)(dppe)_2]$$
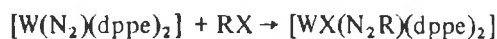
The competition between 2-bromobutane and N_2 shown in the flash experiments provides direct evidence for the proposed mechanism of formation of C–N bonds in these systems [2] in which homolytic fission of the R–X bond takes place at the metal centre [2] which has only one N_2 coordinated. The C–N bond may be formed either between the alkyl radical derived from the alkyl halide or one derived from the solvent by alkyl radical attack, and the one remaining coordinated dinitrogen. This first direct observation of a transient intermediate in the photochemical reactions of dinitrogen complexes indicates that it is the metal centre with only one coordinated N_2, and possibly of reduced coordination number, produced by photo-excitation and subsequent recombination with one N_2 molecule which is highly reactive towards carbon–halogen bonds. Systems of this kind have an obvious potential for the photochemical fixation of nitrogen using sunlight, and we are at present extending the work to other systems.

Acknowledgements

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7 Assignments based on relative intensities of N–N absorptions of isotopomers under limiting conditions. Detailed arguments to be published elsewhere.
8 We have been unable to observe any long-lived emission which would indicate the presence of an excited state of the complex, and an excited state with a lifetime long enough to take part in the reactions with the rate constants we have measured (*ca.* 0.1 s or longer) is most unlikely in a stystem like $[W(N_2)_2(dppe)_2]$ which contains such a heavy atom as W.