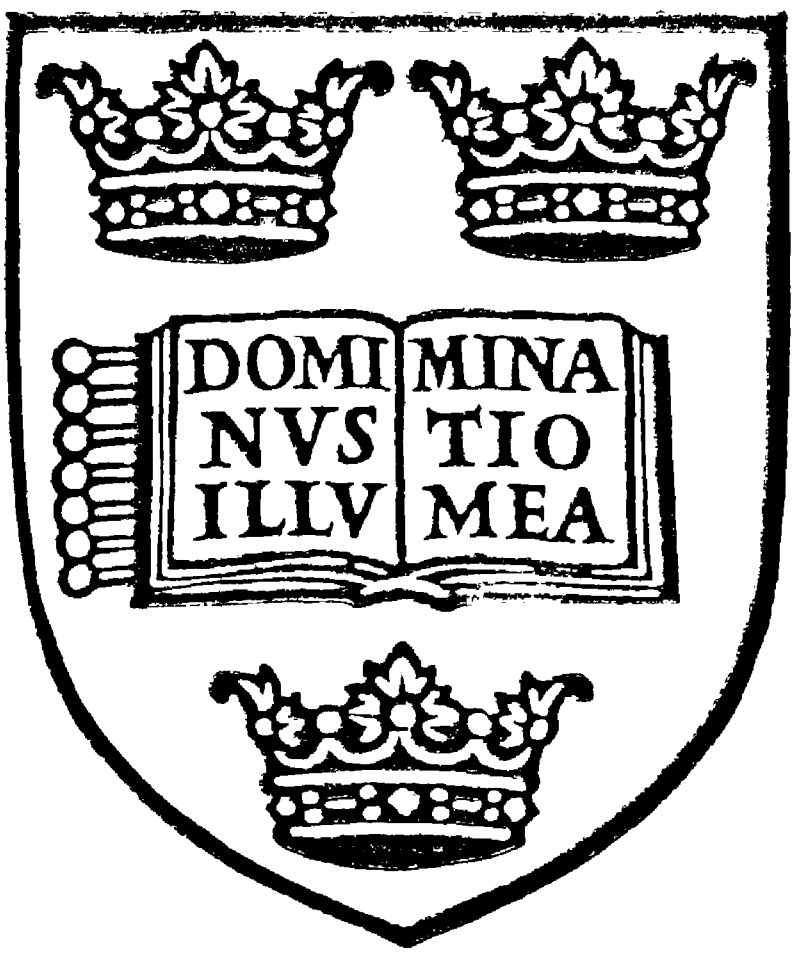

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THE OXIDATION OF OLEFINS PROMOTED BY TRANSITION METAL COMPLEXES

by

Robert Alun John B.Sc.

Wolfson College, Oxford

1981

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ASLIB ABSTRACT

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The Oxidation of Olefins promoted by Transition Metal Complexes

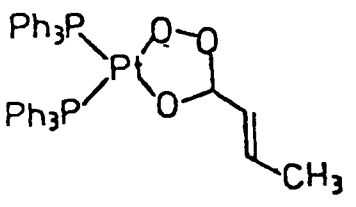
The oxidation of olefins by transition metal complexes leading to epoxide or ketonic products has been reviewed, with an emphasis on non-free radical processes.

The formation of cycloadducts by reaction of bis(triphenylphosphine)-platinum(0)dioxygen with the α,β-unsaturated carbonyl compounds trans but-2-enal, propenal, cyclohex-2-en-1-one, exo 2-methylenecyclohexan-1-one and 3-phenyl-prop-2-enal was investigated by ^{1}H- and ^{31}P- nuclear magnetic resonance (n.m.r.). The cycloadducts derived from trans but-2-enal and propenal were thermally unstable in solution and further reacted to form stable, isolable complexes. The mechanism by which the cycloadduct cis[4-trans(prop-2-enyl)-1,1-bis(triphenyl-phosphine)platina-2,3,5-trioxacyclopentane], I, was transformed into cis[trans-(5-formyl-4-methyl)-1,1-bis(triphenylphosphine)platina-2,3-dioxacyclopentane], II, was investigated by ^{1}H- and ^{2}H-n.m.r. utilising trans 4-[$^{2}H_{3}$]but-2-enal. A mechanism which involved both exchange of free trans but-2-enal with I and reaction to give II was proposed; a computer model, based upon numerical integration of the alternative rate equations was in good agreement with this proposition.

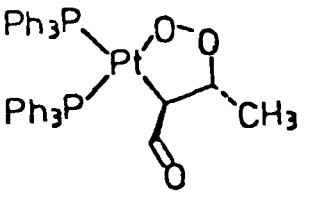
The chemical reactivity of II with a variety of reagents was explored. In particular, the reaction of II with trifluoroacetic acid gave trans 2-formyl-3-methyloxirane in high yield and stereoselectivity.

The dynamic behaviour of cis[bis(triphenylphosphine)(2',3'-η)(trans-but-2-enal)platinum(0)] was observed by variable temperature ^{31}P-n.m.r. and explained by the interconversion of carbonyl rotamers.

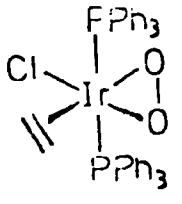
The preparation of iridium(I) olefin and peroxo complexes has been described Chlorobis(triphenylphosphine)(1,2-η)(ethene)dioxygen iridium(I), III, and related complexes were found to oxidise terminal olefins to their methyl ketones stoichiometrically, by a non-free radical process. The mechanism has been discussed.



I



II



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To Mum, Dad
and Eeva.

INTRODUCTION

The discovery in 1774 of oxygen by Priestley and subsequent explanation of combustion by Lavoisier heralded a new era in chemistry. Since the turn of this century a formalism has been given to the basic concepts of free-radical processes in autoxidation. The last twenty-five years has seen a surge of interest in homogeneous catalysis by transition metals bearing small activated molecules, including dioxygen.

The activation of molecular dioxygen to selective and catalytic transfer of oxygen to reactive substances finds dual application in the petroleum industry and in synthetic chemistry.

Several comprehensive and detailed reviews of the oxidation of organic compounds by transition metal complexes have appeared recently[1], and I have drawn upon these extensively. This Introduction will describe the oxidation of olefinic substrates catalysed by transition metal complexes with an emphasis on non free-radical pathways. The source of delivered oxygen will, in most cases, be derived from dioxygen or hydroperoxide.

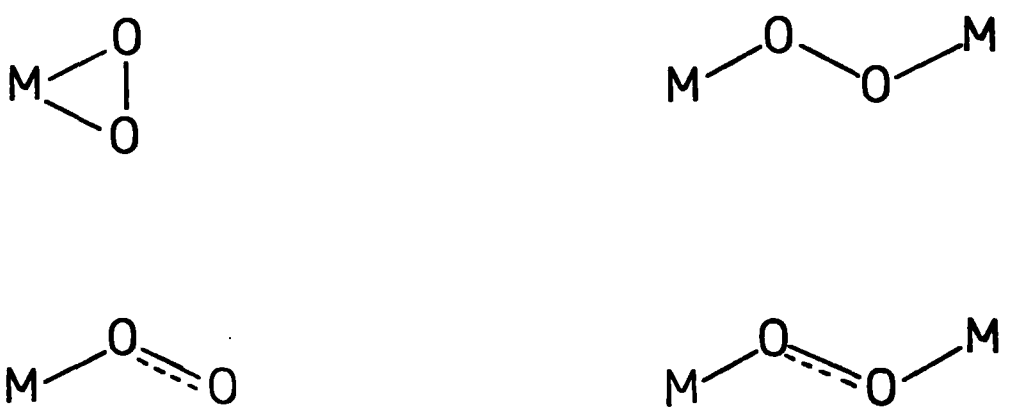
Before attempting such a review it is pertinent first to describe some of the physicochemical aspects of metal complexes containing coordinated dioxygen with special reference to the experimental work described herein.

1. PHYSICOCHEMICAL ASPECTS OF TRANSITION METAL DIOXYGEN COMPLEXES

The binding of dioxygen to transition metals has been reviewed recently[2], making attempts to rationalise and verify the body of diverse and sometimes incorrect information that had developed since the discovery of dioxygen - containing 'natural' and synthetic metal complexes. More recent molecular orbital calculations[3] generally reinforce the simple bonding description presented here.

All known dioxygen metal complexes may be divided conveniently into two broad groups according to the characteristics of the dioxygen ligand; superoxo (by loose analogy to superoxide ion, $O_2^{-\cdot}$) and peroxo (similarly to peroxide, O_2^{2-}). Furthermore, the oxygen may be coordinated to one or more metal centres (Fig. 1).

Figure 1



Bonding. Peroxometal complexes, often referred to as η-1 or 'side bonded', are usually diamagnetic. Many iridium, rhodium and platinum complexes have been shown by X-ray crystallographic analysis to have this structure. Ground state dioxygen is paramagnetic with the two unpaired electrons occupying degenerate $1\pi g^*$ orbitals. Two π-bonds are formed by filling of the partially occupied orbitals by the filled d-orbitals of the metal. A σ-bond is formed by donation of electrons from the filled $^1\pi_u$ orbital of dioxygen with an unfilled d-orbital of the metal (Fig. 2).

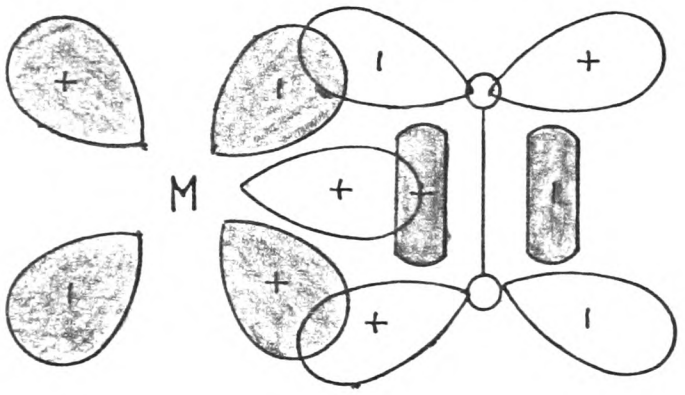
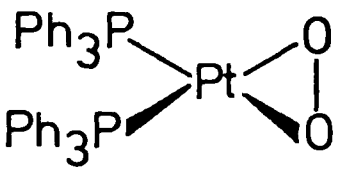


Figure 2

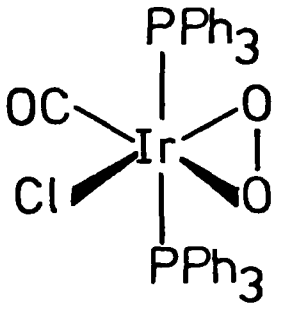
Back-donation into antibonding orbitals accounts for a decrease in O-O bond dissociation energy and vibrational frequency and an increase in the interatomic distance. C.N.D.O. - M.O. studies[3] have estimated the values of $1\sigma_g - \pi_u$ donation and $d\pi - \pi_g^*$ back donation and confirmed the equality of the metal oxygen bond lengths. Further, they have predicted the relative orientation of dioxygen and other ligands. The $d\pi - \pi_g$ interaction makes the Ir-O bond

most stable in 5-coordinate Ir(I) complexes and the Pt-P bond in 4-coordinate Pt(0) complexes. Thus, in the former the metal dioxygen plane is perpendicular to the metal phosphine plane and in the latter it is in the same plane as the Pt-P bonds (Fig. 3).

Figure 3



(1)



(2)

Numerous X-ray crystal structure determinations[2] show that most peroxo complexes have O-O bond lengths of between 1.40 and 1.49 Å.

Superoxo complexes are paramagnetic in which the bonding has been described[4] as containing a σ-bond formed between one of the oxygen lone pairs and the d_{z^2} orbital of the metal. Some back donation from one of the occupied dπ orbitals to the partially filled $1\pi_g^*$ orbital of dioxygen may increase O-O bond length. The unpaired electron resides in the $3d\pi - 1\pi_g^*$ molecular orbital, although E.S.R. studies show the formalism $\overset{+}{M}(III) - O_2^-$ is

preferred to M(II) - O_2 in CO complexes[5] (Fig. 4).

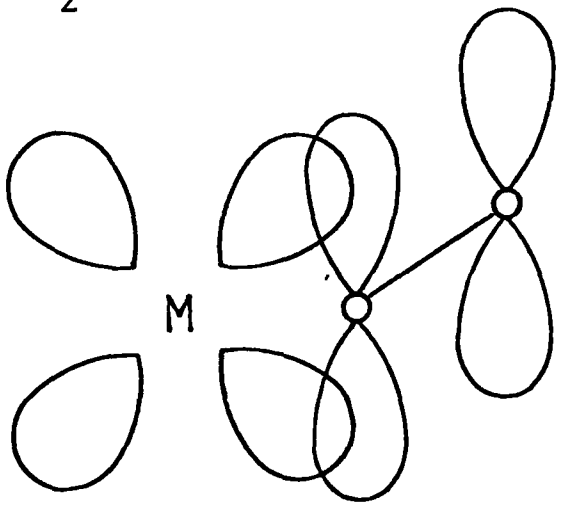
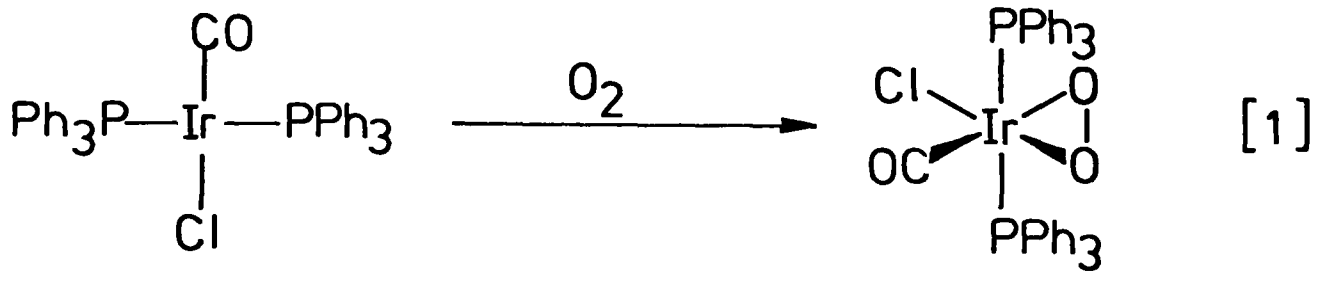


Figure 4

Preparation. Vaska[6] was the first to report the preparation of a peroxo complex, by reaction of the 4-coordinate phosphine complex [1] with molecular dioxygen in solution.

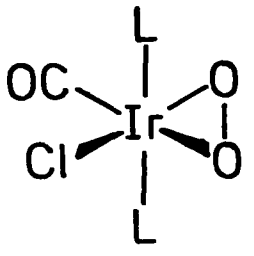


[1]

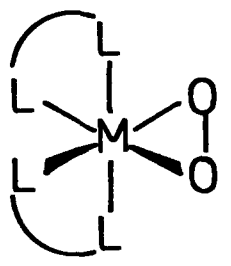
This method of preparation is generally applicable to 16-electron complexes of iridium. X-ray crystal data for this and analogous complexes (Table 1)[2] indicate little variation

in O-O bond length in changing ancillary ligands.

Table 1

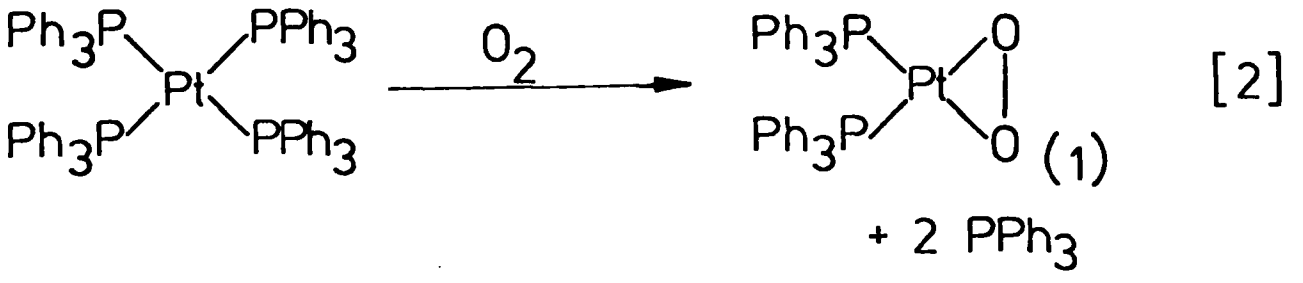


L	X	Bond length/Å
PPh_3	Cl	1·30
PPh_3	Br	1·36
PPh_2Et	Cl	1·47



M	L	Bond length/Å
Rh	Ph_2P PPh_2	1·42
Ir	Ph_2P PPh_2	1·52
Co	Ph_2P PPh_2	1·42

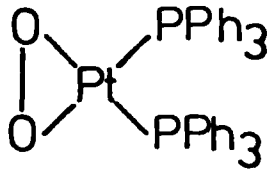
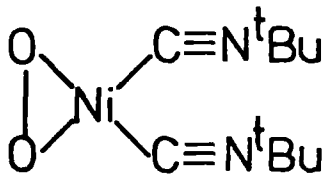
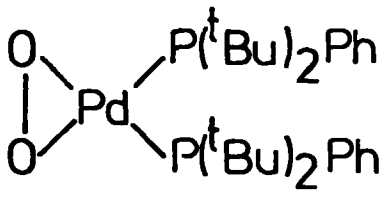
Wilkinson[7] first characterised a dioxygen complex of platinum [2].



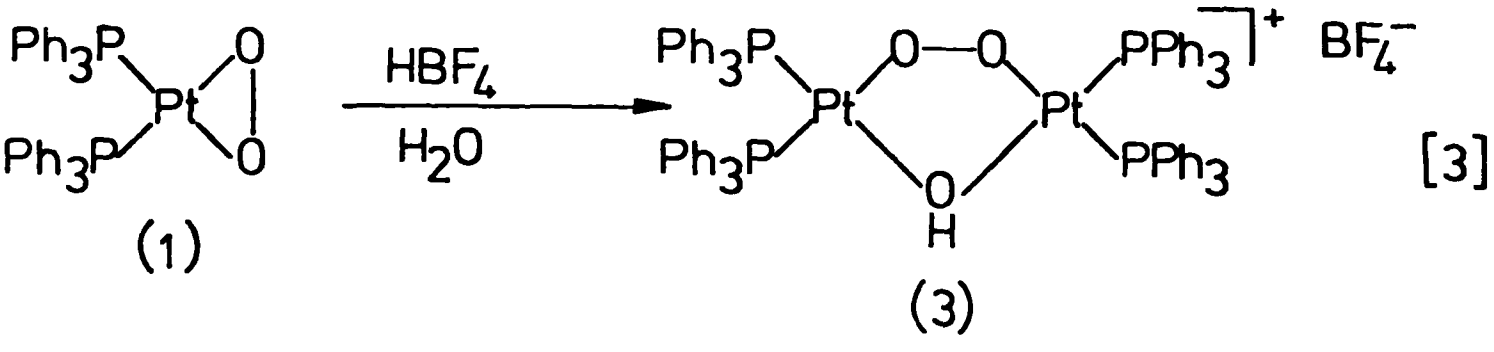
[2]

Group VIII d^{10}-metal complexes (Ni(0), Pd(0), Pt(0)) generally react with dioxygen, with ligand displacement, to give the peroxo complex. An X-ray crystal structure of the complex in Reaction (2) confirms its square planar configuration[8]. Table 2[9] shows the negligible variation in O-O bond length for some representative d^{10}-metal complexes.

Table 2

	Bond length/Å
	1·45
	1·45
	1·37

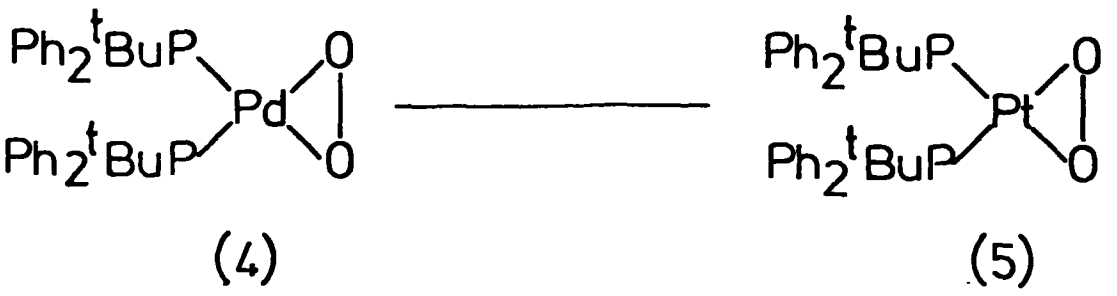
Ugo[10] has prepared a bridging peroxo platinum dimer by reaction of Wilkinson's dioxygen complex with aqueous fluoroboric acid [3].



(1) (3) [3]

Infra-red Spectra. Both peroxo and superoxo complexes give rise to highly characteristic absorptions in their infra-red spectra. The oxygen stretching frequency, ν_{O_2}, in peroxo complexes can be assigned in the range 800 - 900 cm^{-1}, but since the band is not derived from a "pure" O-O stretching vibration, the mass of the metal and auxillary ligands must play some role in determining the observed frequency. The superoxo ligand displays ν_{O-O} near 1100 cm^{-1} in metal complexes bearing one metal-dioxygen bond.

Reversibility of Addition. Few peroxo complexes are known to be able to bind dioxygen in a reversible manner. Some exceptions are displayed in Fig. 5.



(4) (5)

Figure 5

Early attempts[13] to rationalise why some compounds were reversible while analogous ones were thermally stable were founded on poor or insufficient data. Otsuka[9] has attempted to explain why is a reversible oxygen carrier while its platinum analogue

is not, on the basis of stereoelectronic effects in terms of the inter-ligand angle. He suggests that the small difference between the inter-ligand angle, PPdP (115.4°) and PPtP (113.1°), arising from a geometrical difference, accounts for the difference in behaviour.

Biological Complexes. Many naturally occurring biological molecules are known to bind dioxygen[2].

The reversible dioxygen carriers myoglobin and haemoglobin are responsible for oxygen storage and transport respectively. Many classes of oxygenase, like the monooxygenase cytochrome P-450, transfer oxygen to organic substrates under enzymic control.

Haemoglobin and myoglobin contain 5-coordinate high spin iron(III) bound to a porphyrinato group and a single axial imidazole provided by the proximal histidine group from a polypeptide globin. The presence of a single coordination site and favourable one-electron oxidation potential suggest dioxygen bound in a superoxo manner. Crystalline iron superoxo derivatives of simple synthetic analogues of oxymyoglobin have been prepared and characterised by X-ray crystallography [14]. This has revealed, albeit with limited precision the angular nature of the superoxo bond. More accurate crystallographic data has been obtained for simple cobalt macrocyclic dioxygen complexes. This structure shows the angle CO-O-O to be 120° and the O-O bond length to be 1.28 ± 0.02 A[15]. All these dioxygen complexes exhibit an infra-red O-O stretching vibration around 1105 - 1160 cm^{-1}.

The role of cytochrome P-450, the mixed function monooxygenase of liver microsomes has now been extensively studied[16]. They catalyse numerous transformations of lipid metabolism and oxidative detoxification of drugs and other xenobiotic substances. The ability of these and simpler structural models to oxidise olefins *in vitro* is discussed later.

2. THE OXIDATION OF OLEFINS PROMOTED BY TRANSITION METAL COMPLEXES

Fifty per cent of the chemicals needed in industry are derived from the oxidation of petrochemicals[17]; to meet this demand more efficient and selective catalysts are required which utilise cheap sources of oxygen[18]. The use of homogeneous and heterogeneous catalysis in the oxidation of organic substrates has recently received much attention in review literature[1], but the intention in this Introduction is to consider only aspects of the oxidation of olefins.

Free-radical vs. Coordination Catalysis. It is essential to make an important distinction in the oxidation chemistry of olefins at the outset. The O-O bond is relatively weak and may be broken in a homolytic or heterolytic fashion. Homolytic cleavage usually results in the formation of oxygen centred radicals. Transition metals may catalyse the formation of such radical species which can effect the oxidation of olefins often in an unselective manner. The metal is then only responsible for the initiation of the oxidative process. Alternatively, substrates may be oxidised by 'coordination catalysis' at the metal centre and radical intermediates are absent. It is difficult to distinguish between these processes, particularly when they operate in competition. The literature[17] contains many examples (vide infra) of oxidations, catalysed by transition metals, which were ascribed to coordination catalysis, whereas later, more careful work has revealed them to be free-radical reactions. The ubiquitous nature of free-radicals in oxidation mechanisms suggests a brief description of such systems.

2.1 Free-Radical Pathways[1a,19]

Transition-metal complexes most commonly generate free-radicals by catalysing the homolytic decomposition of hydroperoxides. Cobalt and manganese complexes are found to be most effective. Oxidative and reductive cleavages of alkyl hydroperoxides together constitute a means of generating alkoxy and alkylperoxy radicals

$$2ROOH \xrightarrow{[Co^{II,III}]} RO\cdot + ROO\cdot + H_2O$$

The radicals so formed propagate by a branching chain sequence

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

Complexes of rhodium and iridium, which are in the same group as cobalt in the periodic table, initiate similar redox steps in the decomposition of alkyl hydroperoxides, further free-radicals being produced autocatalytically.

Fenton's Reagent. In the presence of certain metals, particularly iron(II), the mild oxidising ability of hydrogen peroxide is considerably enhanced. The combination of hydrogen peroxide and iron(II), known as Fenton's reagent, proceeds by a free-radical mechanism which is a slight modification of that proposed by Haber and Weiss[20] (Scheme 1).

Scheme 1

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III}(OH) + HO\cdot$$

$$Fe^{III} + H_2O_2 \longrightarrow Fe^{II} + HO_2\cdot + H^+$$

$$Fe^{II} + HO\cdot \longrightarrow Fe^{III}(OH)$$

$$Fe^{III} + HO_2\cdot \longrightarrow Fe^{II} + O_2 + H^+$$

$$HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot$$

The synthetic applications of Fenton's reagent have been reviewed recently[21]. Althought it is reasonable to suppose that hydroxyl radicals are responsible for attack on organic substrates, Groves[22] has shown in a series of elegant stereochemical studies on the hydroxylation of alcohols to their diols that other pathways are available, and may proceed by means of the ferryl ion, Fe(IV) = O.

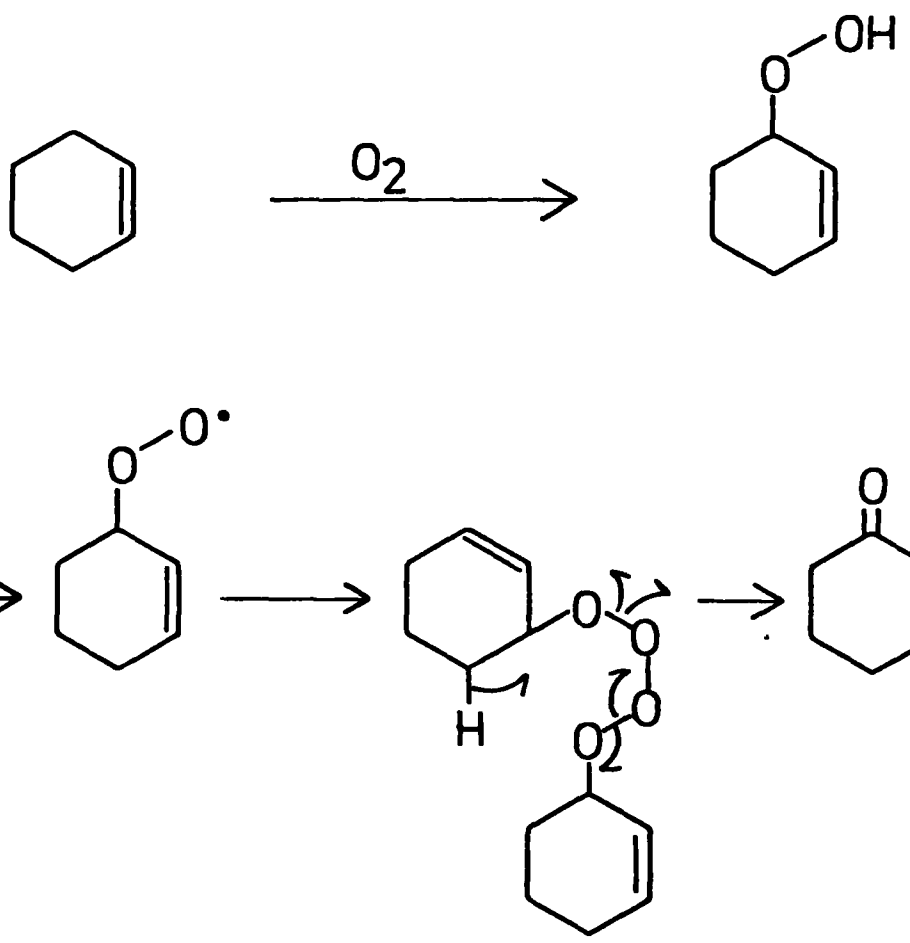
Metalloporphyrins of cobalt, manganese, rhodium and iron, in various oxidation states catalyse the oxidation of olefins by dioxygen. With cyclohexene at least, the alcohol, ketone and epoxide products are produced via the breakdown of a hydroperoxide intermediate[23].

Olefin Oxidation. Collman[24] tentatively invoked 'coordination catalysis' in the oxidation of cyclohexene to mainly 2-cyclohexene-1-one by dioxygen, catalysed by $IrI(CO)(PPh_3)_2$, a complex known to coordinate dioxygen. Soon afterwards Ugo[25] showed that such reactions exhibited the characteristics of a radical

chain process, initiated by decomposition of hydroperoxides, as described above. The cyclohexenyl hydroperoxide is formed by attack of dioxygen on the allylic radical produced by allylic hydrogen abstraction.

Coordination of dioxygen is incidental although coordination of the hydroperoxide is possibly involved (Scheme 2).

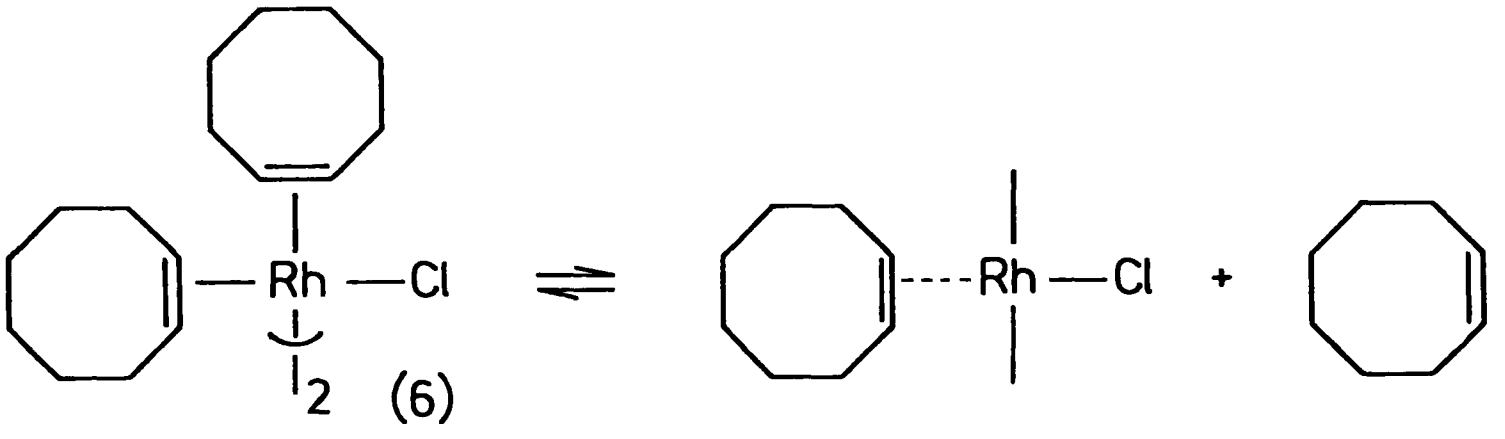
Scheme 2

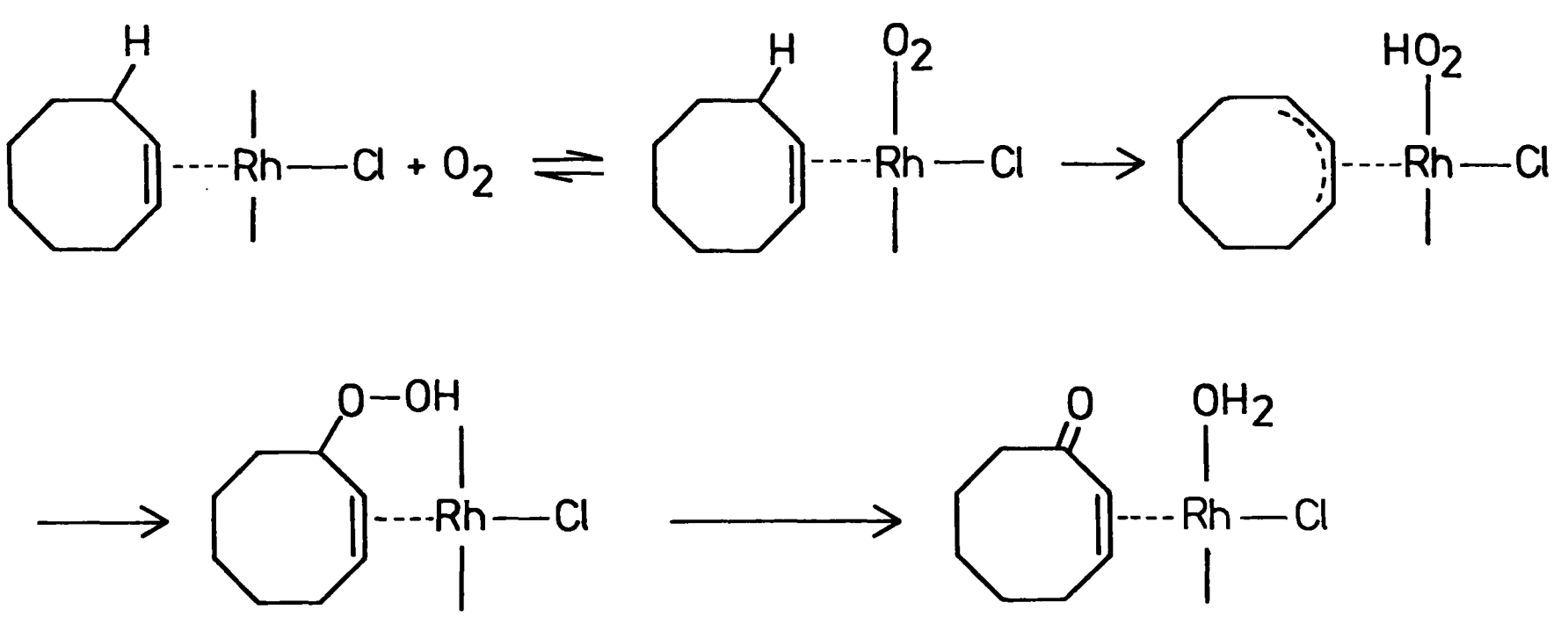


Similarly, James[26] invoked formation of a hydroperoxide intermediate in the oxidation of cyclooctene catalysed by rhodium(I) complexes. Scheme 3 shows how hydrogen atom abstraction

by coordinated dioxygen leads to a hydroperoxide intermediate which subsequently decomposes on or off the metal.

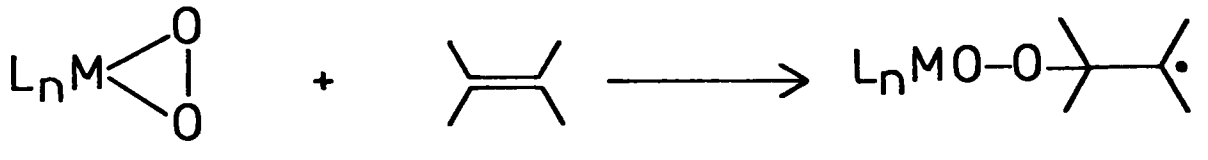
Scheme 3





When the olefinic substrate is unable to undergo allylic hydrogen abstraction, or when the metal is inert to hydroperoxide decomposition, radical pathways may still dominate but alternative means of their generation must be proposed

Scheme 4



(Ref. 27)

$$M(acac)_3 + O_2 \longrightarrow M(oxide) + CO_2 + R^{\bullet}$$ (Ref. 28)

The remaining Introduction lists and discusses transition metal promoted oxidations of olefin substrates, to yield epoxide or ketonic product with generally high selectivity.

2.2 Coordination Catalysis I: Formation of Epoxides

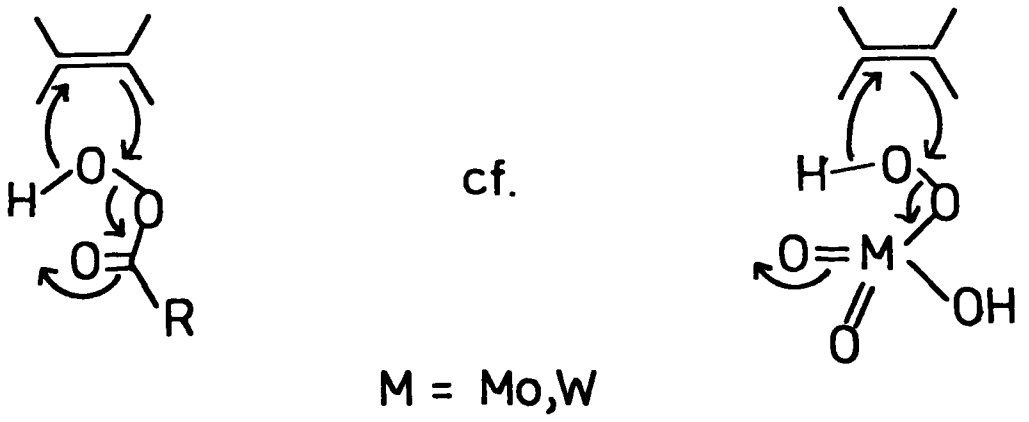
Epoxides are vital building blocks in synthesis, both in industry and the laboratory. They are raw materials for a wide variety of organic substances, including glycols, alkanolamines

and polymers such as polyesters and epoxyresins[29]. Frequently epoxides are intermediates in laboratory syntheses[30]. The most common source of oxygen in these reactions is an alkyl hydroperoxide, but other sources, including dioxygen will also be considered here.

2.2.1 Hydrogen Peroxide

Nearly fifty years ago Milas[31] discovered that hydrogen peroxide, in the presence of certain acidic metal oxides e.g. OsO_4, MoO_3, V_2O_5, catalytically converted olefins to their glycols. It was later shown that many of their oxidations proceed *via* an epoxide intermediate, which is hydrolysed under the reaction conditions. In basic or neutral media selective epoxidation could be achieved. Hydrophilic olefins such as allylic alcohols or α,β-unsaturated acids were the most favourable substrates. Figure 6 illustrates how a mechanism can be drawn analogous to expoxidation by simple peracids

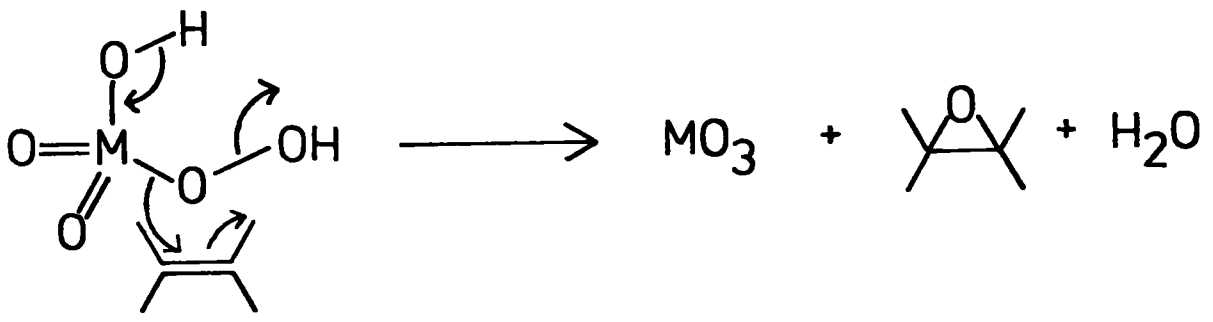
Figure 6



However, other mechanisms can be envisaged, as for example in

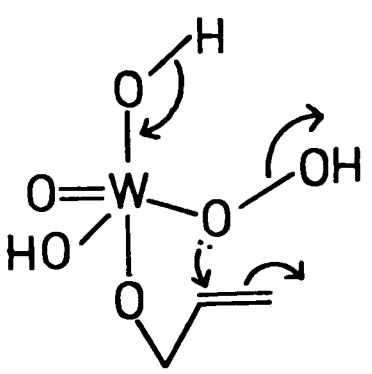
Figure 7.

Figure 7



To account for the exceptional reactivity of allylic pertungstate esters an intramolecular, concerted rearrangement has been proposed[32] (Fig. 8).

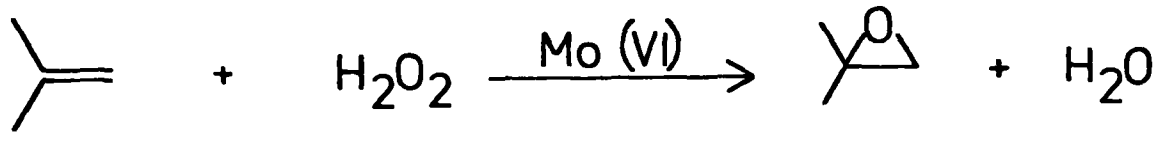
Figure 8

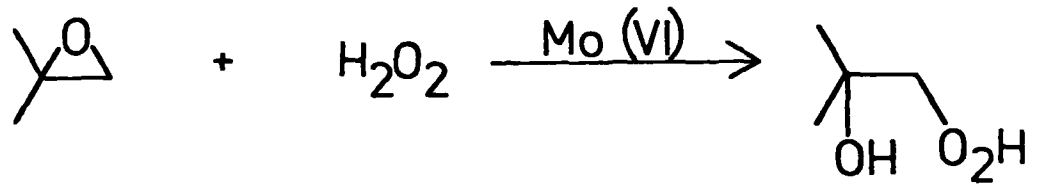


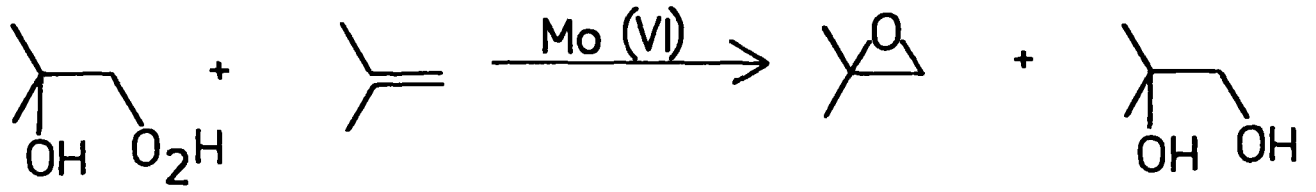
On purely electronic grounds one might expect allylic alcohols to be more slowly oxidised by the electrophilic peracid than more nucleophilic simple olefins. That the reverse is true probably indicates the importance of coordination to the metal through the allylic OH group. Although good yields of epoxide

can be obtained with most functional olefins, simple olefins give low yields or numerous by-products[1c], by, for example, perhydrolysis[33] (Scheme 5)

Scheme 5







The scope of these oxidations is very limited, and on an industrial scale, dangerous and expensive quantities of hydrogen peroxide are required. However, by continuous azeotropic distillation to remove the retarding water, propylene is epoxidised in 85% yield by 70% hydrogen peroxide employing $MoO_2(acac)_2$ as catalyst[34].

2.2.2 Alkyl Hydroperoxide

The earliest reports[35] that alkyl hydroperoxides could, in the presence of certain vanadium (V) salts, yield moderate quantities of epoxide from simple cyclic olefins went quite unnoticed, presumably because of the then exotic nature of

these substances. One presumes that Milas (vide supra) did not extend his pioneering work with hydrogen peroxide to alkyl derivatives because they were not readily available pure in the 1930's. Alkyl hydroperoxides today represent a common tool in the oxidation of olefins in both large and small scale work.

The reaction of alkyl hydroperoxides in the presence of metal catalysts may result in homolytic or heterolytic fission of the O-O bond[1a]. Homolytic decomposition to yield free-radicals has been mentioned above. A heterolytic pathway dominates when a metal is able to withdraw electrons from the O-O bond, making it more susceptible to heterolysis by an attacking nucleophile. This ability of the metal is related to its Lewis acidity - a quantity which increases with higher oxidation state. The oxides CrO_3, MoO_3, WO_3, TiO_2 and V_2O_5 are able to promote the selective, non-radical heterolytic fission of the O-O bond by nucleophiles such as olefins. This subject has several excellent reviews[1c,36].

A priori it could be accepted that either a coordinated hydroperoxide (M-OOR) is the active species, or reaction of the metal with alkyl hydroperoxide produces a peroxometal complex, itself capable of epoxidation. Following Mimoun's discovery[37] (vide infra) that a peroxomolybdenum complex could stoichiometrically epoxidise olefins, several groups[37,38,65] supported a mechanism in catalytic reactions in which the purpose of hydroperoxide

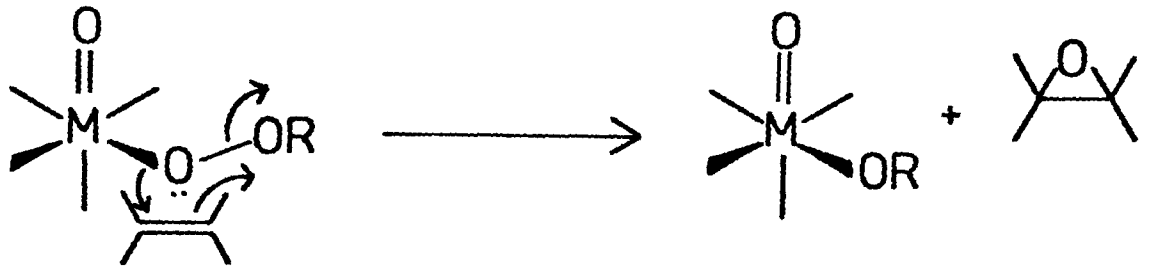
was to generate the active peroxometal species. Sharpless found he was unable to isolate Mimoun's complex in pure form, but that *in situ* it rapidly exchanges with ^{18}O-water at it's oxo position[39] and oxo and peroxo sites did not exchange with each other. By employing a specifically ^{18}O-labelled oxo complex, generated *in situ*, he showed that peroxometal-type intermediates were not taking part in alkyl hydroperoxide epoxidation of olefins, catalysed by molybdenum complexes. He concluded that Mimoun's stoichiometric system could not provide a mechanistic generalisation for catalytic systems involving alkyl hydroperoxides. Sharpless suggested a mechanism which involved activation of alkyl hydroperoxide by coordination to the metal through the oxygen distal to the alkyl group (Scheme 6(a) and (b)).

Sheldon,[40] however, favours a mechanism analogous to the epoxidation of olefins by peracids - involving coordination of the oxygen adjacent to the alkyl group, (Scheme 6(c)). The mechanism outlined in Scheme 6(a) or (b) is more beguiling by virtue of its coordination of the less-hindered oxygen and its accountability for the exceptional reactivity of allylic alcohols. Further, mechanism (a) is generally accepted as more likely[41].

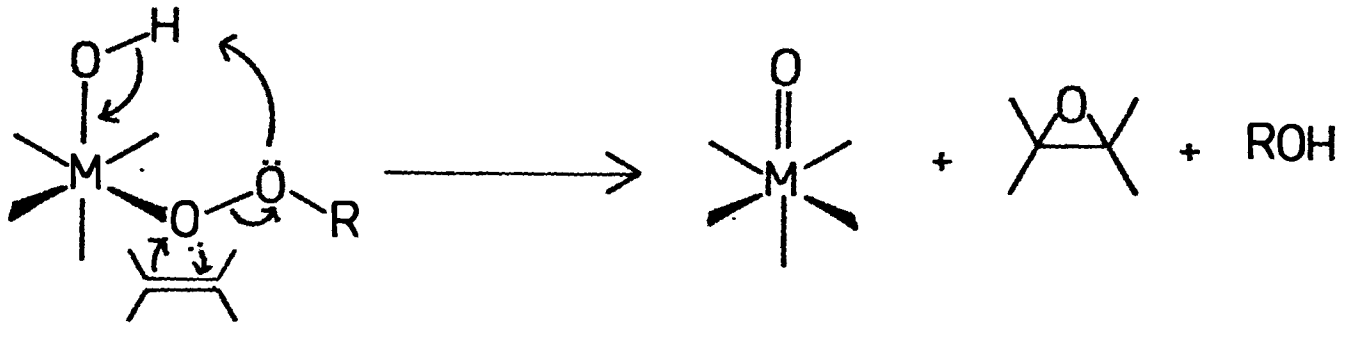
Site- and Stereoselectivity. These effects may arise from factors attributable to either the metal complex or the olefinic substrate. Inherent factors in the olefin may promote differences in reactivity of double bonds (site selection) or in steric

Scheme 6

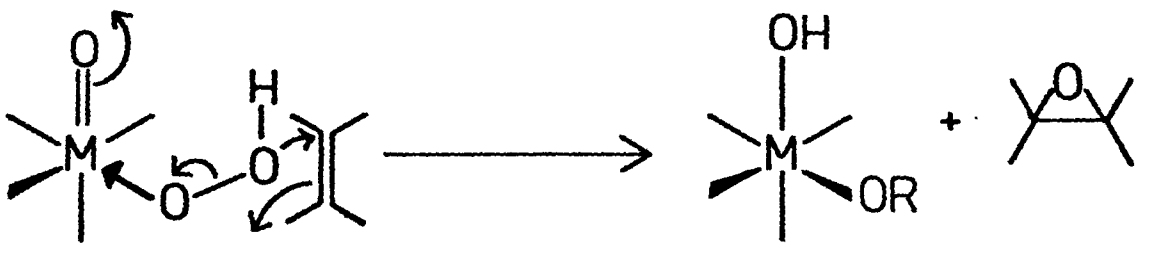
a)



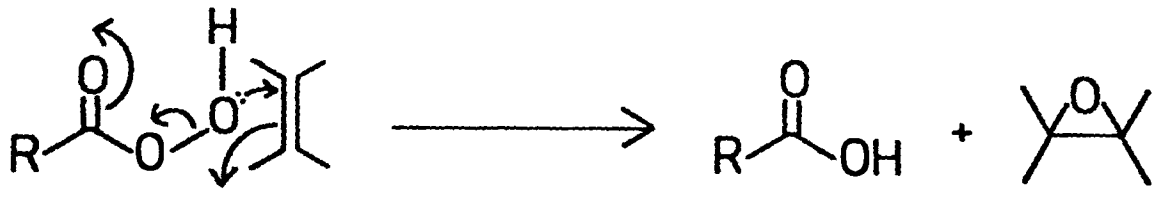
b)



c)

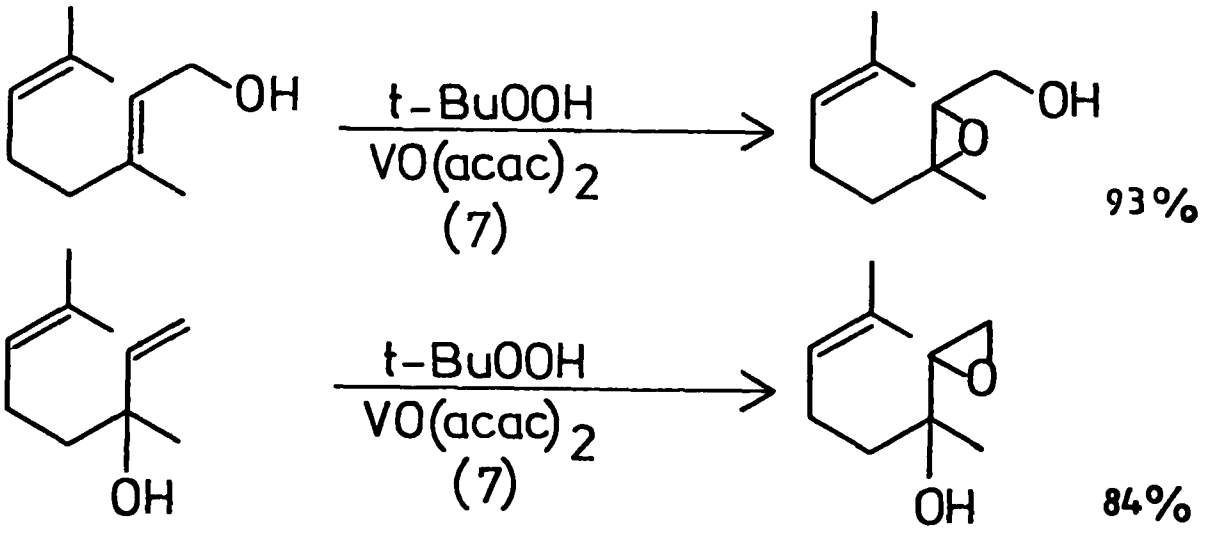


cf:



constraints (stereoselection). In the metal complex, orientation of the substrate by bonding of a functional group (e.g. hydroxyl) may result in preferential transfer to one site (site selection) or to one face (stereoselection). Selectivities which can be achieved using olefinic alcohols as substrates are particularly striking. For example, geraniol and linalool were site selectively epoxidised to their previously unknown monoepoxides by $VO(acac)_2$ with t-butylhydroperoxide[42] (Scheme 7).

Scheme 7

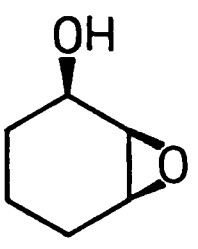


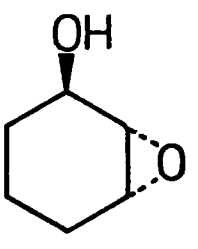
The syn-directive effect of hydroxyl group in the peracid epoxidation of cyclohexene-3-ol to give largely the syn epoxide is now a classic case. Sharpless[42] compared the stereoselection and rate enhancement (measured against cyclohexene as standard) obtained with metal catalysts and perbenzoic acid (Table 3).

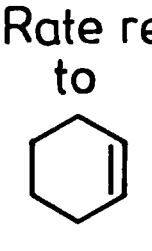
No such effects were detected with the corresponding allylic acetate.

Table 3.









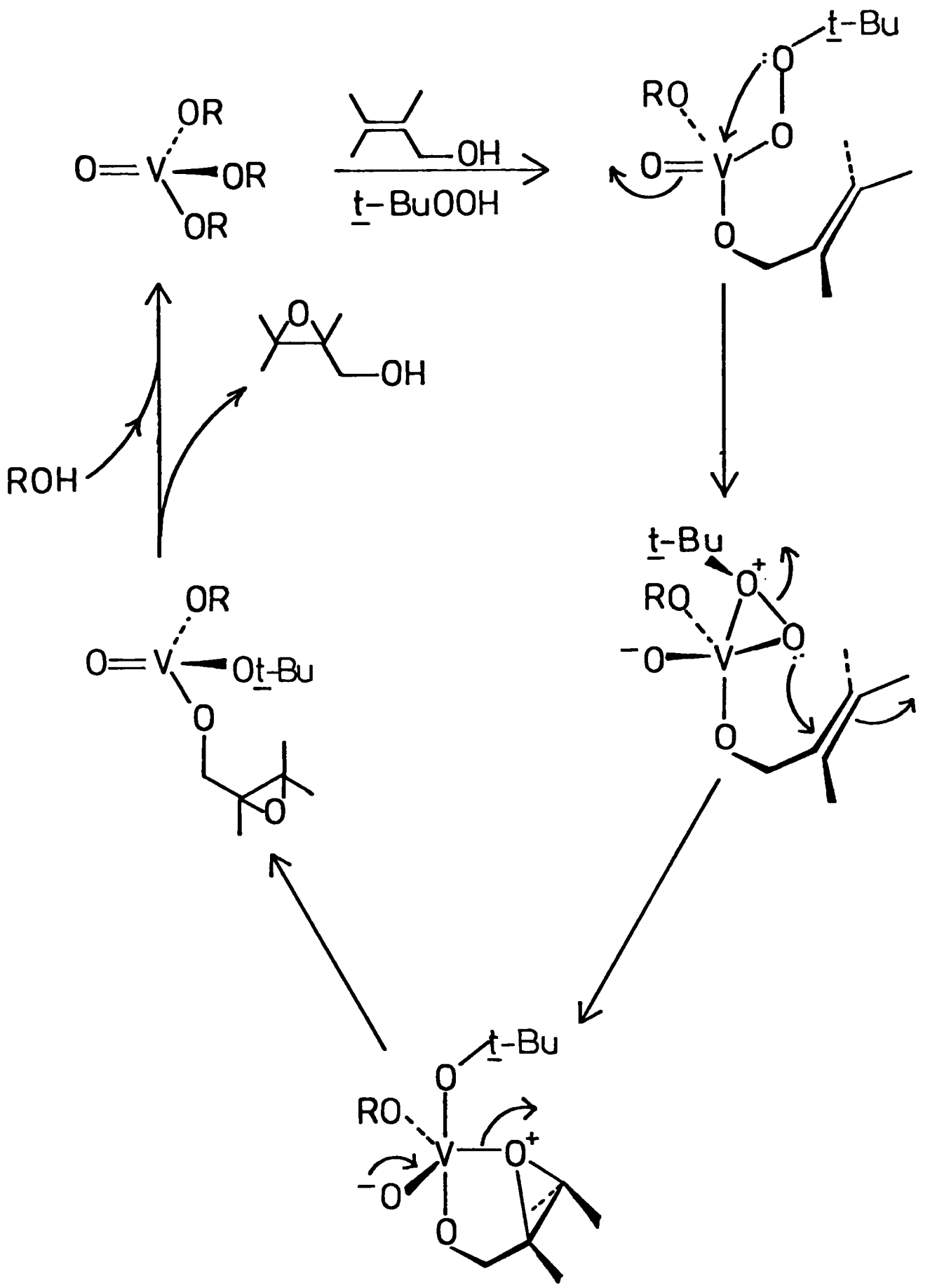
			Rate rel. to
t-BuOOH + $Mo(CO)_6$	98	2	45
+ $VO(acac)_2$ (7)	98	2	200
Perbenzoic acid	92	8	0·5

Such exceptional site- and stereoselection was rationalised on the basis of a mechanism alluded to above where oxygen transfer is enhanced and sterically controlled by coordination of the allylic oxygen to the metal centre (Scheme 8).

Sharpless[36] supposes that oxygen transfer is subject to rigid stereoelectronic requirements. In particular, displacement of the peroxide bond should occur from the back side and along the axis of the O-O bond being broken and he has begun to rationalise stereoselectivity on the basis of stereoelectronically predicted conformations of the alkoxide moiety.

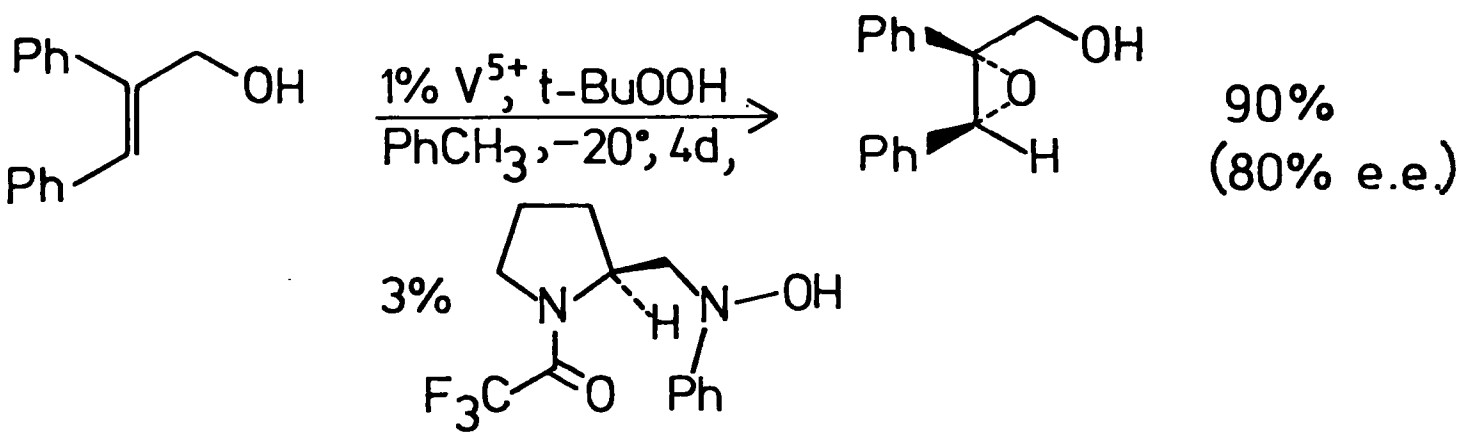
Asymmetric Epoxidation. One attractive feature of the facile vanadium (V) catalysed epoxidation of allylic alcohols is their potential to accomplish asymmetric epoxidations. The first successes were achieved independently by both Yamada[43] and Sharpless[44]. Yamada used a molybdenum catalyst employing chiral

Scheme 8


OR
O=V
OR
OR
OH
t-BuOOH
t-Bu
O
RO
O
O=V
O
O
OH
ROH
OR
O=V
Ot-Bu
O
O
t-Bu
O+
RO
−O
V
O
O
t-Bu
O
RO
V
O+
−O
O

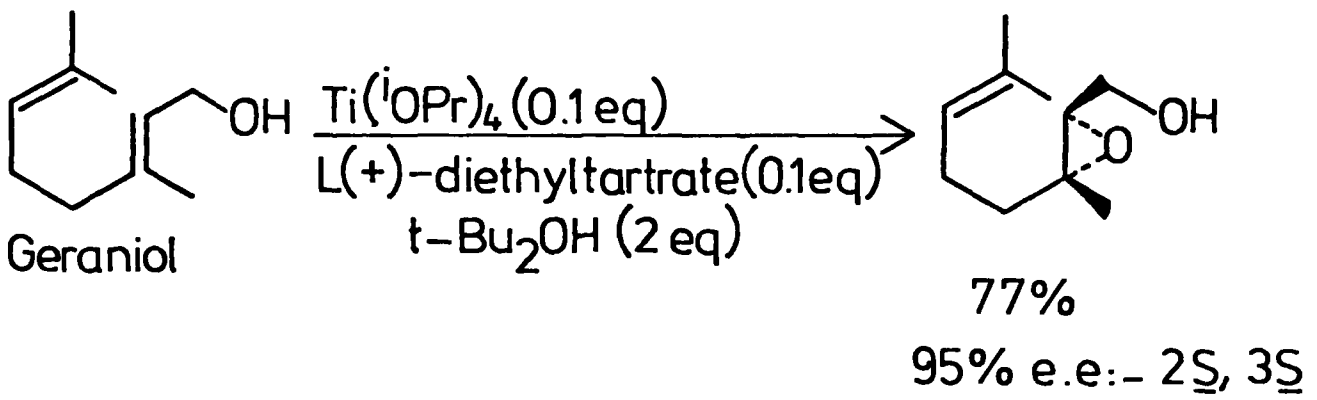
ligands derived from ephedrine, and Sharpless used a Vanadium (V) system bearing chiral hydroxamic acids. Modest (13 - 30%) enantiomeric excesses were obtained with some prochiral allylic alcohols. Since that time Sharpless has developed a ligand capable of rather higher enantioselection, at least in the system cited[45] (Scheme 9).

Scheme 9



Since these initial discoveries Sharpless and Katsuki[46] have described an asymmetric epoxidation of allylic alcohols of truly outstanding enantioselection. The method, based on (+)- or(−)-diethyltartrate, titanium tetraisopropoxide and t-butylhydroperoxide, is capable of very high (90 - 100%) enantiomeric excess and high (70 - 80%) chemical yield in all the substitution patterns of primary allylic alcohols. Geraniol provides a typical example, (Scheme 10).

Scheme 10



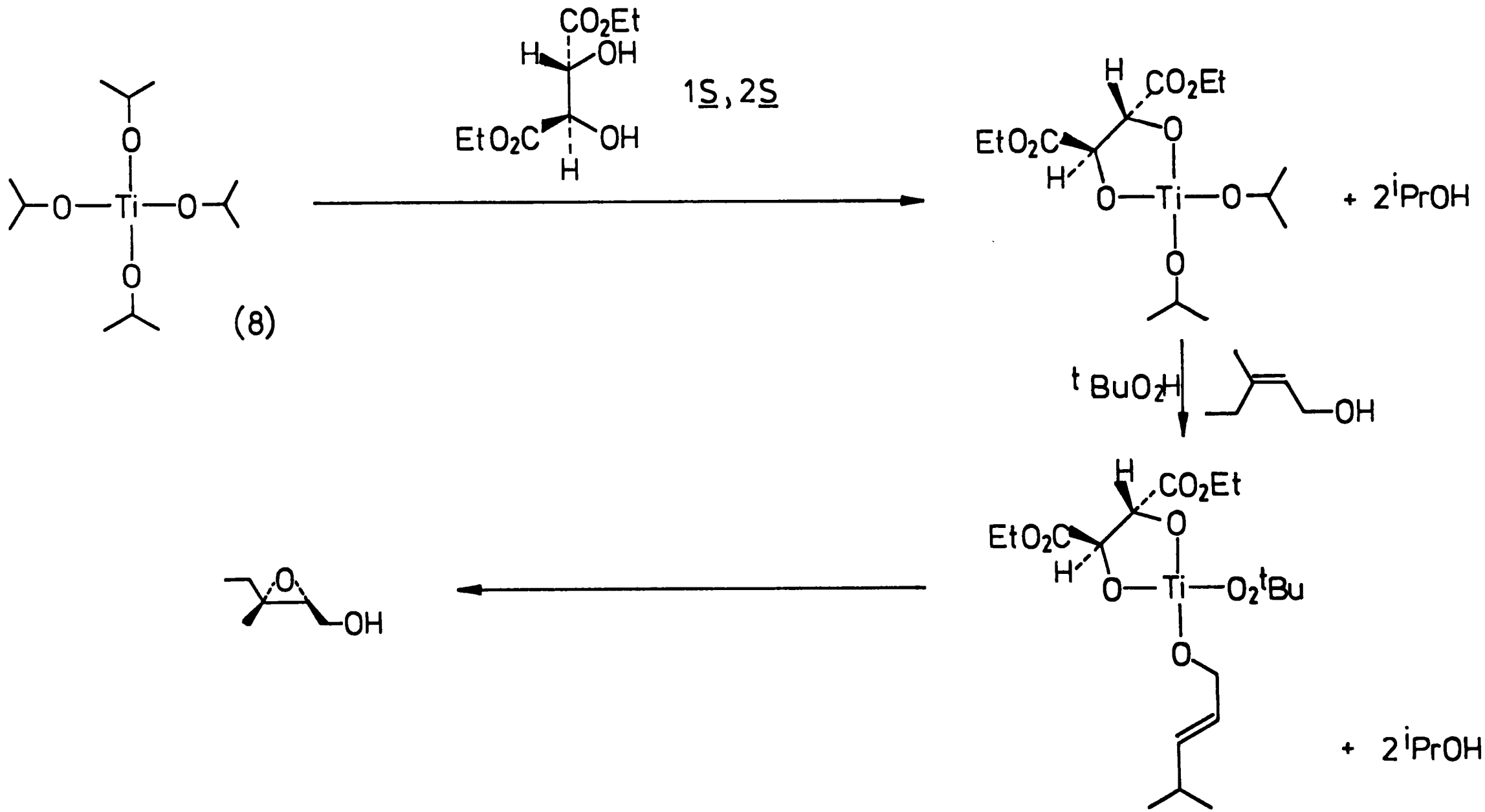
The mechanism by which such high optical purity is obtained has not yet been established, but presumably the reaction proceeds through the pathway illustrated in Scheme 11. The synthetic scope of such asymmetric reactions has been noted by Sharpless for the synthesis of epoxy alcohol intermediates in the construction of complex structures such as methymycin, erythromycin and leukotriene C-1. His partial synthesis of the enantiomers of the gypsy moth sex attractant, disparlure*, exemplifies the utility of chiral epoxy alcohols[47] (Scheme 11).

2.2.3 Peroxometal Complexes

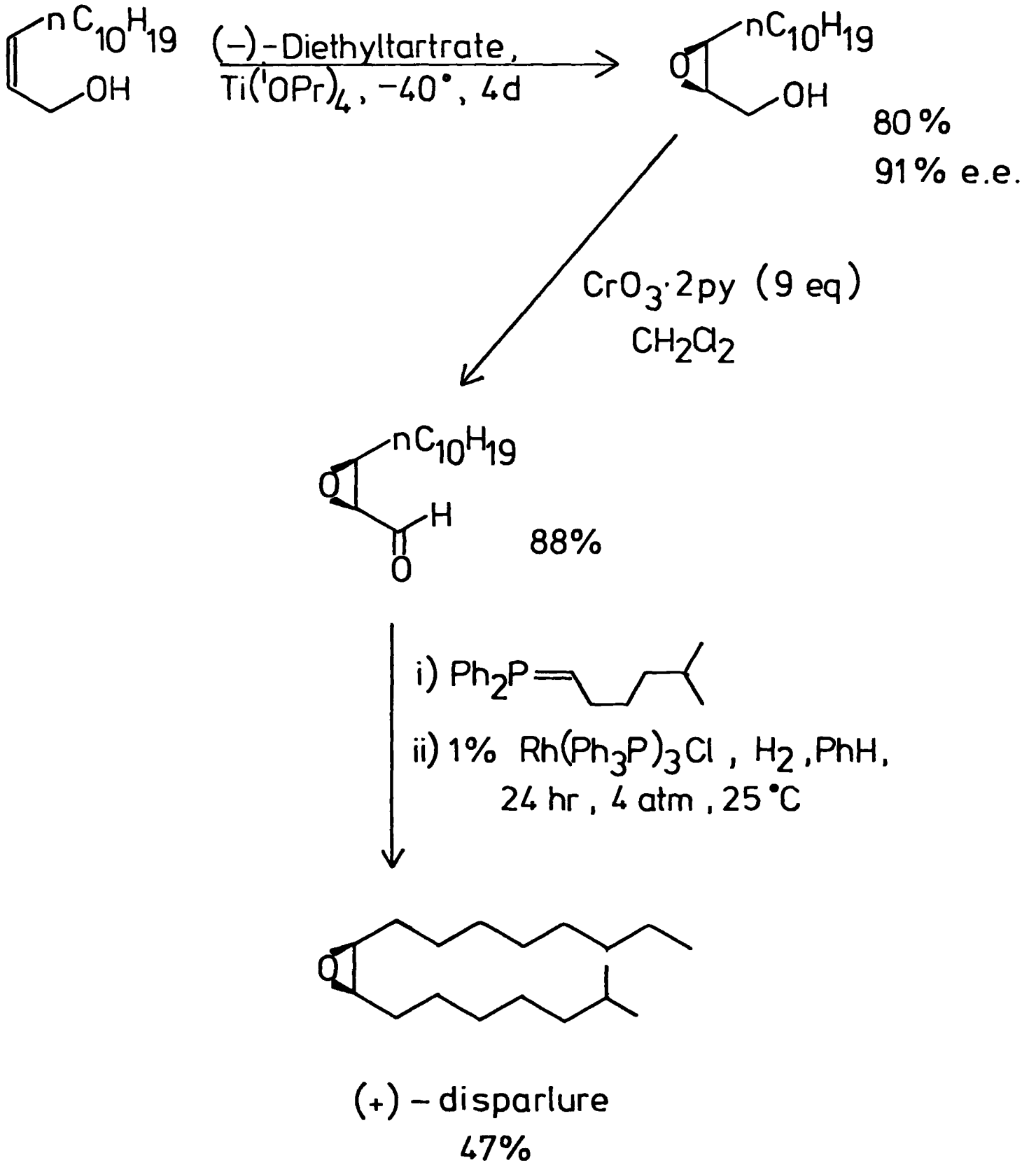
Mimoun[37] has prepared a series of molybdenum (VI) and tungsten (VI) peroxo complexes with the following structure;

*A total synthesis of the enantiomers of disparlure has been reported recently. It employs Sharpless' method for the formation of the chiral epoxy alcohol. See Ref. 47b.

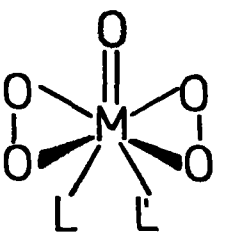
Scheme 11


CO2Et
H
OH
EtO2C
OH
H
1S, 2S
O
Ti
O
O
(8)
H
CO2Et
EtO2C
H
O
O
Ti
O
O
+ 2iPrOH
tBuO2H
OH
H
CO2Et
EtO2C
H
O
O
Ti
O2tBu
O
+ 2iPrOH
O
OH

Scheme 12



(+) – disparlure
47%



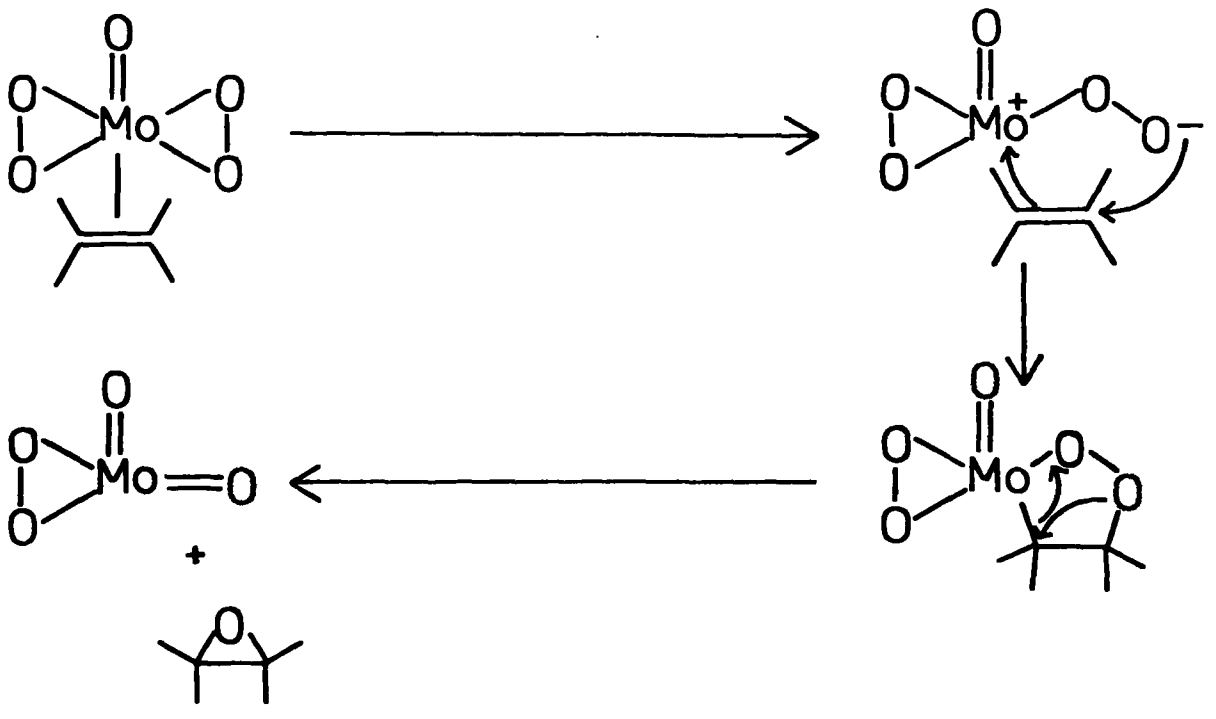
L = py, HMPA (9a,b)

they were found to epoxidise olefins under anhydrous conditions in aprotic solvents. Such peroxometallic species contain highly electrophilic oxygen centres as borne out by the ease of formation of lithium butoxide from n-butyllithium at -78°C. Nucleophilic peroxides such as Na_2O_2 do not form lithium butoxide[48].

In accordance with the electron deficient nature of the peroxo linkage the rate of epoxidation increases with increasing alkyl substitution at the olefinic bond[49].

Mimoun suggests a cyclic mechanism for the oxygen transfer step involving 1,3-dipolar addition to the double bond (Scheme 13).

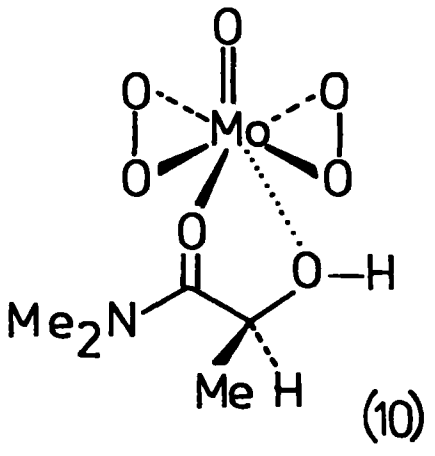
Scheme 13



Sharpless[38a] showed that the transferred oxygen arose only from the peroxide linkage, in the HMPA complex by ^{18}O labelling studies. He also noted however that the relative reactivity of certain olefins paralleled that towards organic peracids, rather than that which might be expected from 1,3-dipolar addition[50], although Mimoun's suggestion could be accommodated if olefin coordination was rate limiting.

An extension to this interesting stoichiometric reaction has been made by Kagan and Mimoun[51]. They synthesised an analogous complex containing the chiral ligand (S)-N,N-dimethylactamide (Fig. 9). Simple, prochiral olefins such as propene or trans-2-butene are epoxidised stoichiometrically to optically active epoxides in up to 34% enantiomeric excess.

Figure 9

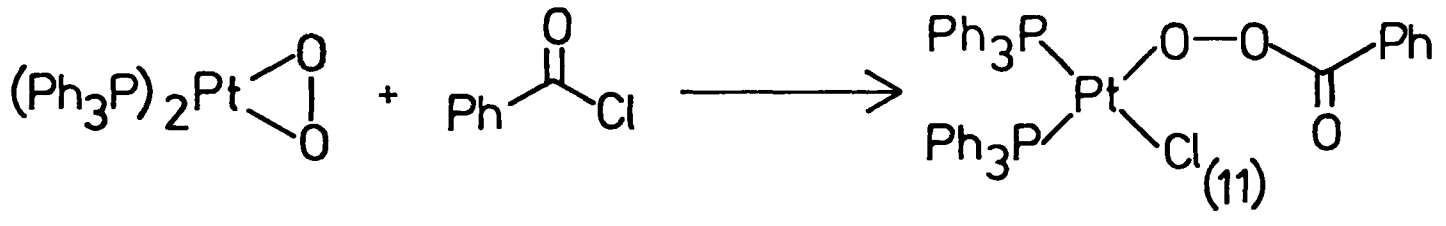


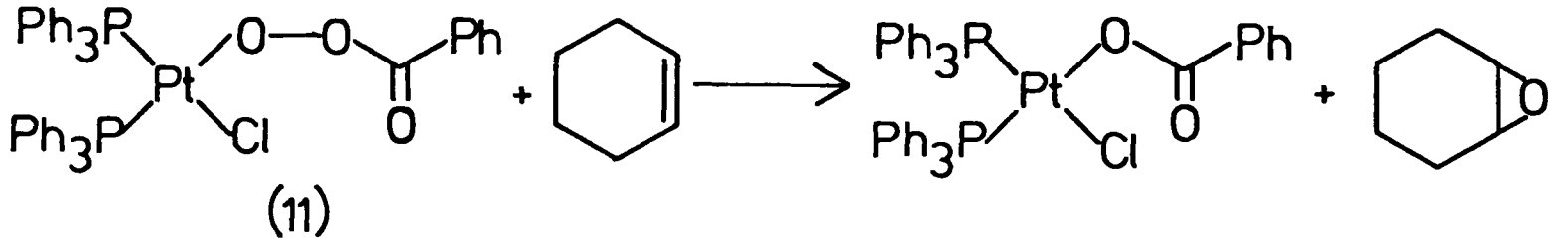
(10)

Oxygen transfer from normally nucleophilic platinum dioxygen complexes has been induced by electrophiles such as benzoyl chloride. The epoxidation of cyclohexene then proceeds via

a peroxybenzoato intermediate* (Scheme 14).

Scheme 14





(11)

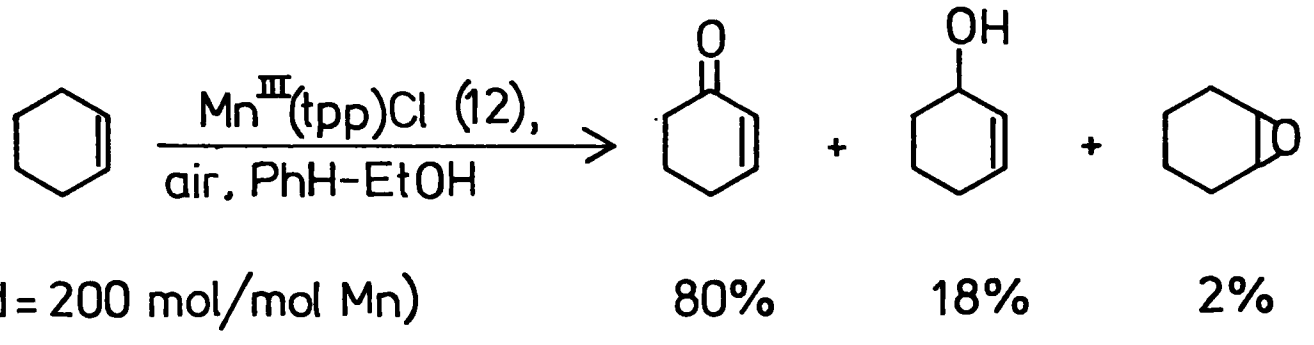
2.2.4 Metalloporphyrins

The search for synthetic models of cytochrome P-450 has uncovered a number of complexes which epoxidise olefins with variable selectivity. These oxidations proceed by means of an intermediate ferryl ion, Fe (IV) = O, believed to be an active species in the biological system. The precise nature of the steps which result in activation of dioxygen by successive electron transfers to ferryl ion are far from clear. Tabashi[53] and Groves[54], however, have studied the epoxidation of olefins by manganese and iron porphyrin complexes. Tabushi notes that the reaction of Mn(III) (tpp)Cℓ with cyclohexene in air catalytically

*The peroxybenzoato intermediate postulated by Kochi has since been isolated and characterised by Otsuka (Ref. 75) and found to be an active epoxidising agent.

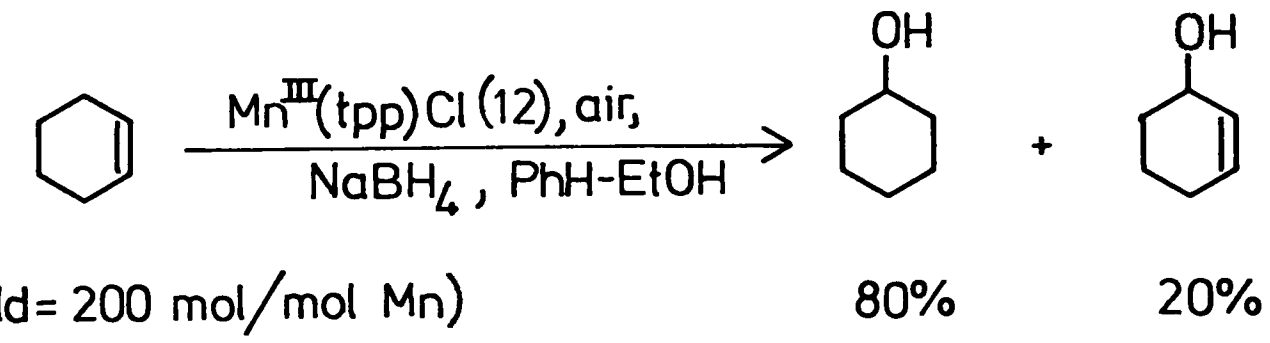
produces a mixture of oxidised compounds. These are formed by release of free-radicals (vide supra)(Scheme 15).

Scheme 15



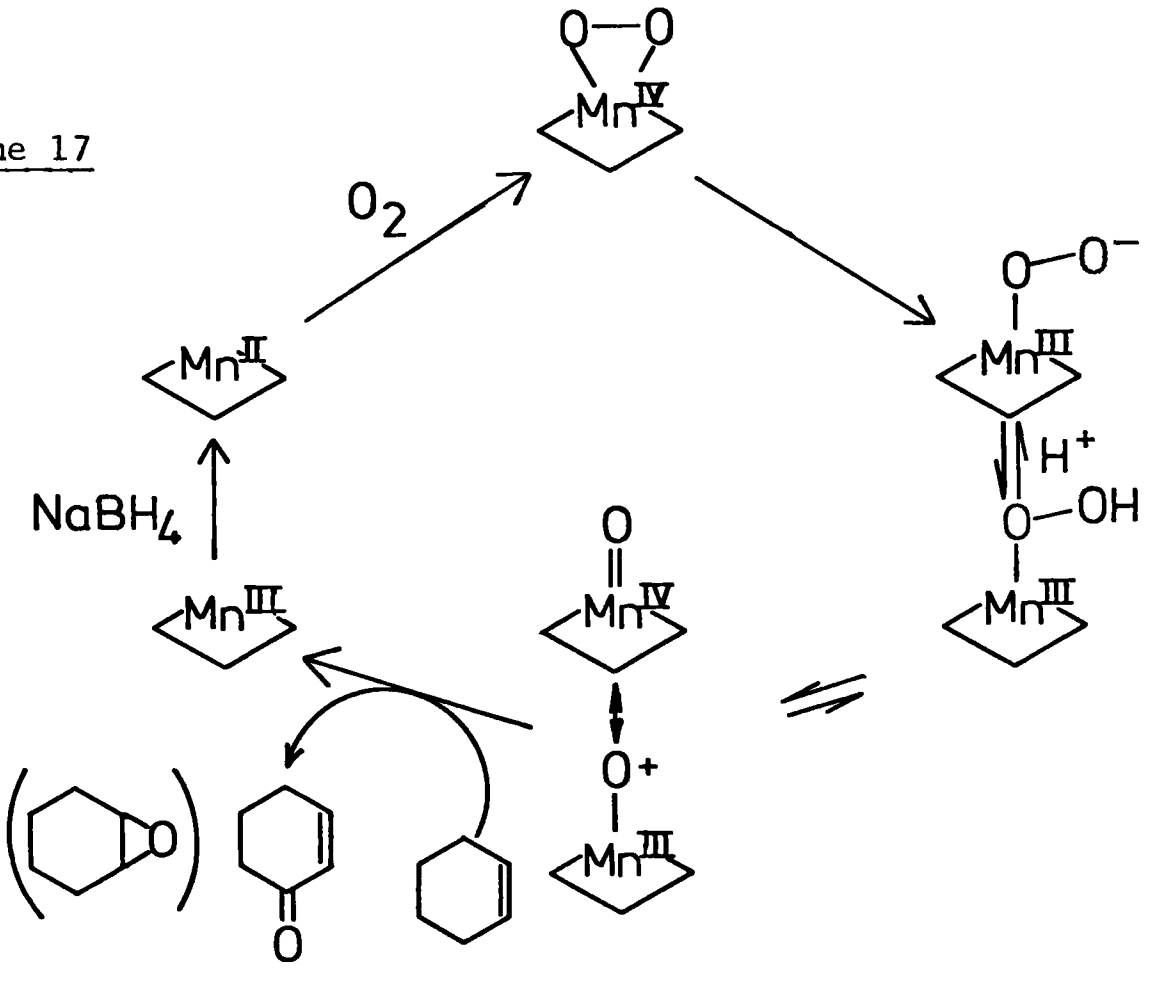
However, the presence of sodium borohydride (perhaps analogous to NADH in vivo) gave a different distribution of products, by a proven non-radical pathway (Scheme 16).

Scheme 16



Tabushi and co-workers produced further evidence that the cyclohexanol was largely derived from epoxide by reduction since the borohydride was present in excess. Tabushi proposes a sequence of reactions for activation of dioxygen, involving the active oxidant Mn(III) = O (Scheme 17).

Scheme 17

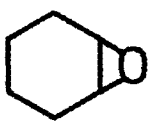
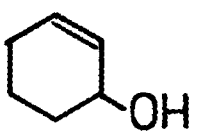
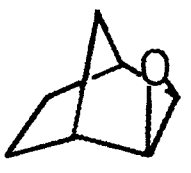
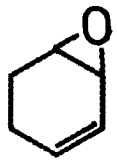
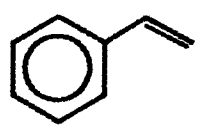
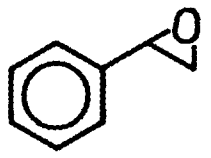
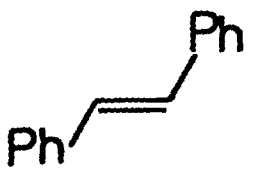
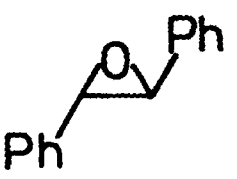


Groves uses iodosylbenzene as an oxygen source and Fe(III)(tpp)Cℓ as catalyst to epoxidise a number of olefins. He noted that cyclohexene was unselective, there was a high specificity for cis-olefins and that the ferryl ion-promoted reaction competes effectively with free-radical pathways (Table 3a).

2.2.5 Heterogeneous Catalysis

The enormous industrial need for ethylene oxide as a basic feedstock prompts the comment that it is produced on a large scale by the 'direct' addition of oxygen over a heterogeneous catalyst. A mixture of ethene and oxygen in some diluent gas is passed over a solid catalyst consisting of silver on α-Al_2O_3 at 250°C. The epoxide is produced with 70% selectivity[55]. Many recent studies[56] support the original view that ethene interacts directly with an oxygenated silver surface, with the absence of hydroperoxides or

Table 3a: Oxidation of olefins with $Fe^{III}(tpp)Cl$/PhIO (13)

Olefin	Product (Yield based on PhIO)	
	 55%	 15%
	 99%	
	 74%	
	 65%	
	 82%	
	 0%	

free-radicals. The method is not generally applicable to higher olefins, giving much lower yields. Even propene is epoxidised in only 25% yield, together with a plethora of by-products.

2.3 Coordination Catalysis II: Formation of Methyl Ketones

The transformation of terminal olefins to methyl ketones is most commonly encountered with the low oxidation state transition metals palladium (0) and rhodium (I). Most generally, the source of oxygen will be water, alkyl hydroperoxide or hydrogen peroxide, or dioxygen. The following review will illustrate several distinctive types of mechanism pertinent to these processes.

2.3.1 The Wacker Process

The industrially important palladium-catalysed oxidation of ethene to acetaldehyde was discovered by Smidt[57] in 1959. The process combines the stoichiometric reduction of palladium(II) with reduction of the metal *in situ* by dioxygen in the presence of copper(I) salts,

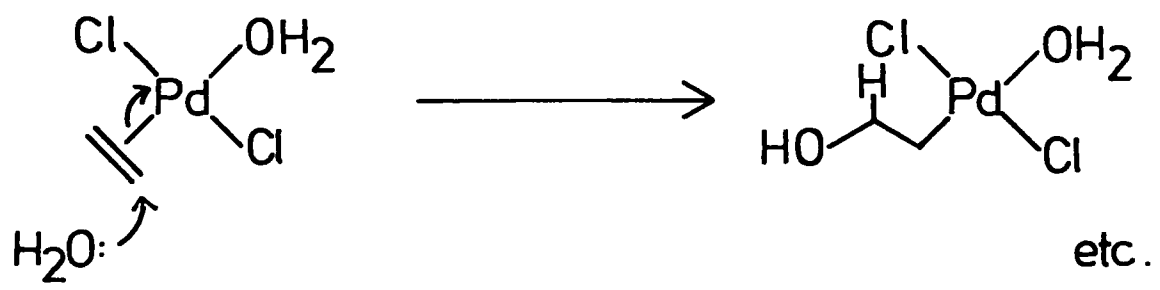
$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$$2CuCl + 2HCl + 1/2\ O_2 \longrightarrow 2CuCl_2 + H_2O$$

It is generally accepted[58] that the key step in this process is

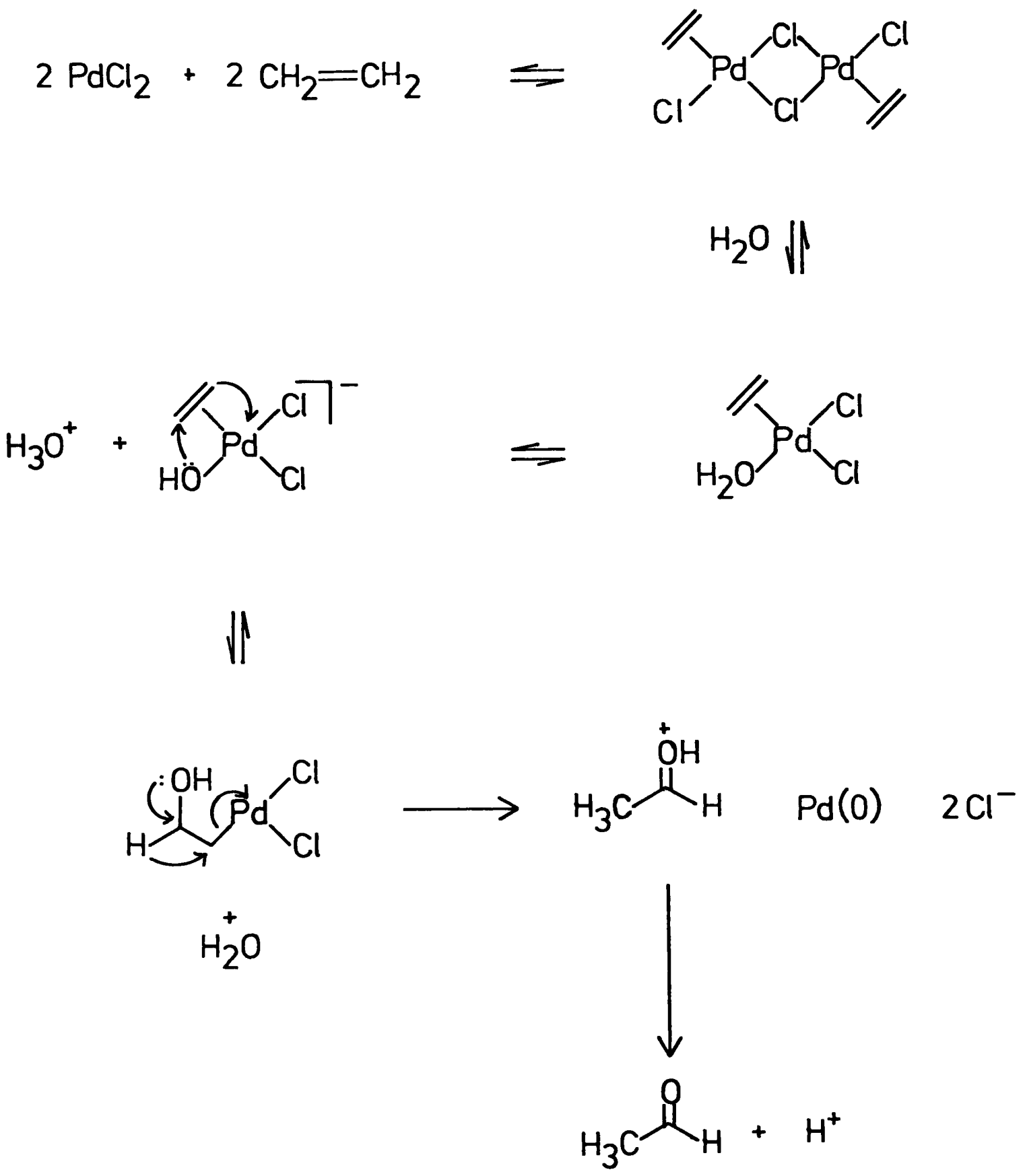
nucleophilic attack of OH^- or H_2O on the Pd-complexed olefin, a mechanism consistent with the kinetic evidence includes prior coordination of the nucleophile[18] to the metal. This mechanism is illustrated in Scheme 18. The crucial step is insertion of the ethene into the Pd-OH bond, followed by a rearrangement. This may be conserted, as shown, or possibly sequential. However, this represents a rare example in which nucleophilic attack is claimed to occur <u>cis</u> with respect to the metal, a claim which cannot be directly probed in this reaction. <u>Trans</u> attack by free H_2O on the coordinated olefin can also be accommodated by the kinetic data and this alternative, proven in analogous systems, has been suggested in recent studies[59]. <u>Trans</u> attack of H_2O is illustrated in Reaction [4].



[4]

Propene is selectively oxidised to acetone and <u>n</u>-butenes give butan-2-one. Higher olefins generally produce mixtures as a result of olefin isomerisation[60], although some changes in solvent[61] or the use of phase-transfer catalysts[62] can improve yields.

Scheme 18

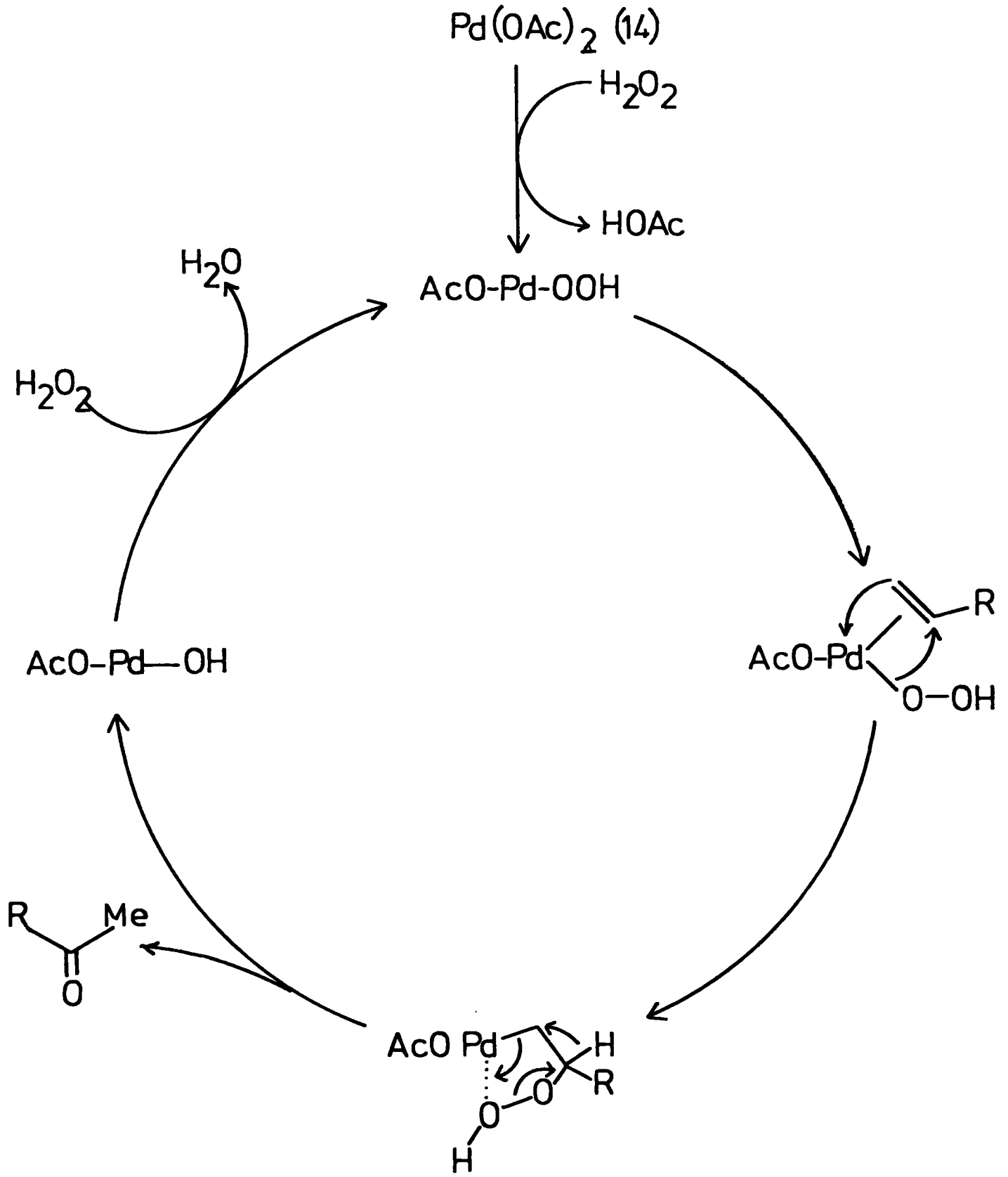

2 PdCl2 + 2 CH2=CH2
Cl
Pd
Cl
Cl
Pd
Cl
H2O
H3O+
+
Cl
Pd
HÖ
Cl
Cl
Pd
H2O
Cl
:OH
Cl
Pd
H
Cl
+
H2O
+
OH
H3C
H
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2 Cl−
O
H3C
H
+
H+

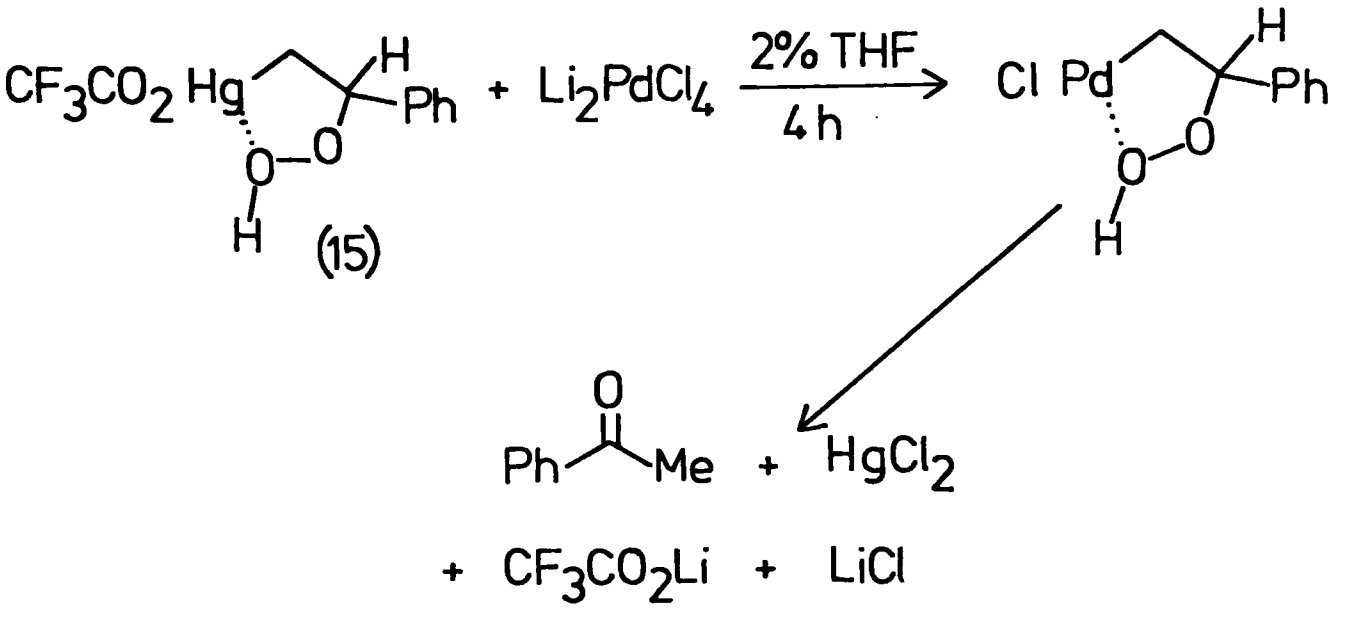
Wacker-type reactions are relevant to many Gp. VIII metal mediated transformations of olefins to methyl ketones, as will be evident from the reamining section of this Introduction. They may participate in the reaction mechanism but in any event need to be excluded from consideration by experimental test.

2.3.2 Hydroperoxides

Recently Mimoun[63] has described a very efficient palladium catalysed oxidation of terminal olefins by hydrogen peroxide, in which only low concentrations of metal salts are required, giving a synthetically useful procedure. The addition of 30% aqueous hydrogen peroxide to a solution of $Pd(II)(OAc)_2$ in acetic acid or t-butanol normally results only in evolution of oxygen. However, in the presence of an excess of 1-octene, octan-2-one is observed to be a major product. The use of a high Pd:1-octene ratio and of excess hydrogen peroxide results in a highly selective and catalytic oxidation of the olefin. The rate and selectivity of this reaction was unperturbed by the presence of free-radical inhibitors and Scheme 19 shows how the key step in Mimoun's mechanism is an internal rearrangement of a pseudocylic peroxidic intermediate. Evidence from a system containing $H_2{}^{16}O_2$ - $H_2{}^{18}O$ ruled out the source of oxygen for methyl ketone formation to be water, in a Wacker-type process. Only terminal olefins are oxidised to methyl ketones, internal and cyclic olefins remain inert. Mimoun claimed that evidence for the pseudocyclic intermediate comes from the exchange reaction between $Na_2PdC\ell_4$ and $CF_3CO_2HgCH_2CH(Ph)OOH$, affording acetophenone in good yield[64][5].

Scheme 19

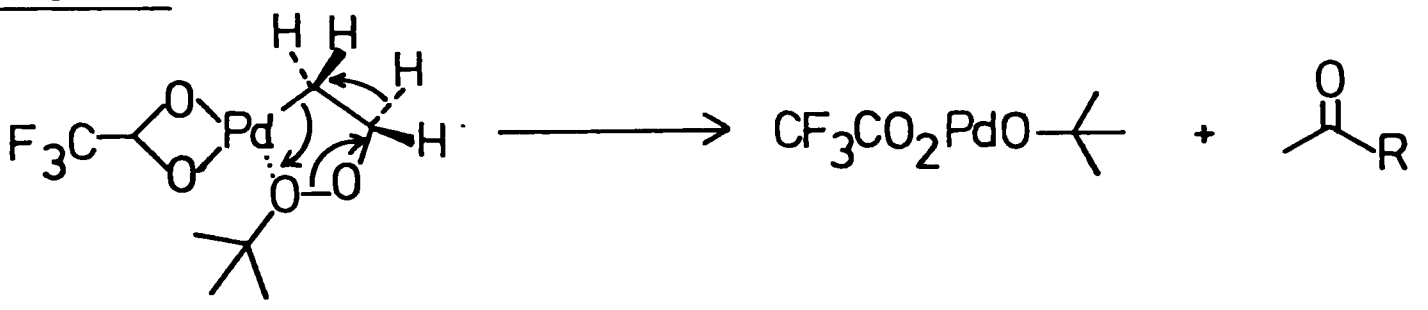

Pd(OAc)2 (14)
H2O2
HOAc
AcO-Pd-OOH
H2O
H2O2
AcO-Pd—OH
AcO-Pd
R
O—OH
R
Me
O
AcO Pd
H
R
O
O
H



[5]

The reactivity of olefins with hydrogen peroxide is similar to that in an analogous complex $[CF_3CO_2PdO\text{-}\underline{t}\text{-}Bu]_4$.[65] Mimoun proposes that this tetramer, formed from $Pd(II)(CF_2CO_2)_2$ and t-butyl hydroperoxide in benzene solution, oxidises terminal olefins to methyl ketones via the pseudocycle shown in Fig. 10.

Figure 10



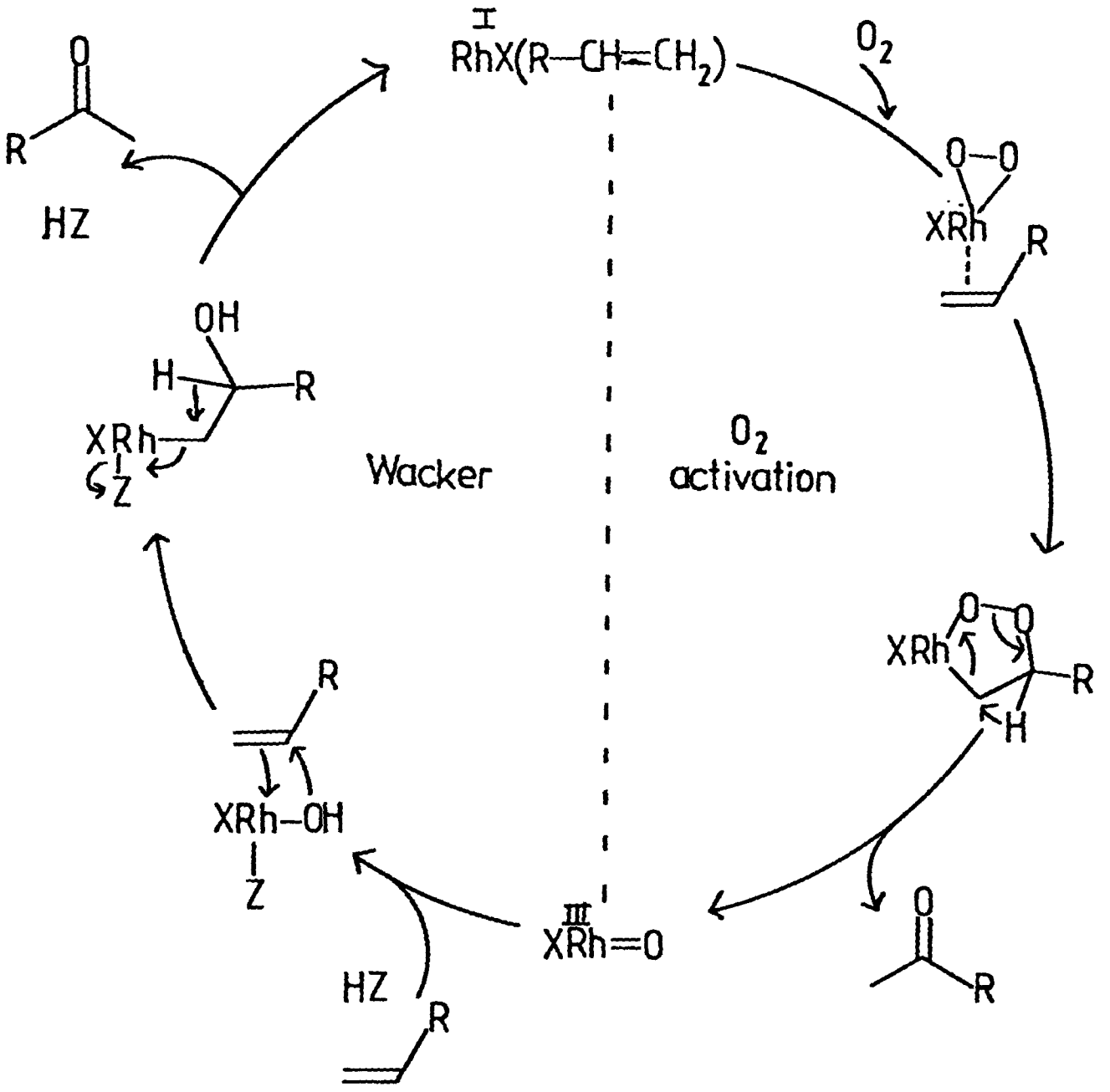
The ketonisation can be made catalytic in palladium species in the presence of an excess of t-butylhydroperoxide[66].

2.3.3 Dioxygen

Cationic Rhodium(I) Complexes. Mimoun was intrigued by his observations that the $RhCl_3$ - $Cu(ClO_4)_2$ couple, or even $Rh(ClO_4)_3$ alone, were efficient catalysts for the selective oxidation of terminal olefins to methylketones by dioxygen in alcoholic solutions at ambient temperature[67]. This led him to suggest a dual mechanism comprising an oxygen activation process and a separate Wacker-type

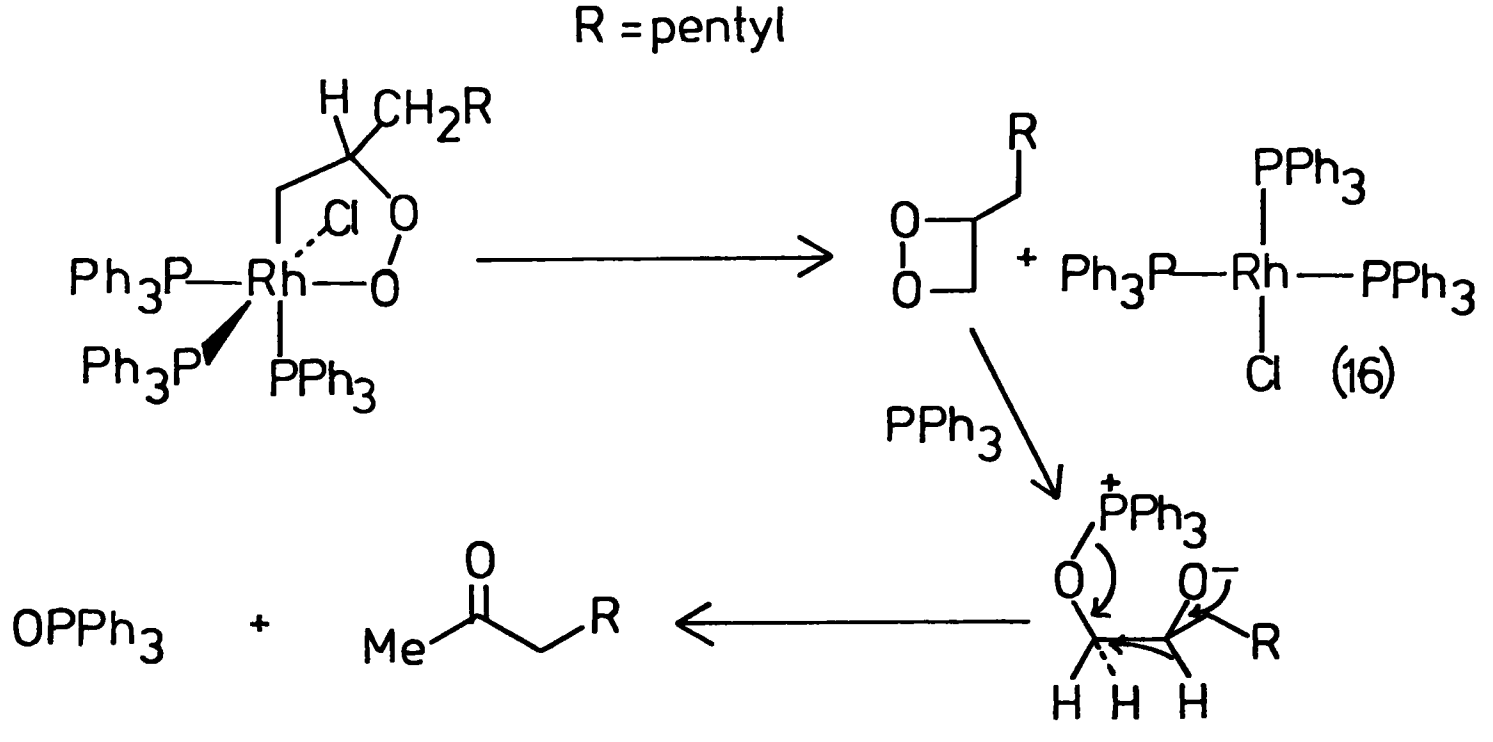
oxidation involving cationic intermediates. Later researches, employing both rhodium peroxo complexes of the general formula $[RhO_2L_4]^+ A^-$ (L = $AsPh_3$; A = $C\ell O_4$, PF_6) and cationic rhodium(I) π-olefinic complexes such as $[Rh(1,7\text{-octadiene})_2]^+ A^-$ strengthened his proposition of a dual catalytic cycle[68]. Scheme 20 illustrates how the five-membered metallocycle, formed by activation of dioxygen, collapses to give one molecule of methyl ketone. The hypothetical Rh(III) = O complex is protonated and the second coordinated olefin subsequently hydroxymetallated, in a manner analogous to the Wacker process, to afford the second mole of methyl ketone. Thus the incorporation of both oxygen atoms, derived from O_2, can be accounted for by this scheme.

Neutral Rhodium(I) Complexes. Read initially reported[69] a novel, non-free-radical oxidation of 1-octene to octan-2-one with concomitant oxidation of triphenylphosphine by oxygenated solutions of $Rh(PPh_3)C\ell$. He later showed[70] how the process could be made mildly catalytic by the presence of excess triphenylphosphine. Mares[71] further studied this system using $H_2\ ^{18}O$ present in the medium, looking for isotopic incorporation in the product ketone. Finding only sufficient ^{18}O-label to account for $H_2\ ^{18}O$-ketone exchange he concluded that oxygen could not be derived from a Wacker-type nucleophilic attack of OH^-. Read has proposed the formation of a metallocyclic intermediate and its collapse to give a dioxetan. Rapid attack by coordinated triphenylphosphine produces a zwitterion which decomposes to products (Scheme 21).


I
RhX(R–CH=CH2)
O2
O–O
XRh
R
O
R
HZ
OH
H
R
XRh
Z
Wacker
O2
activation
R
XRh–OH
Z
III
XRh=O
HZ
R
O
O
XRh
R
H
O
R

SCHEME 20

Scheme 21



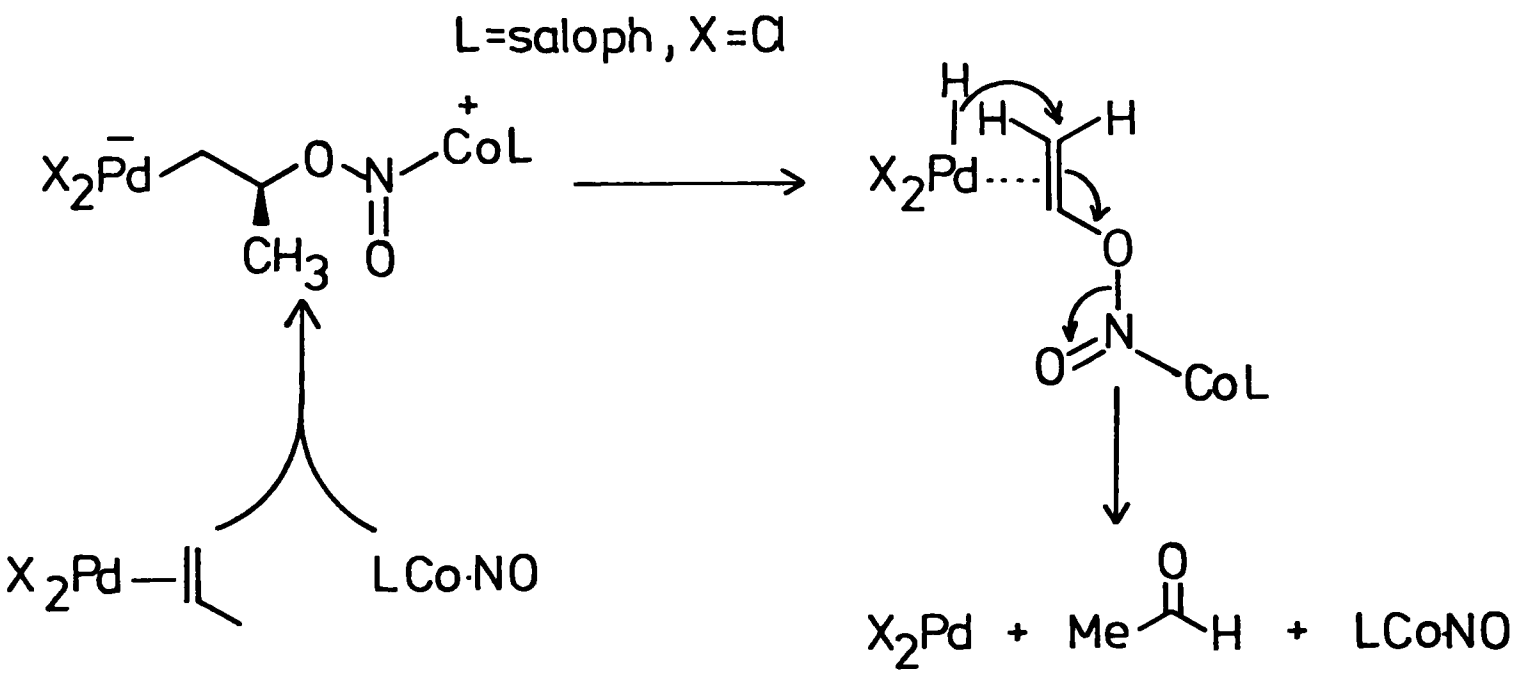
Further comment on this mechanism will be made in Chapter II.

2.3.4 Transition Metal Nitro Complexes

Mares has reported that the nitro complex py. $Co(saloph)(NO_2)$ (saloph = N,N'-bis(salicylidene-o-phenylene)diamino) oxidised triphenylphosphine to its oxide[72] and in the presence of Lewis acids (BF_3, Li^+) extended this oxidation chemistry to organic sulphides and alcohols[73]. More importantly, he enhanced the susceptibility of olefins to nucleophilic attack by their co-ordination to palladium, thereby enabling the cobalt nitro complex to oxidise the olefin to its methyl ketone. The nitro group is clearly reduced to the corresponding nitrosyl but may be reoxidised by dioxygen, making the overall reaction catalytic. Thus ethene yields acetaldehyde and propene acetone in up to 1300% yield (based on cobalt). Mares states that the product forming step

(Scheme 22) involves β-hydride elimination followed by hydride shift.

Scheme 22



Of related interest is the preliminary report by Kelly[74] that the palladium nitro complex $Pd(CH_3CN)_2\ C\ell(NO_2)$ converts, in a marginally catalytic manner, 1-decene to decan-2-one, presumably via an intramolecular analogue of Mares' system.

2.3.5 Metalloporphyrin Complexes

It has been shown above that metalloporphyrin complexes may catalyse the oxidation of olefins by free-radical or 'oxygen-activation' pathways, with variable selectivity. There exists only one example of such a complex which is selectively able to oxidise olefins to methylketones, this was reported by Perree-Fauvet[75]

for the complex Mn(III)(tpp)Cℓ in the presence of dioxygen and $(NBu_4)(BH_4)$. The latter reagent further reduces the ketonic product to alcohol. Thus styrene yields acetophenone (2000% based on Mn) and 1-phenylethanol (1700%). The transformation is inhibited by high concentrations of dioxygen, but the mechanism of oxidation is, as yet, unexplored.

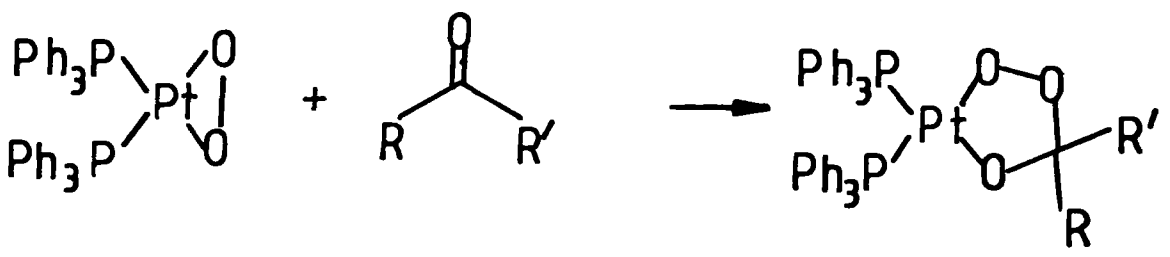
SUMMARY

Olefins may be oxidised in the presence of transition metals by a variety of oxygen donors. The metal may simply initiate the formation of oxygen-centred free-radicals which then attack the olefin in an unselective manner. Alternatively the metal may serve to activate the oxygen source or the olefin to oxidation occurring within its coordination sphere. This latter process yields either epoxide or methyl ketone with high selectivity.

CHAPTER 1

1.1 The Reaction of Carbonyl Compounds and Electrophilic Olefins with Bis(triphenylphosphine)dioxygen-platinum (0)

It was reported concurrently by Wilkinson[76] and Ugo[77] that the peroxo complex, bis(triphenylphosphine)dioxygenplatinum (0),[7] (1), reacted with carbonyl compounds. Cyclic peroxy adducts were formed readily from a wide range of aldehydes and ketones (both cyclic and acyclic). The molecular structure of the representative complex (17) in Figure 11 has been established by X-ray crystallographic analysis[77].



(1)

R,R' = ALKYL
R=R'=Me (17).

Fig. 11

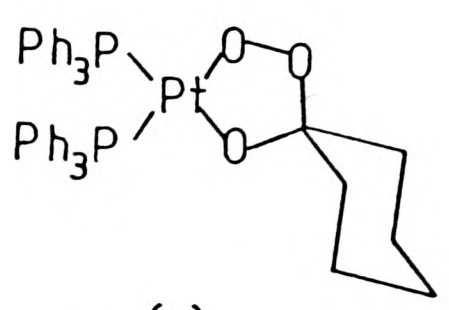
The course of this general class of addition reactions may be followed conveniently by Fourier transform ^{31}P nuclear magnetic resonance spectroscopy. ^{31}P has nuclear spin, $I = \frac{1}{2}$, while only 33.7% of naturally occurring platinum contains the spin active, $I = \frac{1}{2}$, isotope ^{195}Pt. The ^{31}P n.m.r. spectra of platinum complexes

are thus characterised by a central resonance displaying satellites of one-sixth intensity, the distance between the satellites corresponding to the coupling constant $J_{^{195}Pt^{31}P}$.

The phosphorus atoms in (1) are magnetically equivalent by virtue of the molecules' C_2-axis, and appear as a singlet at 17.4 p.p.m. with ^{195}Pt satellites, $^{1}J_{PtP}$ = 4034 Hz. Figure 12 illustrates the ^{31}P n.m.r. spectrum of the cyclic adduct (18) formed in the reaction between (1) and cyclohexanone. In this unsymmetrical complex each phosphorus atom is now magnetically inequivalent and so appears as a separate doublet, with P-P coupling, $^{2}J_{P1P2}$ of 20 Hz. Coupling of each phosphorus atom to ^{195}Pt gives two pairs of satellites with $^{1}J_{PtP1}$ = 3504 Hz., and $^{1}J_{PtP2}$ = 3487 Hz.

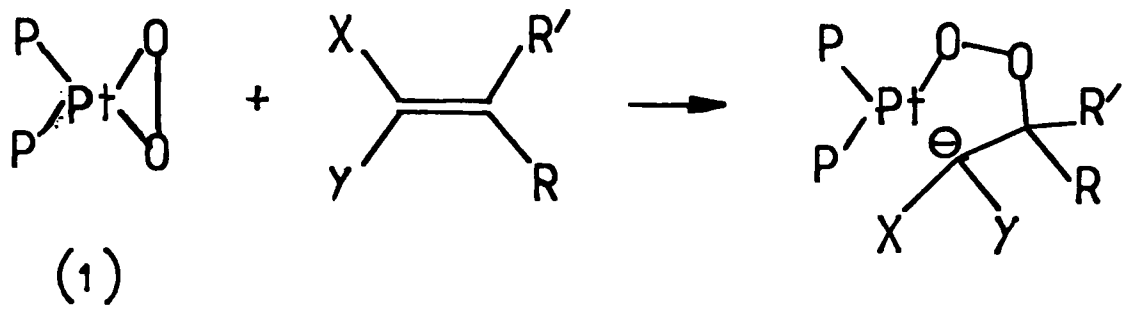
Sheldon[78] demonstrated for a series of electrophilic olefins an interesting addition reaction of (1). Figure 13 illustrates how olefins, geminally disubstituted with strongly electron withdrawing groups, undergo a 1,3-dipolar cycloaddition via a stabilized carbanionic intermediate.

It was therefore of interest to determine the course of the reaction with an unsaturated carbonyl compound since initial addition might involve either a perketyl complex or the metallacycle derived from 1,3-dipolar cycloaddition. The ultimate goal was transfer of oxygen from the dioxygen complex to the olefinic double bond.

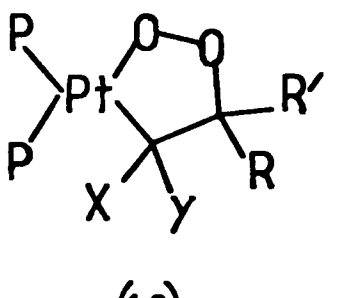


(18)

Fig.12 ^{31}P NMR [36·4 MHZ]



	R′	R	X	Y
	CN	CN	CN	CN
	H	Ph	CN	CN
	H	Ph	CN	NO_2
(19a)	Me	Me	CN	CN



(19)

P=PPh_3

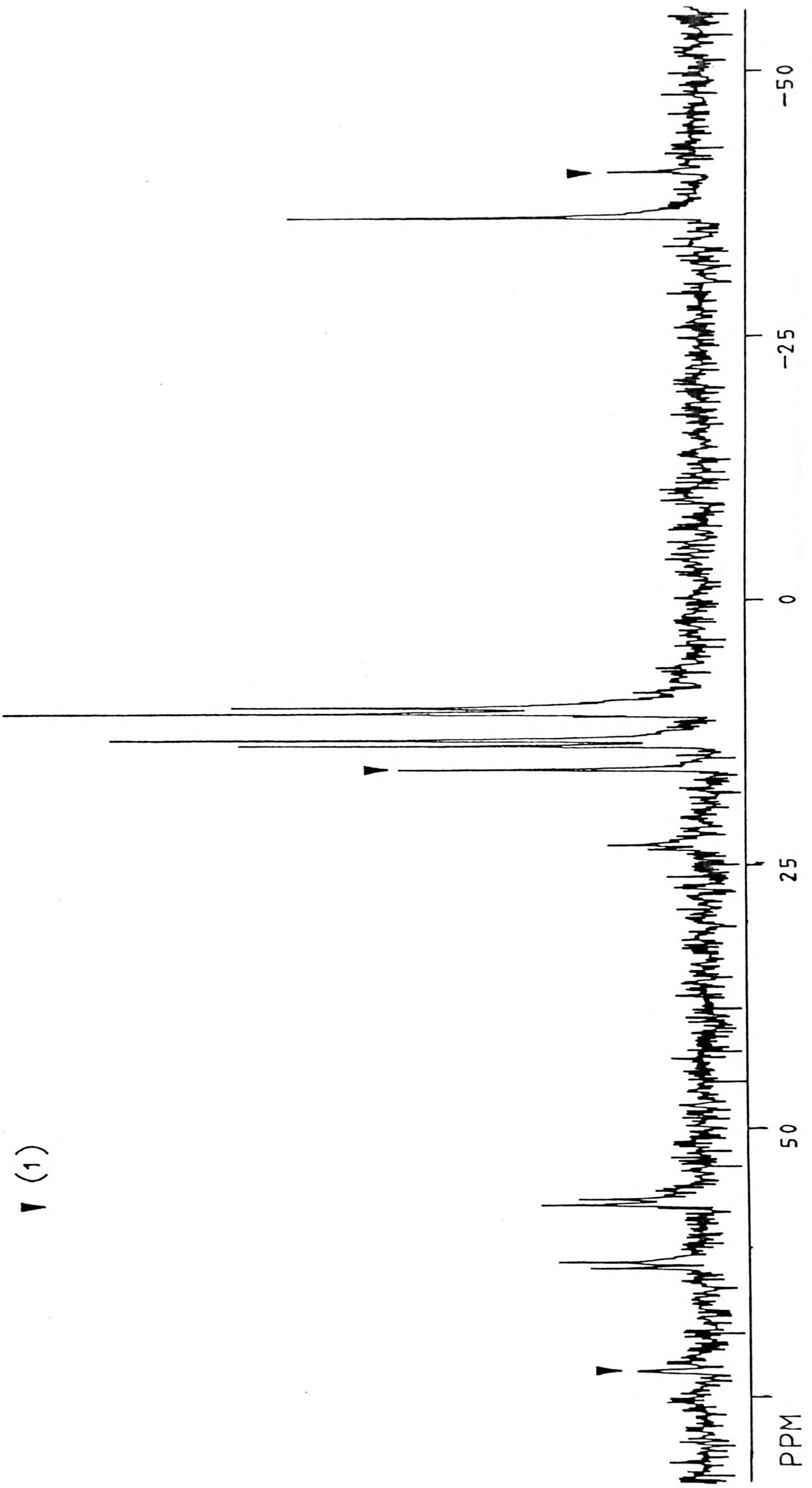
Fig. 13

1.2 Formation of a Perketyl Adduct, (20) by the Reaction of Bis(triphenylphosphine)dioxygenplatinum (0) with trans But-2-enal

The course of reaction between (1) and a range of α,β-unsaturated carbonyl compounds was followed conveniently by ^{31}P n.m.r. (36.43 MHz). Thus, when 3 molar equivalents of trans but-2-enal, (20), were added to a solution of (1) in dichloromethane in an n.m.r. tube, which was then sealed under argon and kept at 21°C, the ^{31}P n.m.r. spectrum revealed, after 2.5 hr, the appearance of signals corresponding to the perketyl adduct (Figure 14). At about 1/20 the rate, a minor species was also observed to appear. After 18 hr (Figure 15) all dioxygen complex has disappeared. Evaporation of most of the solvent followed by trituration with toluene gave a white solid which was recrystallised to give a species whose ^{31}P n.m.r. spectrum corresponded to the major component. This characteristic ^{31}P n.m.r. spectrum is consistent with a perketyl structure, (20), derived by cycloaddition of the dioxygen complex to the carbonyl group of trans but-2-enal, since it had two inequivalent phosphorus nuclei which are both trans to an electronegative atom.

Further evidence for this structure came from the ^{1}H n.m.r. spectrum (300 MHz) of the recrystallised complex (Figure 16). The low field aldehydic proton resonance at 9.0 p.p.m. has disappeared and becomes coincident with the olefinic protons at 5.65 p.p.m. The spectrum is simple in appearance with broad resonances centred at 5.40 and 5.65 p.p.m. Further, the carbonyl stretching frequency, $\nu_{C=O}$, present in the infra-red spectrum of trans-but-2-enal is

Fig. 14 ^{31}P NMR [36.4 MHZ]



▼ (1)

Fig.15 ^{31}P NMR [36.4 MHZ]

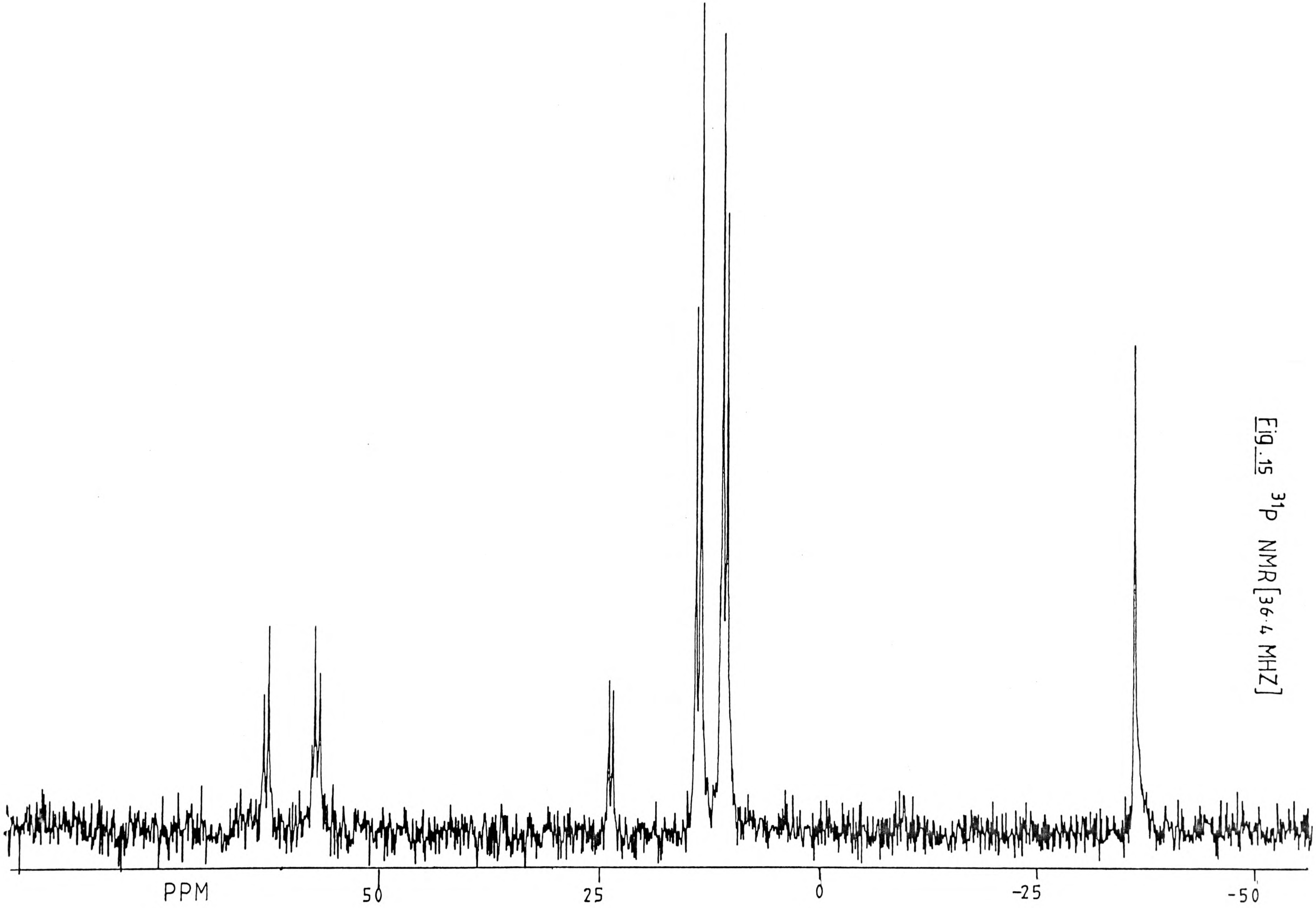
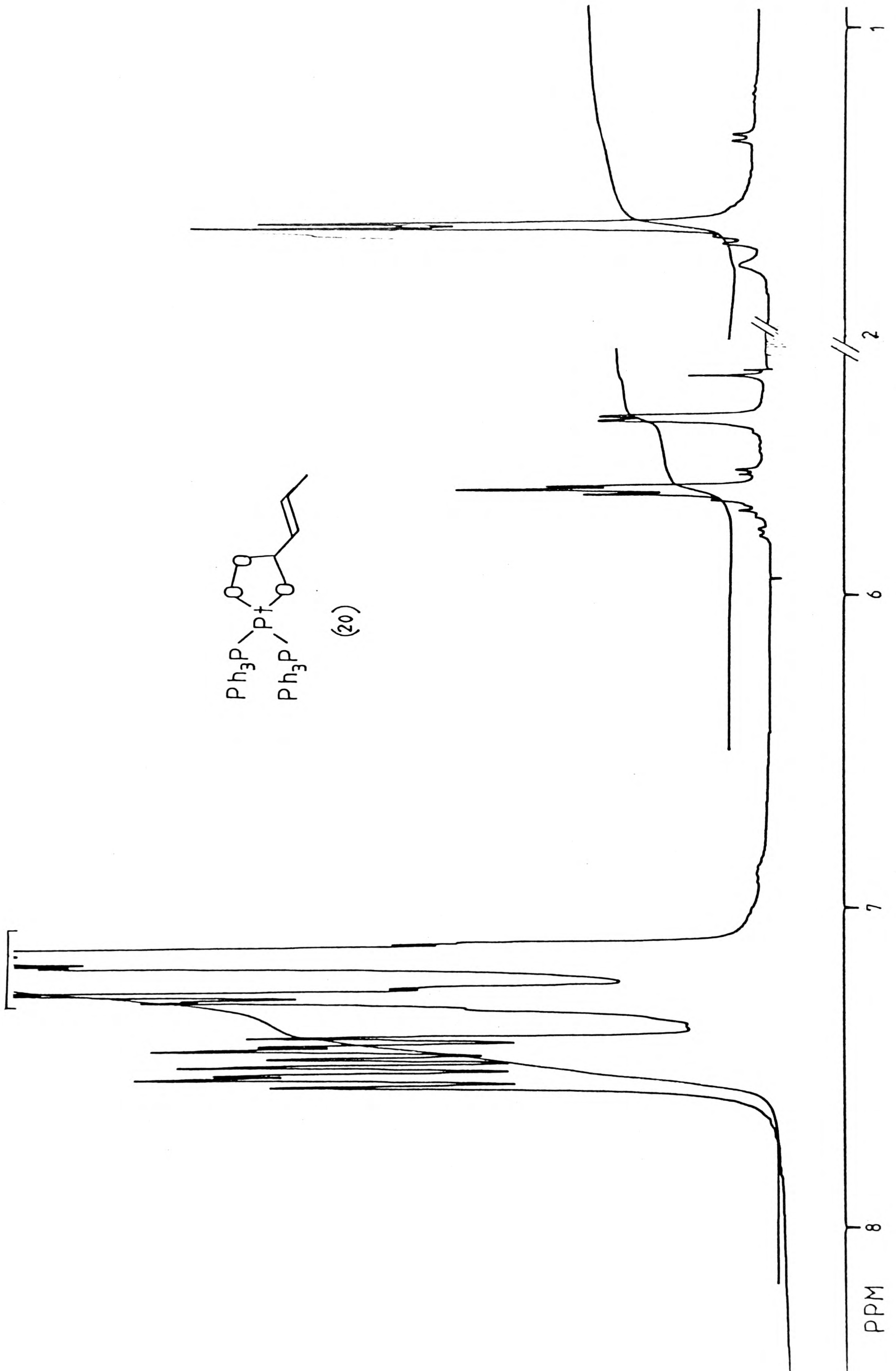


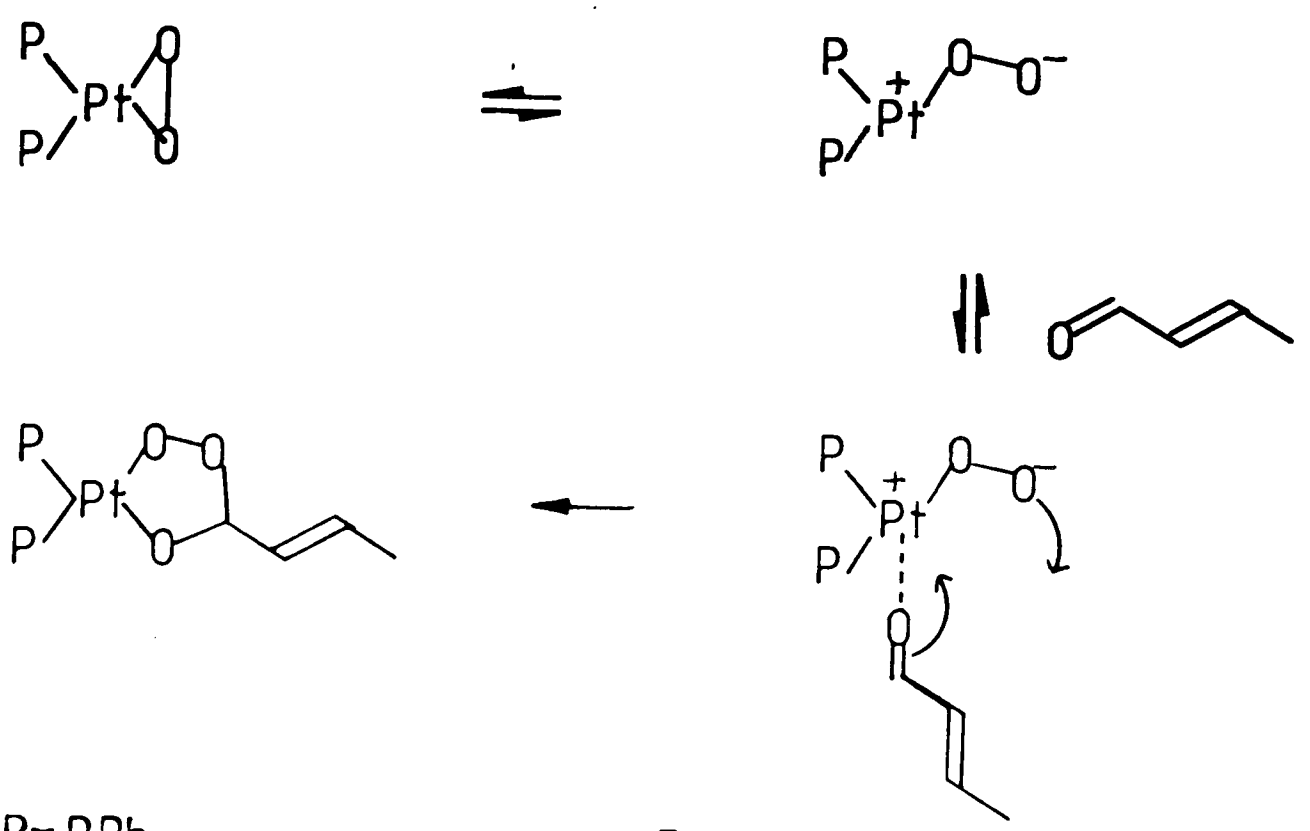
Fig.16 ^{1}H NMR (300 MHZ)



absent in the complex. The characteristic intense band due to the O-O stretching in the parent dioxygen complex has become too weak to be identifiable, although the O-O stretch in perketyl complexes is generally found shifted to higher frequency[79].

The perketyl complexes are thermally unstable and so it has not been possible to obtain mass spectral data.

Ugo[80] has provided evidence that prior binding of the carbonyl group at the vacant coordination site of the formally d^8 Pt(II) complex is an important feature of this class of cycloadditon reactions. The retarding effect of good donor solvents such as dimethylformamide, the presence of severe steric constraints upon the incoming carbonyl compound and rather negative values of $\Delta S^{\ddagger}$ strongly suggest a bimolecular association. Figure 17 illustrates how the mechanism may be viewed as a nucleophilic attack by the platinum bonded peroxidic[81] anion to the coordinated carbonyl group of <u>trans</u> but-2-enal. The reaction is promoted by the enhanced electrophilic character of the carbonyl carbon atom, when the carbonyl group is coordinated to the metal.



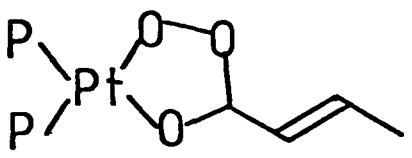
P= PPh$_3$

Fig. 17

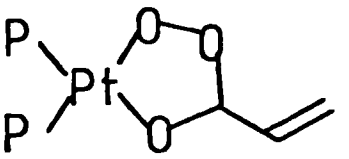
Otsuka[79] has demonstrated by ^{18}O-labelling studies that the insertion of the carbonyl group of ketones proceeds with retention of the O-O moiety derived from dioxygen.

Other α,β-unsaturated carbonyl compounds also formed perketyl adducts. They are listed with spectral data in Table 4. Data for complex (18), the cyclohexanone adduct, is given for comparison. The table illustrates the similarity of chemical shift and coupling constant for the whole range of these structurally related complexes.

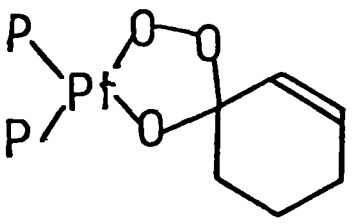
Over a period of days, at ambient temperature, in the presence of free trans but-2-enal, signals originating from complex (20) decreased in intensity in the ^{31}P n.m.r. spectrum. Concomitantly, and without the appearance of intermediates, the minor species' signals (as in Figure 15) became predominant. Inspection of the ^{31}P n.m.r. spectra indicated that the secondary adduct was formed in about 90% yield. A little (ca. 5%) decomposition product $(Pt(PPh_3)Cl_2]$ and triphenylphosphine oxide (ca. 5%) were also identified by their characteristic resonances. This secondary adduct is thermally stable under all conditions tested. Similar behaviour was observed with (21) (vide infra) but in all other cases the decomposition or rearrangement products gave complex ^{31}P n.m.r. spectra which were not readily interpreted. For this reason attention was concentrated on the adducts obtained with trans but-2-enal.



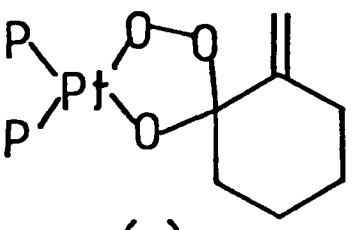
(20)



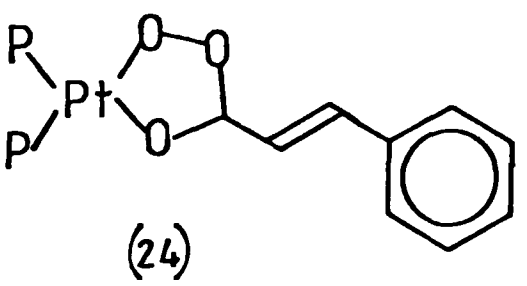
(21)



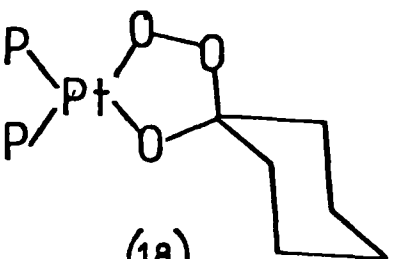
(22)



(23)



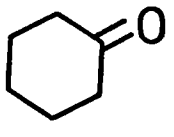
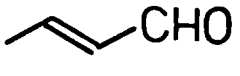
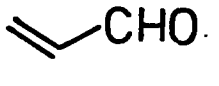
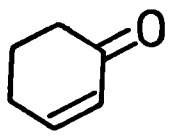
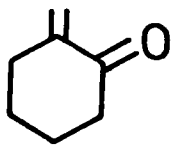
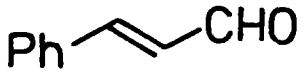
(24)



(18)

P = PPh_3

Table 4. ^{31}P n.m.r. Data* for Perketyl Adducts

Carbonyl Compound	Complex	δP^1	δP^2	J_{PtP1}	J_{PtP2}	J_{PP}
	18	11.4	14.7	3504	3487	20
	20	13.7	10.9	3567	3353	16
	21	13.3	10.9	3350	3320	20
	22 †	6.0	12.4	3560	3400	18
	23 †‡	12.1	12.1	3526	3326	20
	24 §	13.0	11.4	3568	3362	13

*$CH_2C\ell_2$; 21°C; 36.43 MHz; δ (p.p.m. H_3PO_4 (85%)), J (Hz)

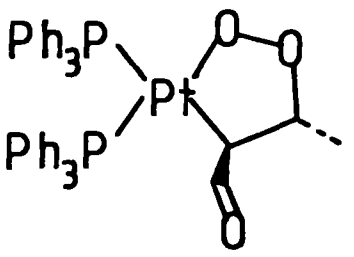
†Solutions of complexes were unstable. Resulting spectra were too complex to analyse but signals corresponding to phosphine oxide and $[Pt(PPh_3)_2C\ell_2]$ were identified.

‡Coincidence of signals for P_1 and P_2 led to a singlet as central resonance, but AB quartet sideband structure.

§This complex was only very slowly decomposed in solution whence products resulting from reaction with solvent were identified.

1.3 Characterisation of the Secondary Adduct of (1) with trans But-2-enal

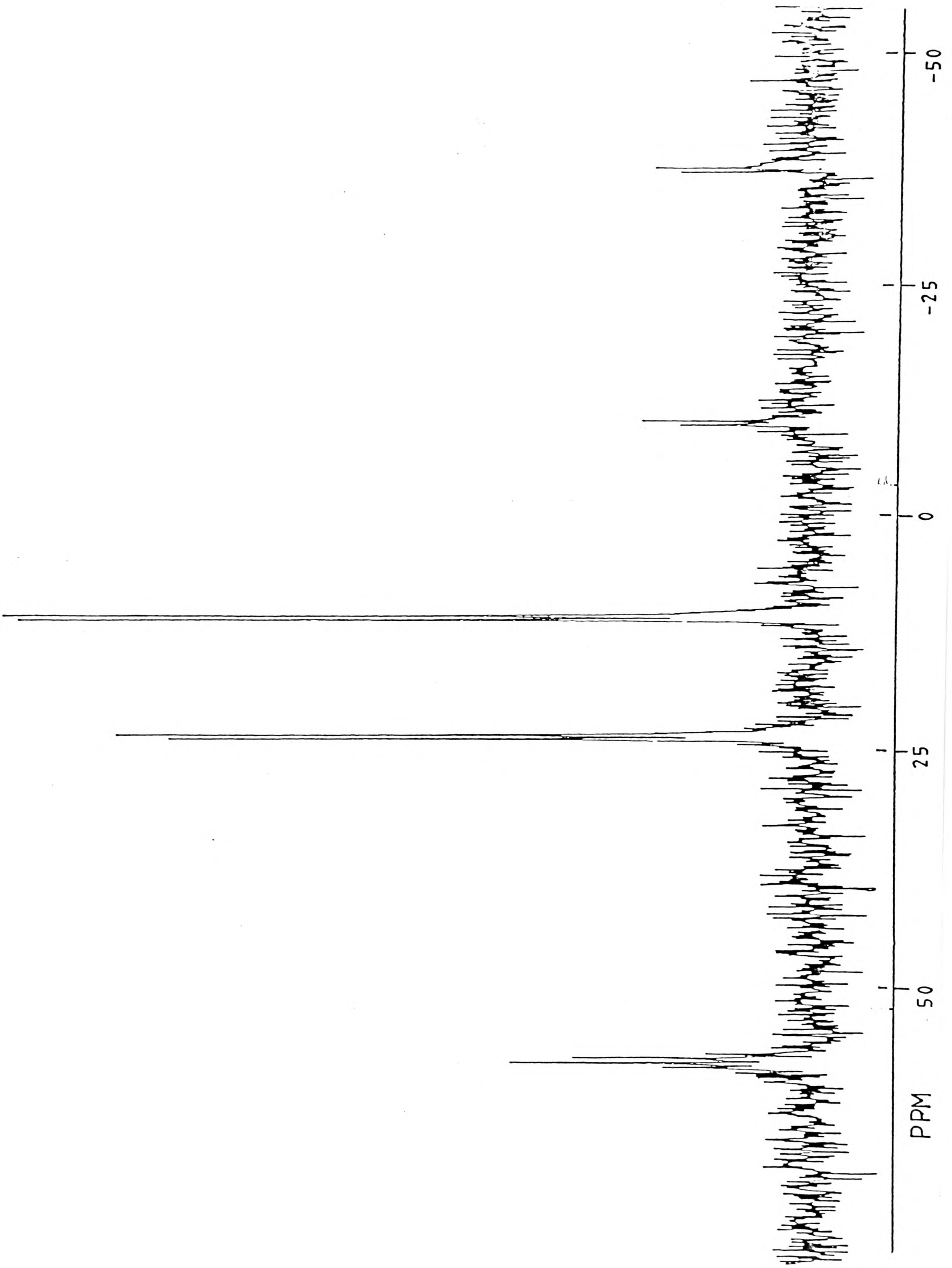
The secondary adduct of (1) with trans but-2-enal could be isolated in pure form as an air-stable white crystalline solid, (25). The ^{31}P n.m.r. spectrum of (25) in dichloromethane, Figure 18, was essentially the same as that obtained from the reaction mixture. Most pertinently, one phosphorus resonance has moved 10 p.p.m. downfield with decrease in $^{1}J_{PtP}$ from 3567 Hz, in the perketyl complex (20), to 2426 Hz. This large decrease in coupling constant suggested that the moiety trans to the perturbed phosphorus was exhibiting a larger 'trans-effect' than the perketyl oxygen*. The field-desorption mass spectrum of (25) gave a parent ion of molecular mass 820 (the same mass as the perketyl adduct (20)). A strong absorption at 1665 cm^{-1} in the infra-red spectrum of (25) suggested the presence of a carbonyl group. A product formally representing peroxyplatination of trans but-2-enal was considered first.



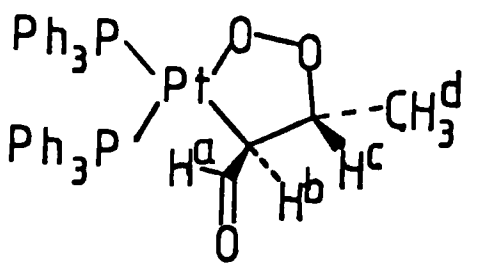
(25)

*The 'trans-effect' of ligands is a factor influencing $^{1}J_{PtP}$. For example, in the complex cis-[chloromethyl bis(triethylphosphine) platinum], (26), $^{1}J_{PtP}$ (trans to chloride) = 4179 Hz and $^{1}J_{PtP}$ (trans to methyl) = 1719 Hz. In this respect halide resembles oxygen in trans influence. See Ref. 82.

Fig.18 ^{31}P NMR (36·43 MHZ)



This structure was confirmed by the ^{1}H n.m.r. (300 MHz) spectrum, shown in Figure 19, and tabulated in Table 5.

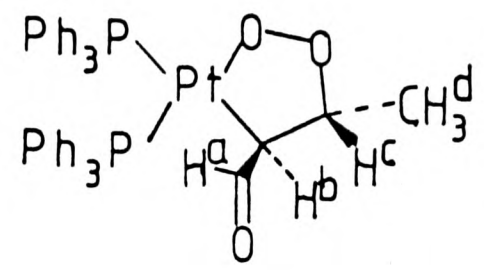


(25)

Table 5 ^{1}H n.m.r. data for (25)

Resonance	δ p.p.m	Coupling Constants Hz	
H^a	9.0	$^{3}J_{ab}$	3
H^b	3.1	$^{3}J_{ab}$	3
		$^{3}J_{bc}$	12
		$^{2}J_{Ptb}$	79
		$^{3}J_{P^1b}$	6
H^c	3.6	$^{3}J_{dc}$	6
		$^{3}J_{bc}$	12
		$^{4}J_{P^1c}$	1.5
$CH_3{}^d$	1.3	$^{3}J_{dc}$	6
Ph^e	7.2-7.6	-	

Notably, the resonance at 9.0 p.p.m. was ascribed to the aldehydic proton H^a. The proton α to platinum exhibits satellites with $^{2}J_{PtH}$ = 79 Hz.* The stereochemistry about C2-C3 was assigned



(25)

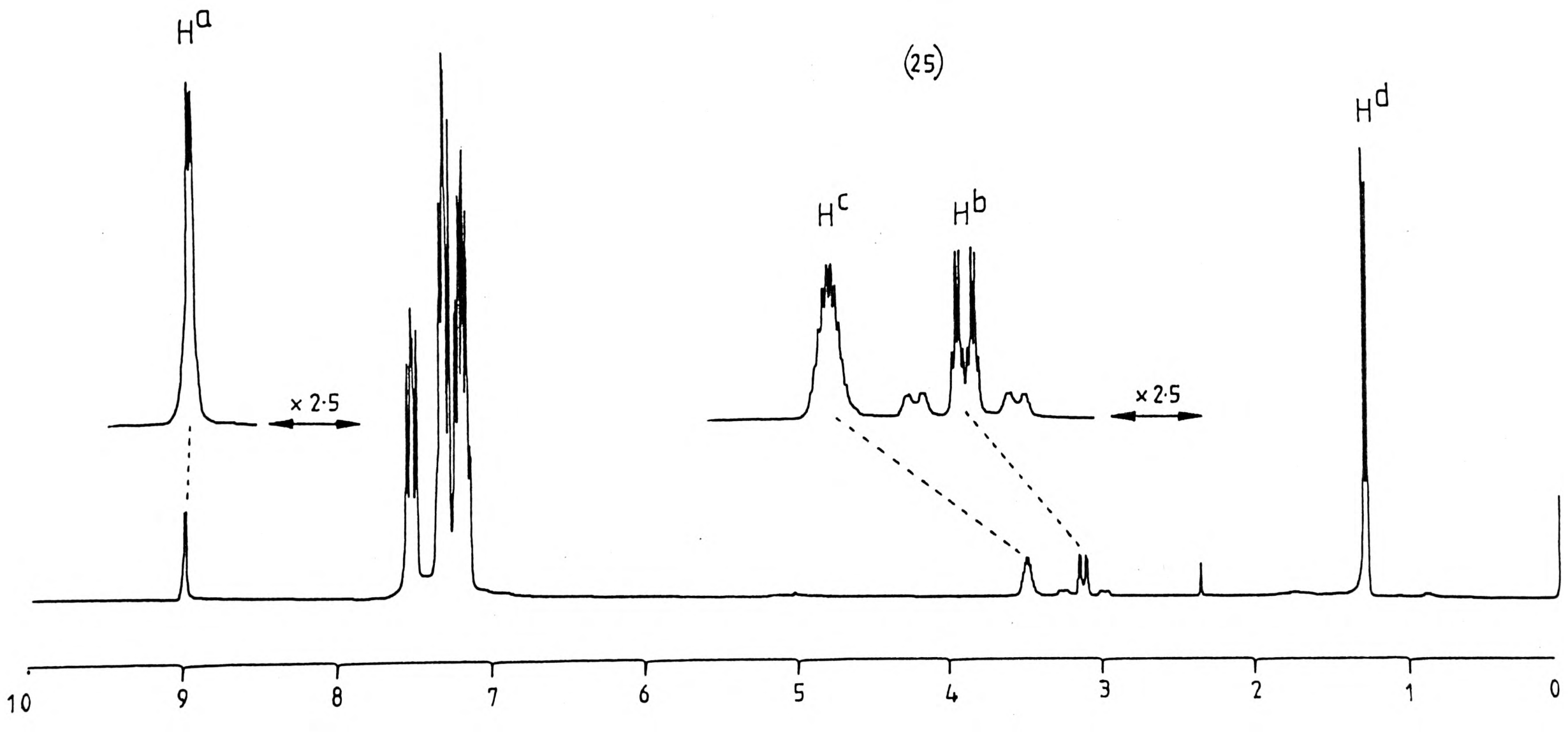
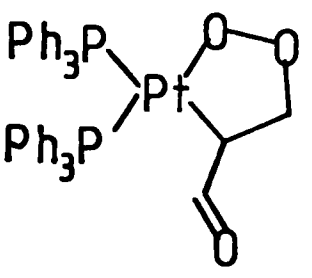


Fig.19 ^1H NMR[300 MHZ]

as trans because of the large vicinal coupling constant of 12 Hz between H^b and H^c. Figures 20 and 21 illustrate a full analysis of the spin systems for H^b and H^c respectively.

A solution of the perketyl adduct of propenal, complex (21), behaved similarly to that of trans but-2-enal, quantitatively forming a new species in the presence of free aldehyde. The ^{31}P n.m.r. spectrum revealed a characteristic widely spaced pair of doublets with ^{195}Pt satellites suggesting structure (27).

Figure 22.



(27)

ppm. Hz

δP^1 23.34 $^1J_{PtP^1}$ 2400

δP^2 10·6 J_{PtP^2} 3320

$J_{P^1P^2}$ 18

Secondary Adduct of Propenal and Complex (1) with ^{31}P n.m.r. Data

*At 300 MHz the ^{195}Pt satellites appear to be broadened, whereas the same sample run at an operating frequency of 90 MHz gave much sharper satellites. This broadening at higher fields may be due to ^{195}Pt chemical shift anisotropy - a relaxation process strongly dependent upon the strength of the observing magnetic field (Ref. 83). In some cases the satellites may disappear. For an example in Pt(II) square planar nucleotide complexes see Ref. 84 .

**An alternative configuration in which H^b and H^c are eclipsed would also be consistent with the large coupling constant. In the following discussion it has been assumed that the trans geometry of the initial olefin was maintained in the complex.

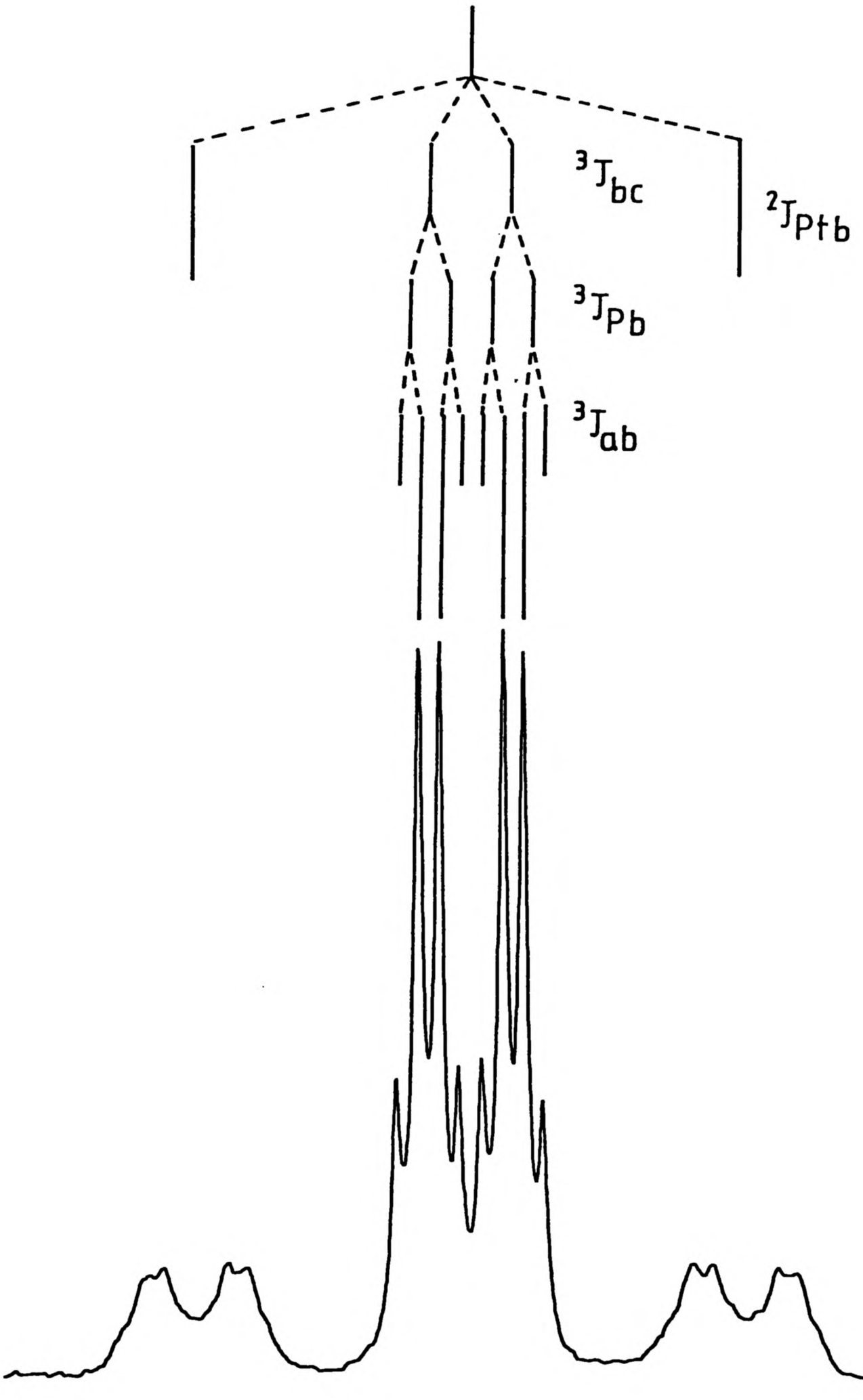


Fig. 20 ^{1}H NMR [300MHZ]

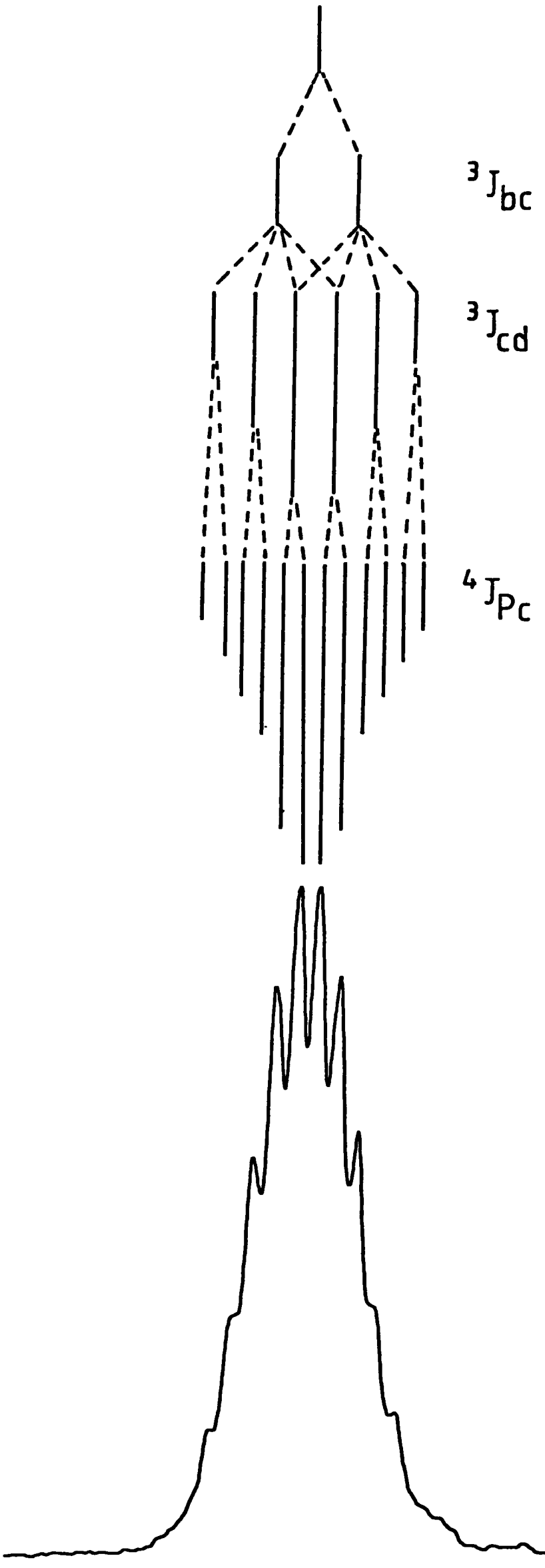


Fig. 21 ^{1}H NMR [300 MHZ]

Green and co-workers have reported[85] a metalladioxacyclopentane of similar structure to (25) or (27). Reaction of $Pt(cod)_2$ (28), with but-1-en-3-one produces the intermediate olefin complex (29) which, at low temperature, adds dioxygen with loss of one but-1-en-3-one to produce the metallacycle, (30) (Figure 23). Complex (30) was characterised by ^{13}C and ^{1}H n.m.r. although, at least for the latter, resonances attributable to the cyclooctadiene ligand masked diagnostic resonances in the metallacycle.

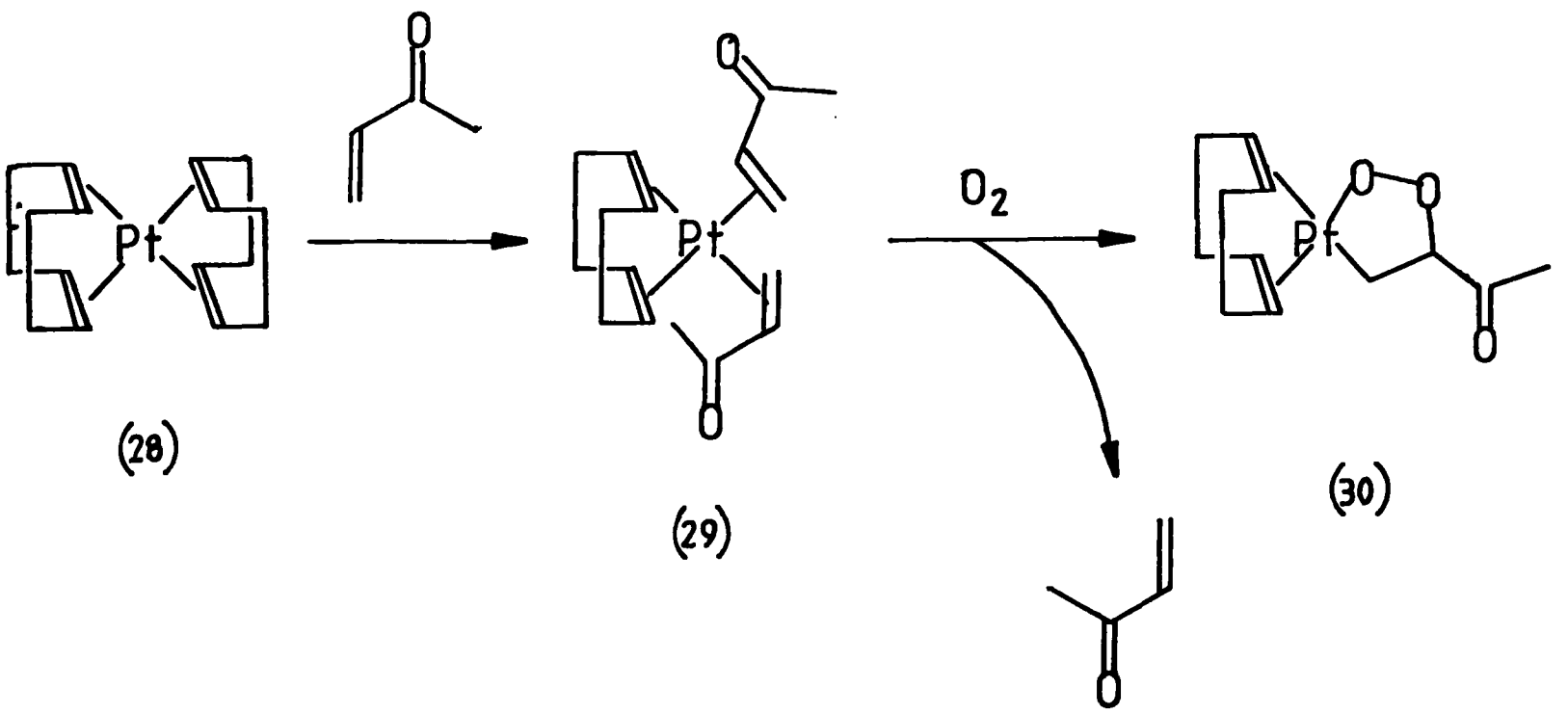


Fig.23

According to these authors peroxymetallation of but-1-en-3-one has occurred in the opposite regiochemical sense to complex (25), making the carbonyl group β to oxygen rather than platinum.

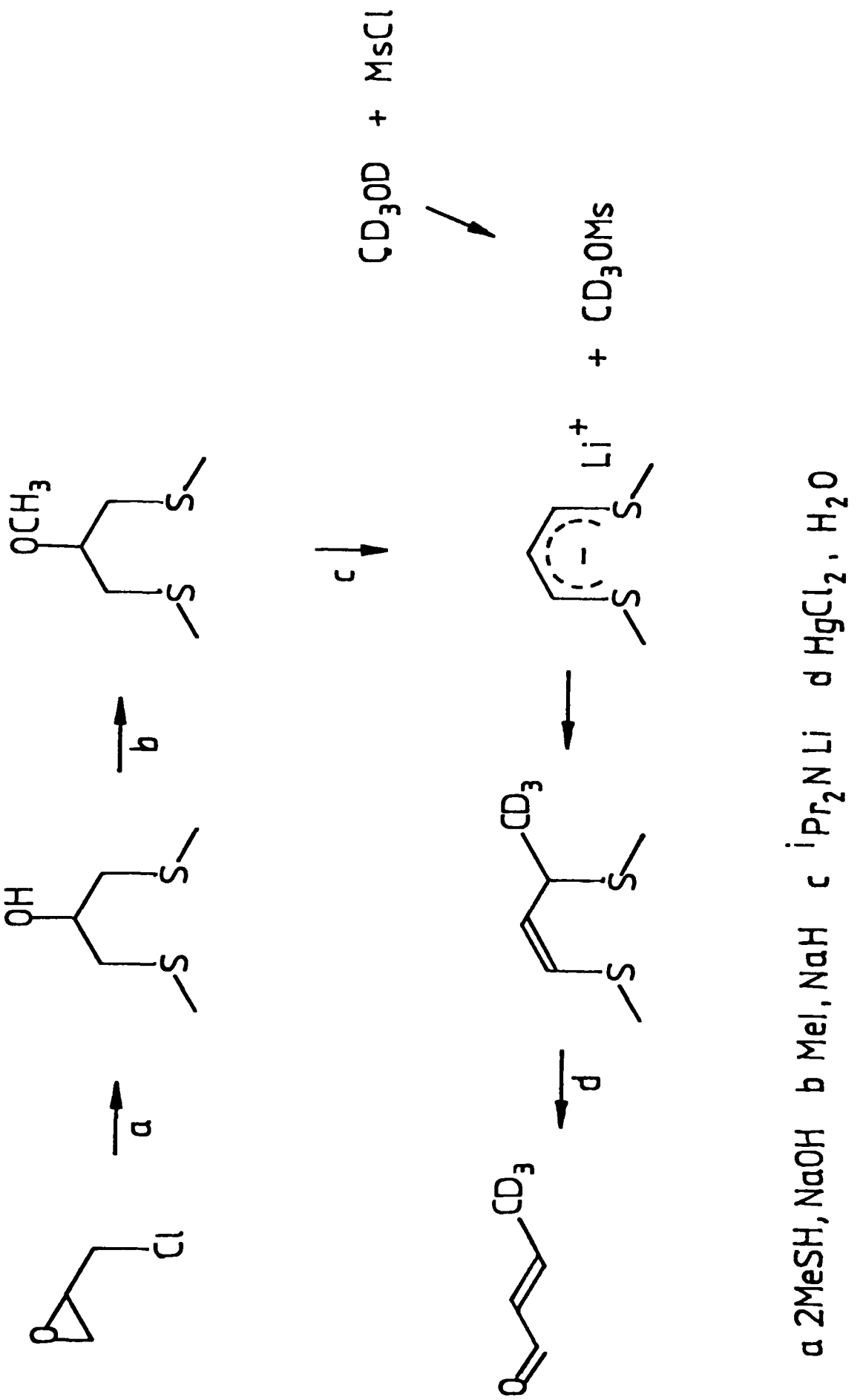
1.4 Mechanistic Studies on the Formation of the Metalladioxacyclo-Pentane (25)

In order to gain insight into the mechanism by which the metalladioxacyclopentane, (25), was formed we undertook the synthesis of specifically deuterated trans but-2-enal. Figure 24a shows how incorporation of a deuterated methyl group was achieved. Addition of methyl-d_3 methanesulphonate to the formyl-vinyl anion equivalent 1,3-bis(methylthio)allyllithium[86] gave a product which could be oxidised by aqueous mercury(II)chloride to the required compound.

The perketyl adduct (31) was then obtained in pure crystalline form and characterised by ^1H n.m.r., (Figure 24b). Deuteration caused the methyl doublet at 1.6 p.p.m. to disappear and some simplification of coupling pattern at 5.65 p.p.m.

The formation of the metalladioxacyclopentane product in the presence of 3 or 10 molar excess of unlabelled but-2-enal was followed by ^1H n.m.r. (300 MHz). The results (Table 6) clearly indicated that the perketyl adduct underwent exchange with free aldehyde. Concomitant with this process was the formation of the metalladioxacyclopentane by attack of free trans but-2-enal upon the perketyl adduct. Both processes were dependent upon the concentration of free but-2-enal.

Fig. 24a



a 2MeSH, NaOH b MeI, NaH c $^{i}Pr_2NLi$ d

Fig.24b ^1H NMR [300 MHZ]

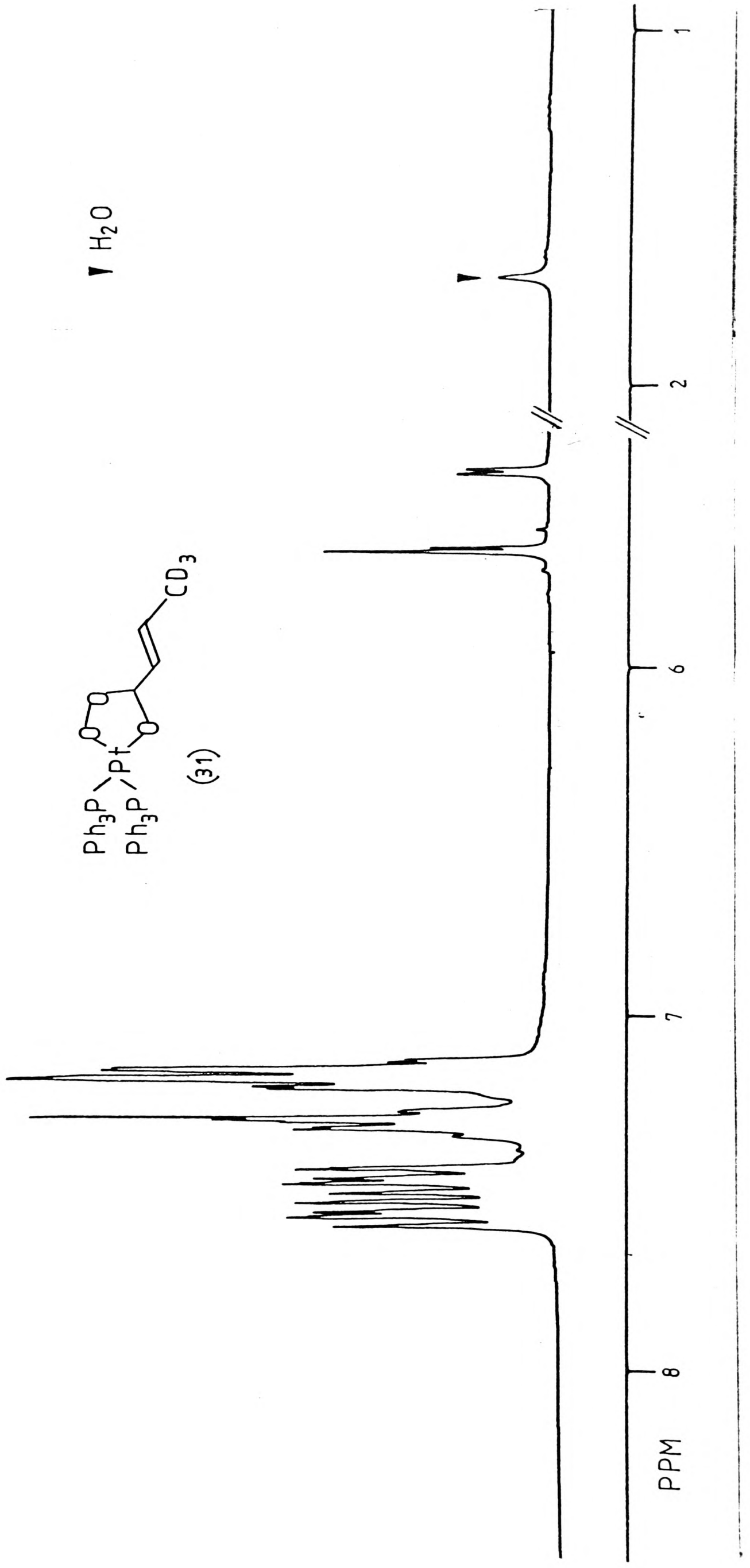


Table 6

t/hr‡	%Extent Exchange in perketyl adduct		%Extent Exchange in product		%Extent of Product formation	
	A*	B†	A	B	A	B
3	12	42	77	94	18	28
6	-	49	-	96	-	38
8.5	45	83	83	100	32	44

*Column A: 3 molar excess but-2-enal

†Column B: 10 molar excess but-2-enal

‡Temperature kept at 40°C.

Data from ^2H n.m.r. spectra was also obtained (see Experimental Section). Parallel experiments were set up in which complex (20) and trans but-2-enal-d_3 or complex (31) and trans but-2-enal reacted to afford the metalladioxacyclopentane. They led to qualitatively the same conclusion and provided evidence that the product, complex (25), does not exchange with trans-but-2-enal. Figure 25 illustrates a parallel pair of ^2H n.m.r. spectra.

Three possible pathways to product were envisaged. Scheme (A) illustrates the 'concerted' mechanism in which the product forms by a strictly intramolecular rearrangement of the perketyl adduct which is itself undergoing exchange with trans but-2-enal. Scheme (B) shows how the perketyl adduct reversibly returns

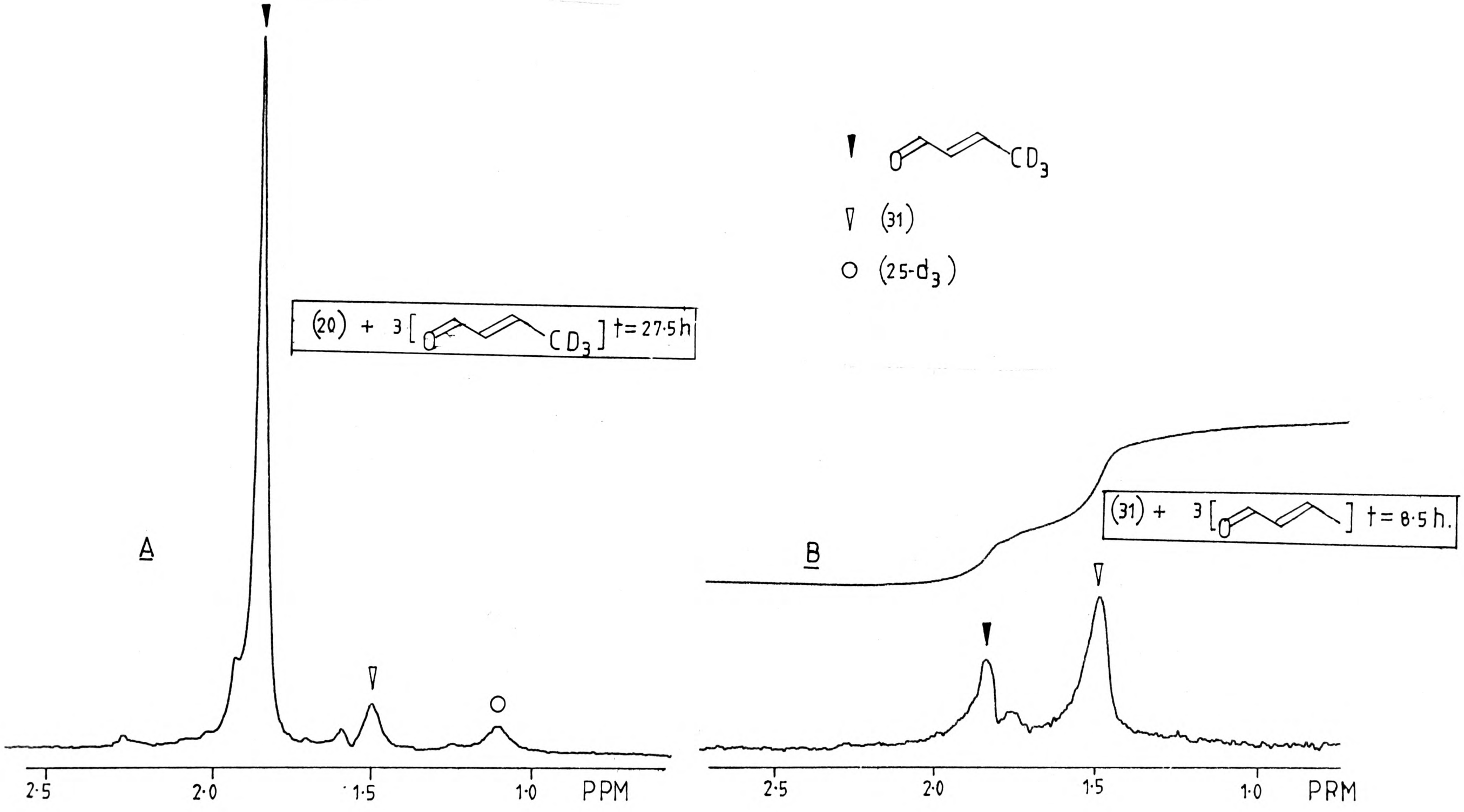


Fig. 25 ^{2}H NMR [46.0 MHZ]

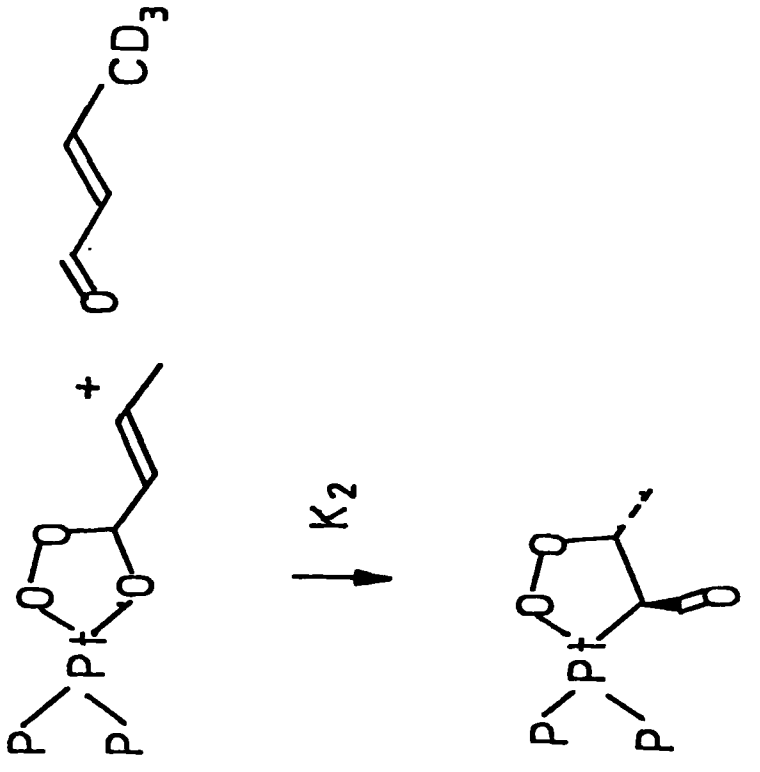
to the dioxygen complex whence it may exchange with trans but-2-enal or form product in a bimolecular reaction. In the third alternative, illustrated in Scheme (C), product may form by means of the attack upon the perketyl adduct of incoming trans but-2-enal, displacing that already bound.

The intramolecular mechanism (Scheme (A)) predicts that the perketyl complex and product are equally exchanged, since the control experiment shows clearly that the product is not labile to exchange. The observation that the product is always more exchanged than the perketyl adduct invalidates this mechanism.

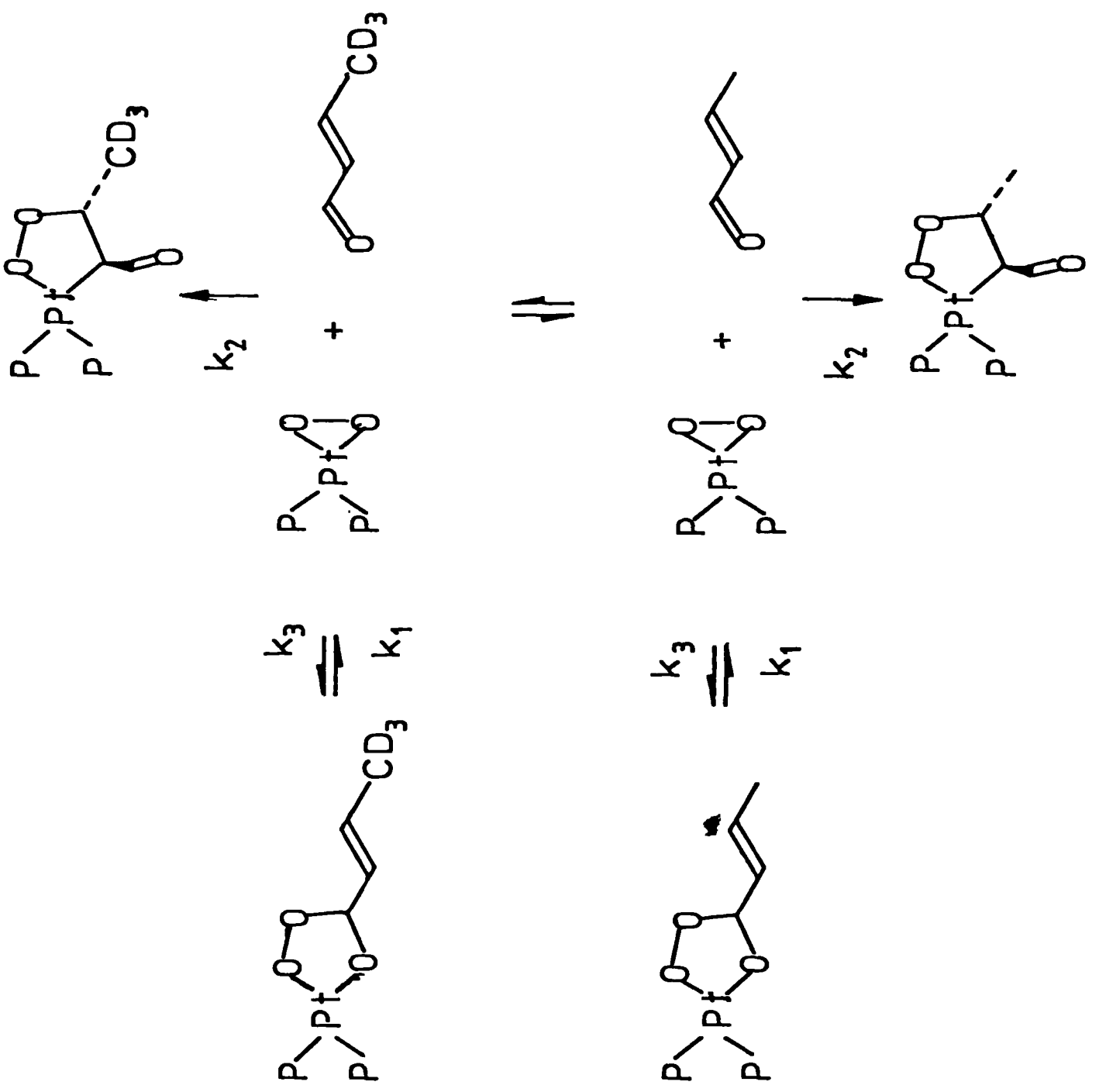
It is not possible intuitively to distinguish the reversible collapse to dioxygen complex (Scheme (B)) from the mechanism shown in Scheme (C). It was tested by a computer program* based upon numerical integration of the rate equation for the mechanism shown in Scheme (B). Since prior observation (^{31}P n.m.r.) had shown that the reaction of the dioxygen complex to form the perketyl adduct was at least 20 times faster than the reaction to form product, values of $k_3 = 20\ k_2$ were utilised and k_1 adjusted so that the steady-state concentration of the dioxygen complex was low, in keeping with the ^{31}P n.m.r. observation. The computer program plots %extent of reaction, %extent exchange in perketyl adduct and %extent exchange in product, respectively. Typical curves,

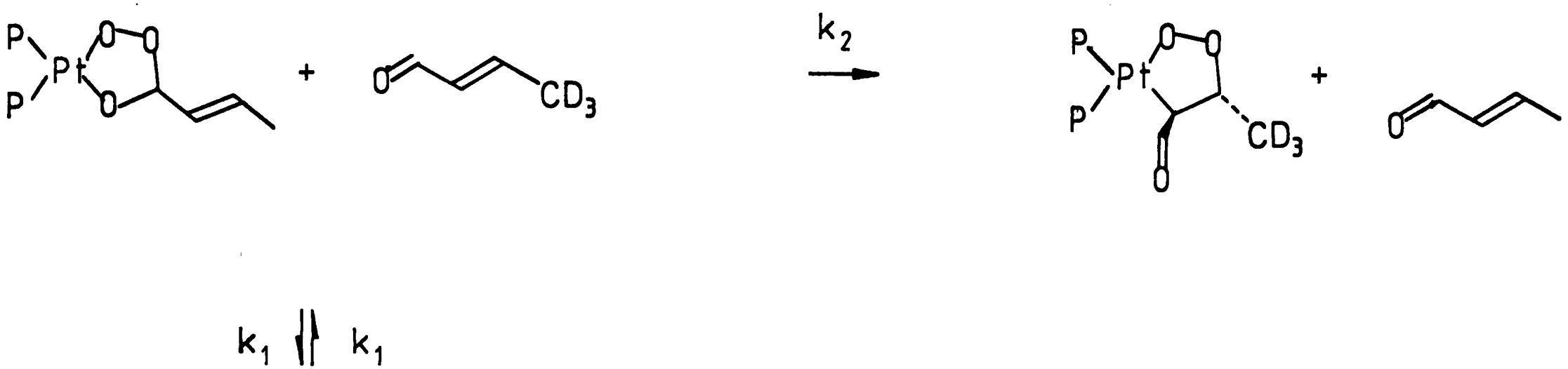
*Written by J.M. Brown (Oxford) and executed on a Hewlett-Packard HP85. The program listing is found in the Appendix.

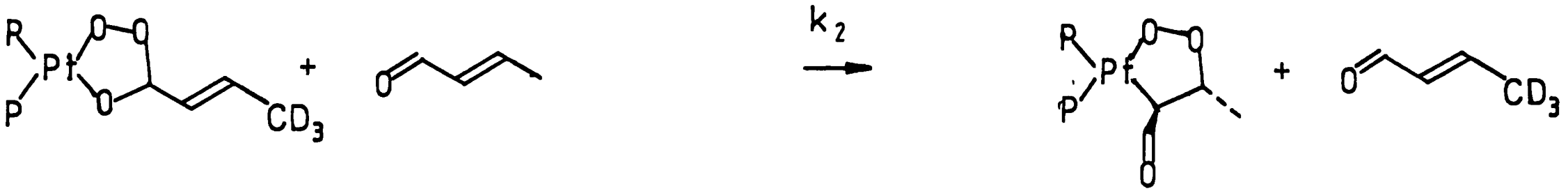
SCHEME A



SCHEME B







P=PPh3

SCHEME C

as for example Figure 26, do not correspond with observation. Most strikingly the predicted extent of product exchange is much lower than is observed. Variation of kinetic parameters did not change these general features. The displacement mechanism appears at first sight to be reasonably in accord with experimental observation. It was tested as above, the program now being written to provide numerical integration according to the rate equation applicable to the mechanism shown in Scheme (C). The fit with experimental data, shown in Figure 27, shows a good internal consistency of parameters, particularly with a 10 molar excess of but-2-enal, given an arbitrary time scale. Little confidence can be placed on the experimental time points because of the nature of removing samples for ^{1}H n.m.r. measurement.

It may be fortuitous that the best fit was achieved when rate of exchange (k_1) = rate of displacement (k_2). However, it also leads to speculation that a common intermediate is involved which, unselectively, partitions between an exchange or a displacement process (figure 28).

Fig. 28

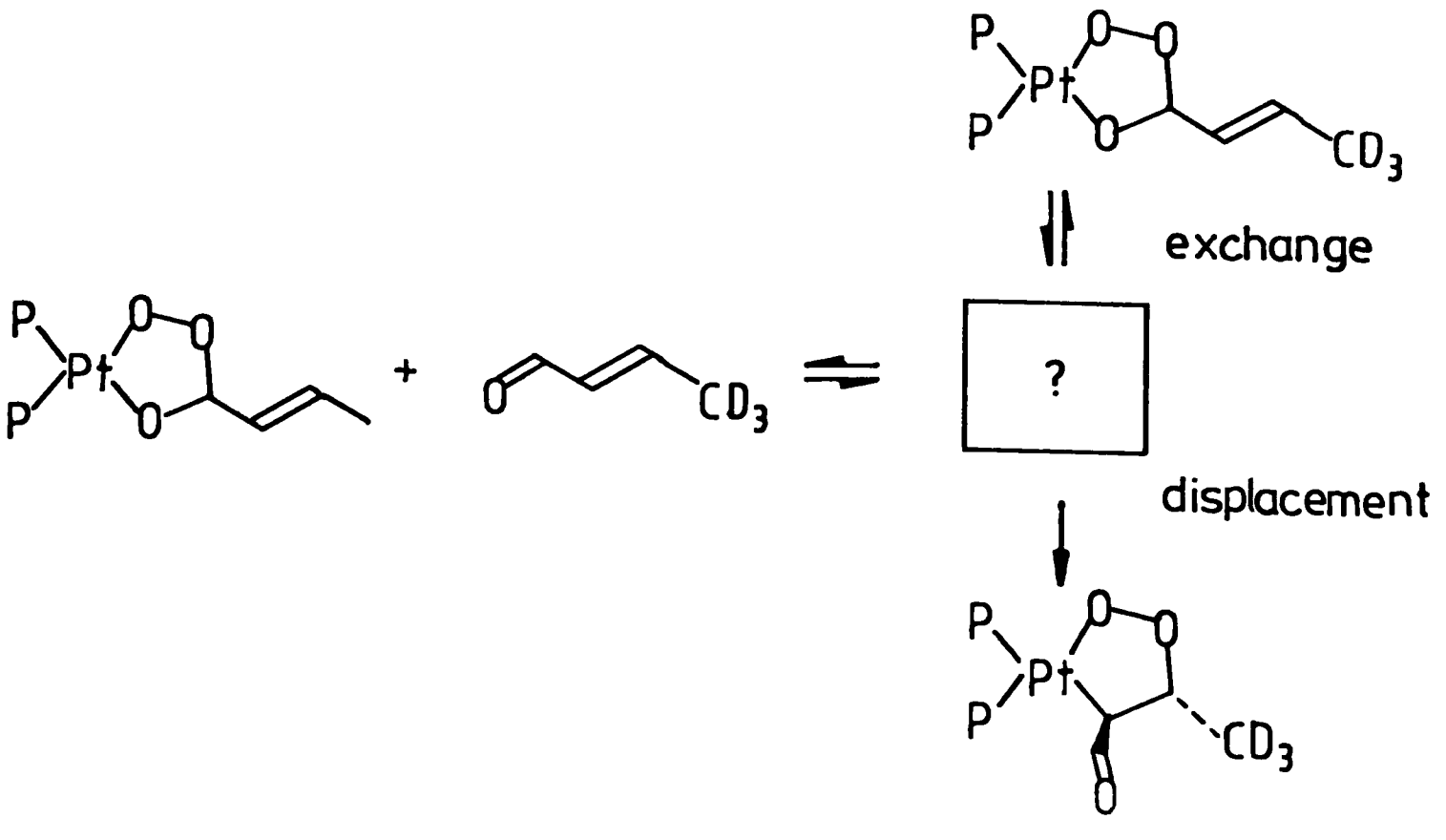
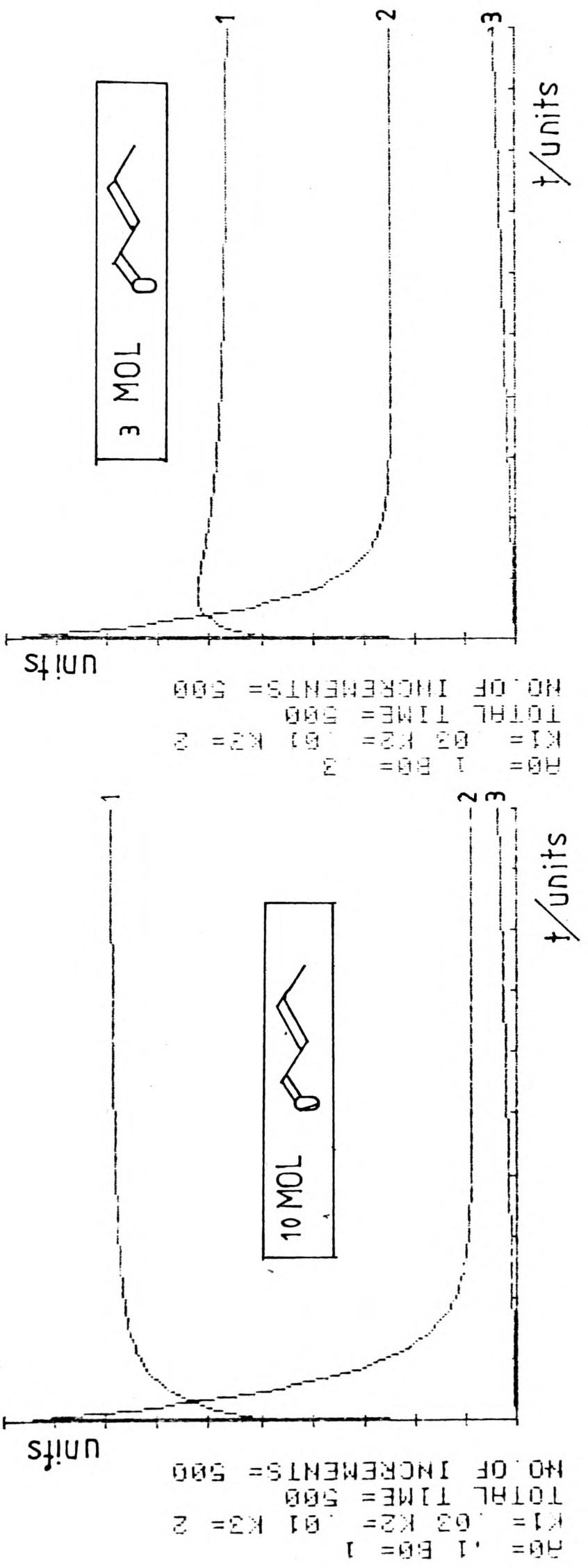
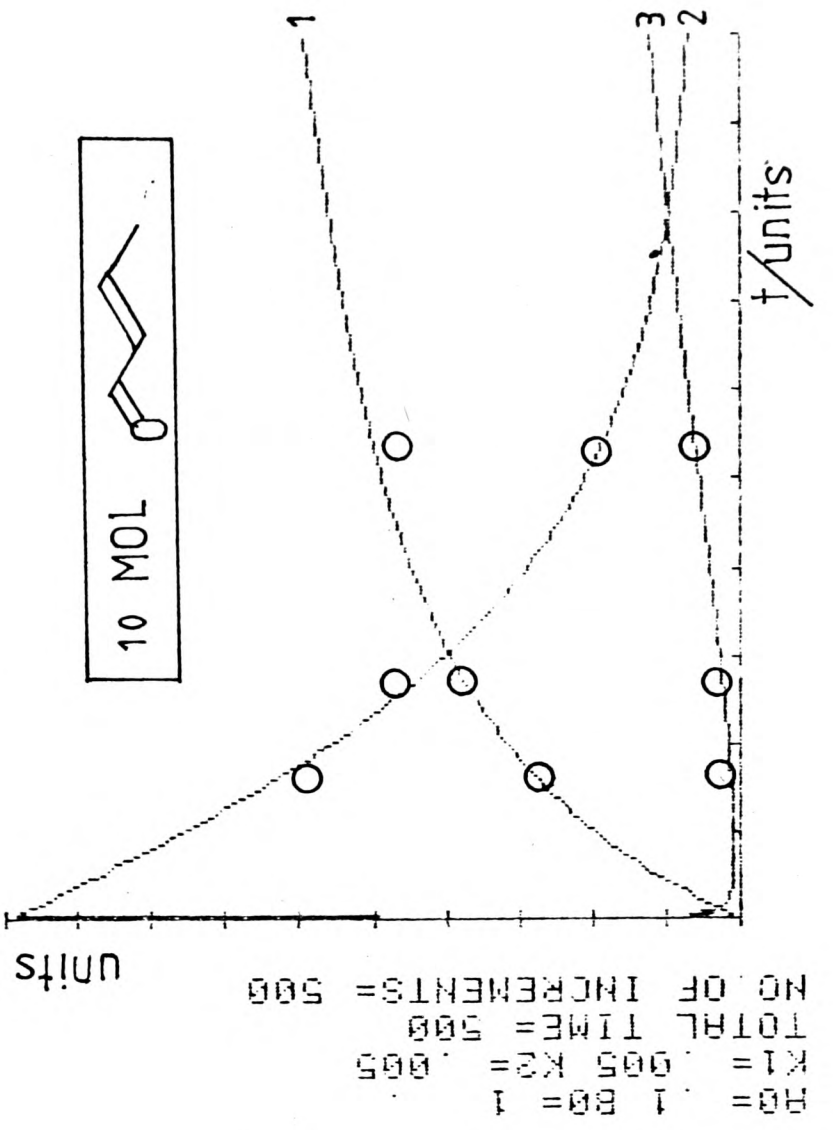


Fig. 26



1 ⁄. reaction
2 ⁄. exchange (31)
3 ⁄. " (25)

Fig. 27

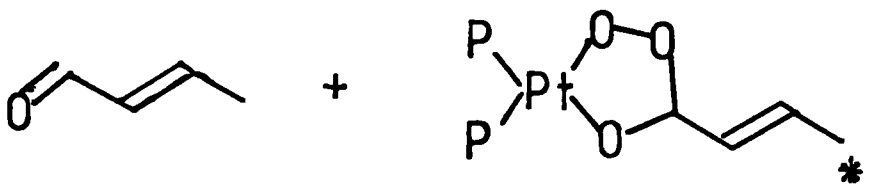


O exptl. pt.

It is reasonable to suppose that trans but-2-enal may act as a bifunctional ligand in its approach to the perketyl complex. One could then envisage nucleophilic attack by the perketyl moiety upon either the coordinated carbonyl group, leading to exchange, or the coordinated olefin leading to the metalladioxacyclopentane as shown in Figure 29. The latter mechanism is equivalent to the cycloaddition of the dioxygen complex to electrophilic olefins as has been noted and illustrated in Figure 13. However Sheldon[78] found that the cycloaddition was limited to olefins geminally substituted with electron withdrawing groups so that, for instance, 1,1-dicyano-2-methylpropene reacted instantly with the dioxygen complex, (1), whilst 1-cyano-2-methylpropene or 1,2-dicyanoethene were completely unreactive. Further, he observed no reaction with the diketone, (32), or the diester (33). This unreactivity was attributed to the steric bulk associated with the ketone and ester groups and the phenyl rings of the coordinated triphenyl-phosphine, making difficult ring closure to a metalladioxacyclopentane (Figure 30).

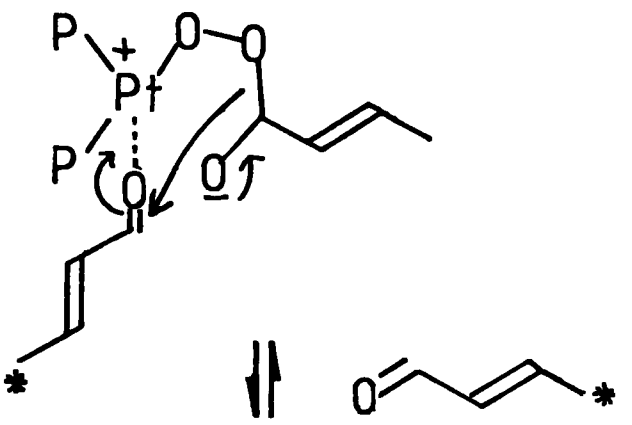
The reaction of the dioxygen complex, cis[bis(tricyclohexyl-phosphine) dioxygenplatinum (0)], (34), with dimethylacetylene-dicarboxylate (Figure 31) is unique in exhibiting an apparently symmetrical rupture of the O-O bond[87].

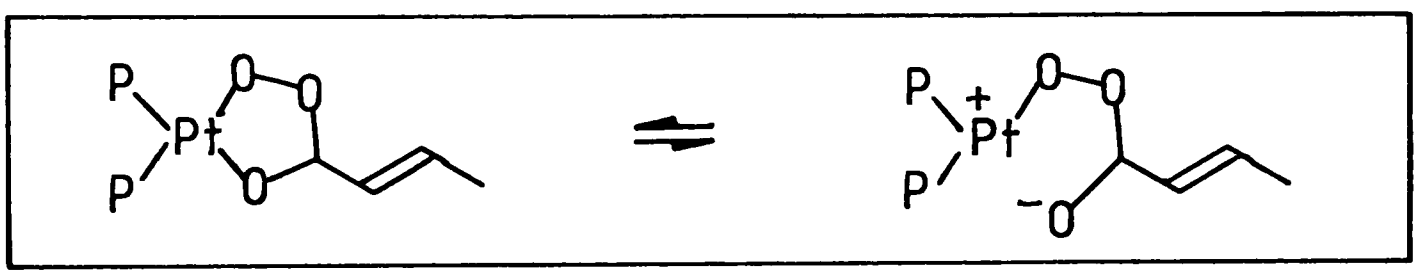
Fig. 29

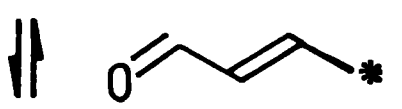




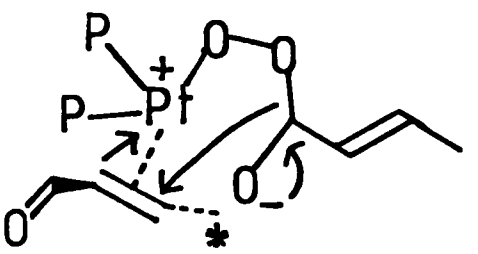
carbonyl attack



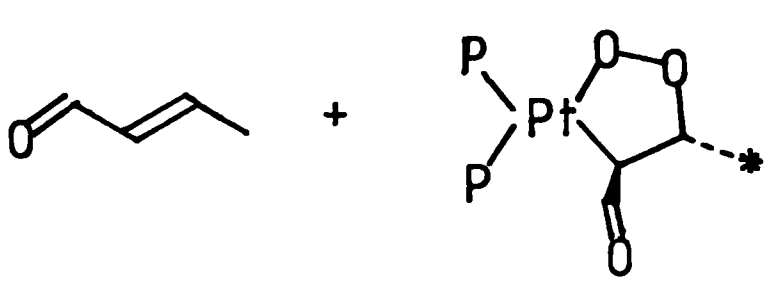




olefin attack

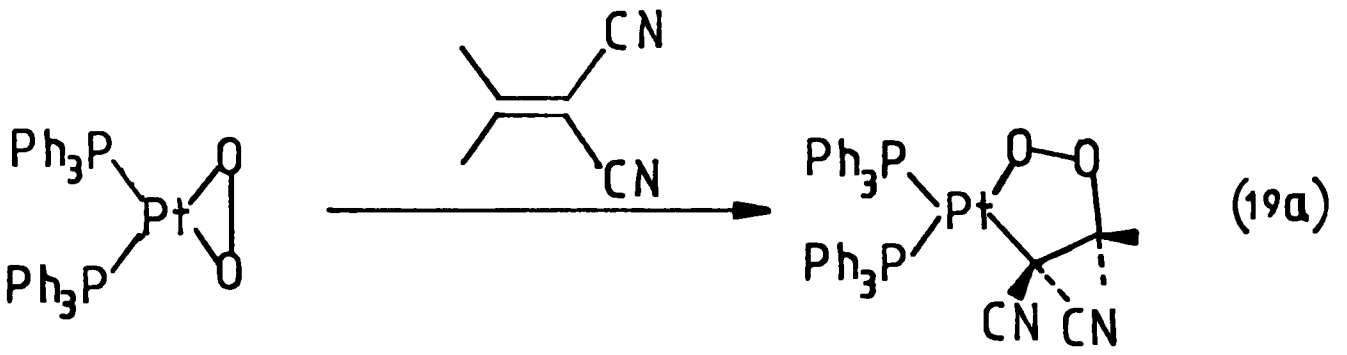




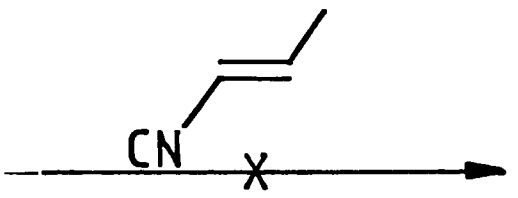


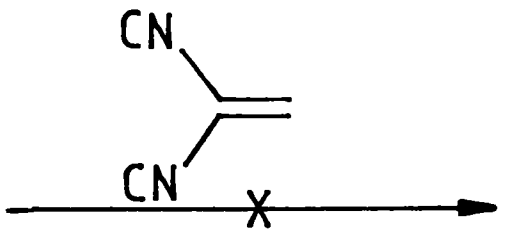
P=PPh$_3$

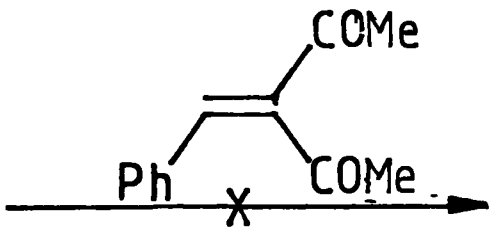
Fig. 30

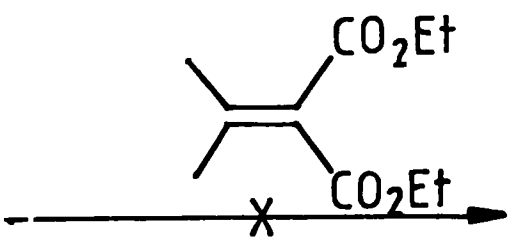

CN
CN
Ph3P
Pt
O
O
Ph3P
Ph3P
Pt
O
O
CN
CN

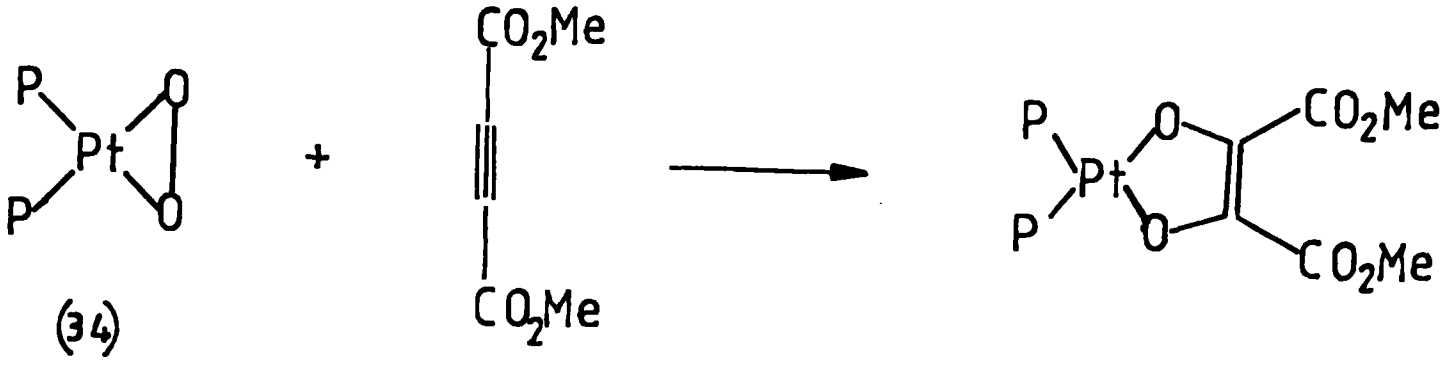
(19a)


CN
X


CN
CN
X


COMe
Ph
COMe
X


CO2Et
CO2Et
X



$P = P(C_6H_{11})_3$

Fig. 31

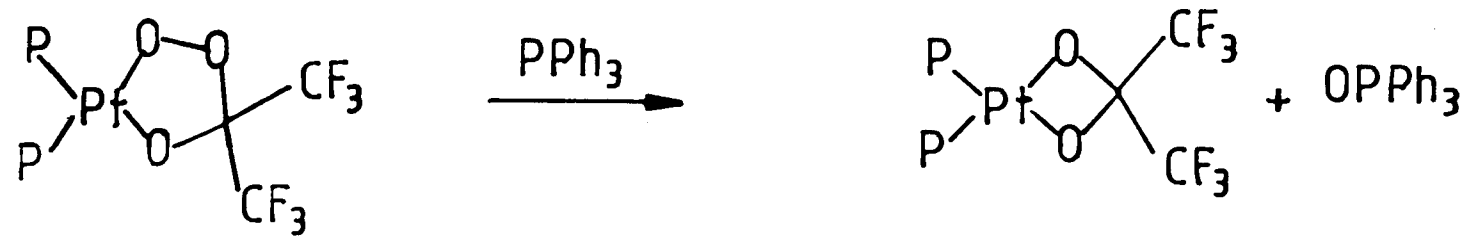
However, the initial formation of a unsymmetrical peroxo complex bearing the intact O-O moiety cannot be excluded, although attempts to identify it spectroscopically at low temperature have failed[79].

1.5 The Chemical Reactivity of the Metalladioxacyclopentane (25)

The following section describes an examination of the chemical reactivity of complex (25). An early objective was the selective removal of one oxygen atom in this complex giving the equivalent of a metallaoxacyclobutane which might fragment to epoxide under appropriate conditions. It was discovered that complex (25) is stable to a wide range of reagents which effect the cleavage of organic peroxides[88]. Reduction of the complex by sodium borohydride is described. Replacement of phosphine by chelating diphosphines and t-butylisocyanide may be achieved. Most importantly, acid hydrolysis leads to epoxide formation.

1.5.1 Attempted Ring Contraction of Complex (25)

It was known from the work of Wilkinson[76] that the perketyl adducts of bis(triphenylphosphine)dioxygenplatinum (0) with perfluoroacetone and acetone could be reductively ring contracted by reaction with triphenylphosphine and dihydrogen, respectively (Figure 32).



P=PPh3

Fig. 32

Similarly the carbon dioxide adduct undergoes ring contraction to the carbonate complex[89] as illustrated in Figure 33.

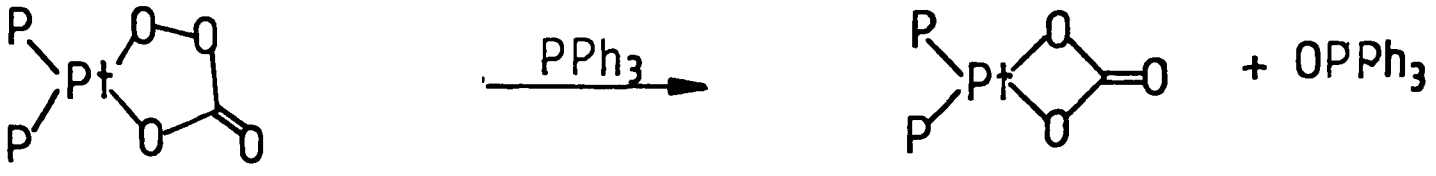


Fig. 33

It had been anticipated that an analogous reductive ring contraction leading to epoxide formation (Figure 34) might occur.

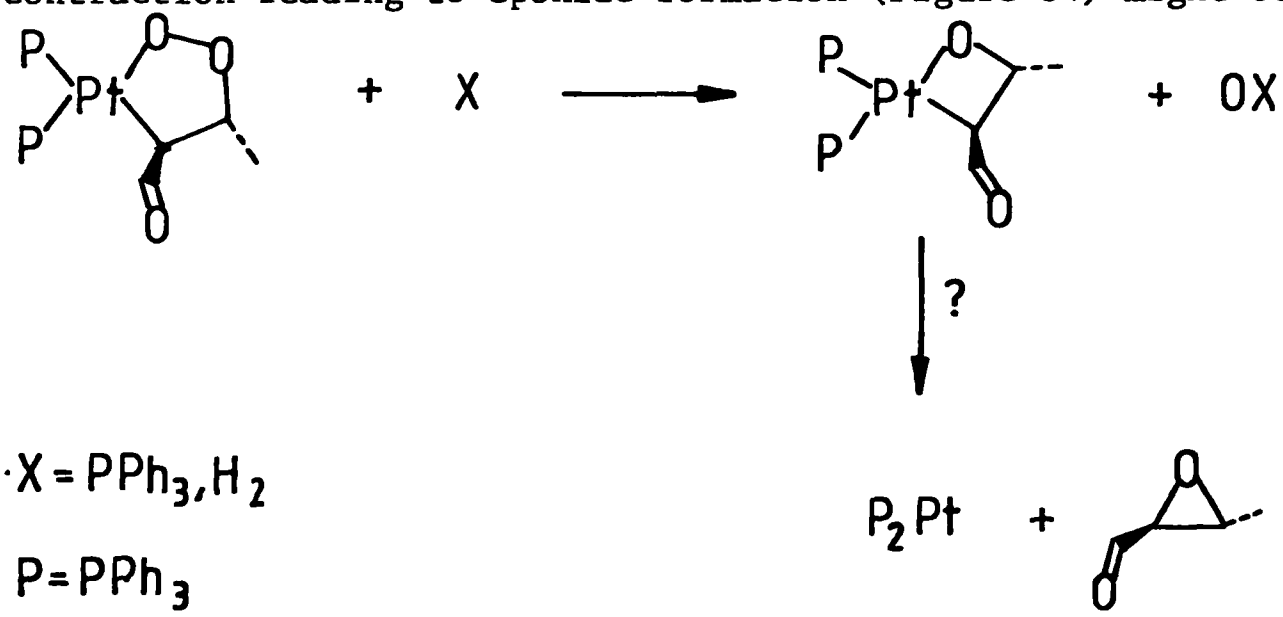


Fig. 34

A solution of complex (25) in dichloromethane was unaffected by a ten molar excess of triphenylphosphine at 40°C for 24 h , however. The adduct was similarly not reduced by dihydrogen at room temperature over 10 days. The very nucleophilic 4-(dimethylamino)-pyridine was not able to effect oxygen abstraction and hence ring contraction even when in excess under conditions of refluxing dichloromethane. A similar lack of reactivity is observed with

the more basic phosphine methyldiphenylphosphine. No change is observed in the metalladioxacycle although the reaction is complicated by ligand exchange.

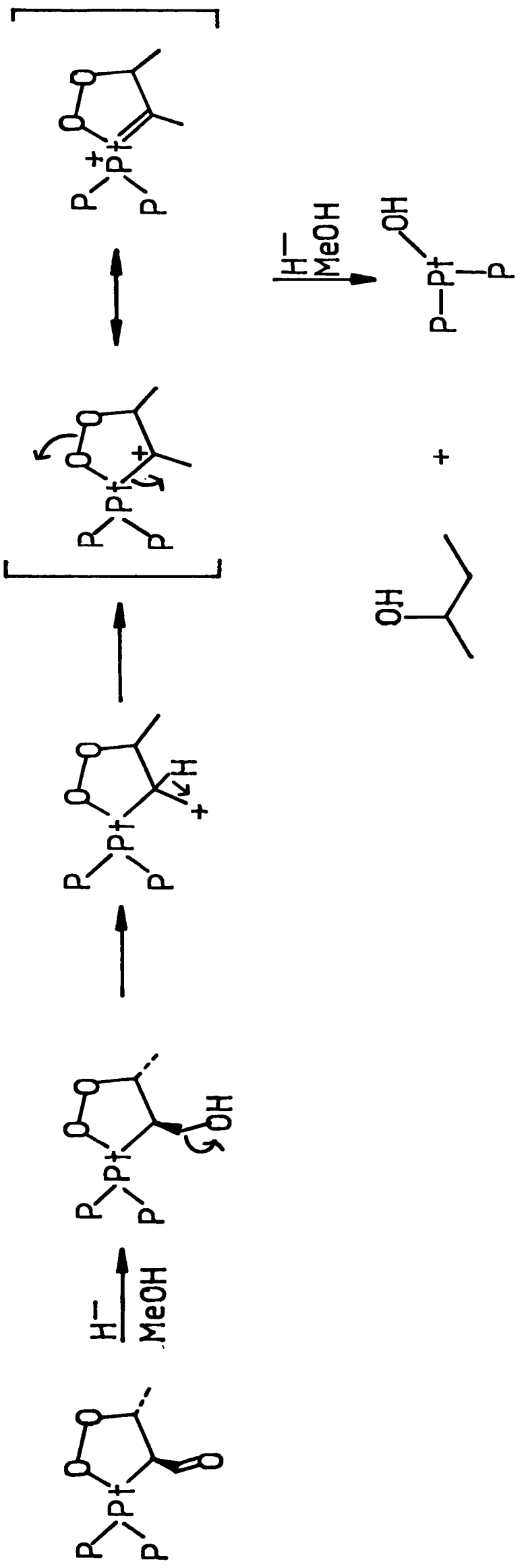
The complex was found to be inert to these reagents even when more forcing conditions of reflux in dichloroethane for 24 h , were employed. It can be concluded that there exists the requirement for electron withdrawing groups such as CF_3 or C = O adjacent to the peroxy linkage to enhance the reactivity to nucleophiles.

1.5.2 The Reduction of Complex (25) by a Hydride Reducing Agent

The addition of a methanol solution of sodium borohydride to (25) dissolved in chloroform resulted in an immediate brown colouration. The volatile products were removed by 'trap-to-bucket' distillation. ^1H n.m.r. and gas chromatography revealed butan-2-ol to be the sole volatile product, formed quantitatively (n.m.r. integration). The platinum containing species gave a brown intractable oil which was not characterisable. It is likely that the reaction proceeds via an initial reduction of the formyl group, followed by loss of OH^- to give a platinum stabilized carbonium ion. This is illustrated in Figure 35.

When the initial adduct, complex (20), was reduced by methanolic sodium borohydride the only observable volatile product (by

Fig. 35



^{1}H n.m.r. and GLC) was that which would be expected[90] from the simple hydride addition to <u>trans</u> but-2-enal itself, <u>trans</u> but-2-en-1-ol (Figure 36).

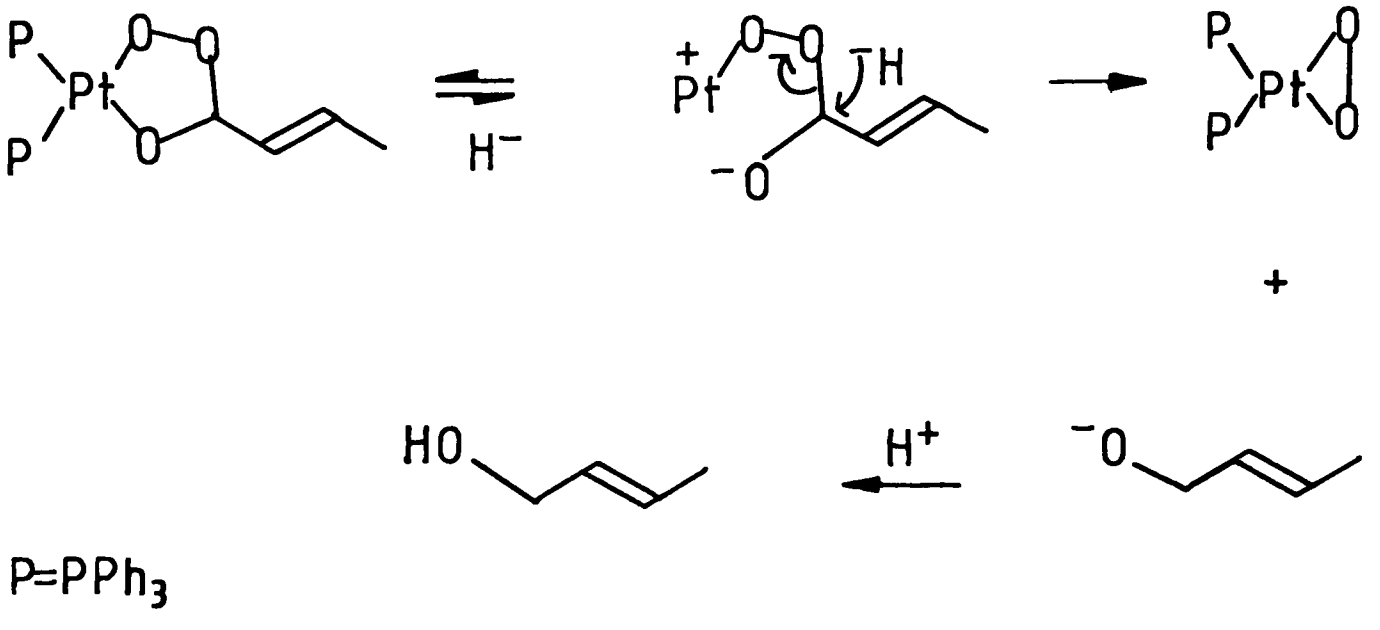


Fig. 36

1.5.3 Reaction of Complex (25) with Carbon Monoxide

Alkyl migrations to bound CO occur frequently in organo-transition metal chemistry[91]. However, when a solution of complex (25) in dichloromethane-d_2 was saturated with carbon monoxide the non-aromatic region of the ^{1}H n.m.r. spectrum revealed only a slow release of <u>trans</u> but-2-enal and minor, unidentifiable, by-products. At room temperature the ^{31}P n.m.r. spectrum of (25) collapsed on admission of carbon monoxide. Cooling the sample to - 70°C sharpened the resonances to give a singlet at 7.7 p.p.m. with ^{195}Pt satellites, $^1J_{PtP}$ 3232 MHz. This corresponded to the complex cis-[bis(carbonyl) bis(triphenylphosphine)platinum], (35), which had been synthesised independently by the method of Chini and Longoni[92]. The broad spectrum presumably is due to chemical exchange of phosphine

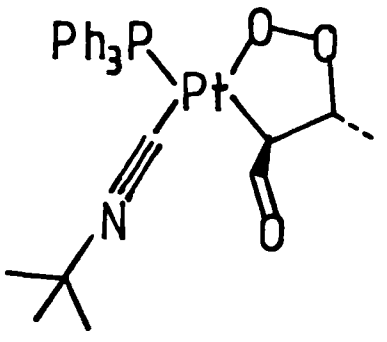
ligands at ambient temperature.

1.5.4 Reaction of Complex (25) with t-Butylisocyanide

Isocyanides are formally equivalent to carbon monoxide[93] although they are stronger σ-donors and weaker π-acceptors. They have an even greater proclivity than carbon monoxide to undergo 'insertion' reactions[94], but complex products are often formed by further transformations.

The addition of one molar equivalent of t-butylisocyanide to a solution of (25) in dichloromethane caused the collapse over several minutes of the ^{31}P n.m.r. spectrum to a broad hump. At $-50^{o}C$ the spectrum became sharpened and a singlet at 14.9 p.p.m. with ^{195}Pt satellites, $^{1}J_{PtP}$ = 2270 Hz, in dynamic exchange with free triphenylphosphine at -10.3 p.p.m. was observed. A white solid obtained from the reaction mixture showed strong infra-red (KBr) absorbances at 2182 cm^{-1} ($\nu_{C\equiv N}$) and 1660 cm^{-1} ($\nu_{C=O}$). The field-desorption mass spectrum gave a parent ion of molecular mass 642/3/4/6 (platinum isotopic distribution) indicating the addition of t-butylisocyanide with concomitant loss of one triphenylphosphine ligand.

Furthermore, the value of 2270 Hz for $^{1}J_{PtP}$ suggests carbon rather than oxygen trans to phosphorus (see Footnote p 59). Structure (36) in which t-butylisocyanide has selectively replaced the phosphine trans to the peroxo linkage was proposed.



(36)

The ^{1}H n.m.r. for (36) was consistent with this structure but not exclusively so. Figure 37 illustrates the ^{1}H n.m.r. (270 MHz) of the reaction half-way to completion, while the figures on the inset show the changes in chemical shift (in p.p.m.) upon substitution of triphenylphosphine by t-butylisocyanide. The large chemical shift change for protons H^a and H^b may be rationalised in terms of the shielding effect of the phosphine phenyl rings. Figure 37b shows how H^a and H^b are shielded and thereby their resonances are shifted upfield. t-Butylisocyanide presents no such effect to the protons and consequently their resonances appear downfield from the original complex.

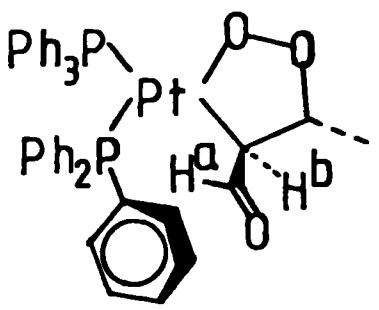


Fig. 37b

Precedent for ligand substitution rather than 'insertion' of t-butylisocyanide comes from the work of Treichel and Heiss[95]. They showed that the complex (37) undergoes loss of phosphine on addition of methylisocyanide (Figure 38), to give a thermally

▼ (25)

○ (36)

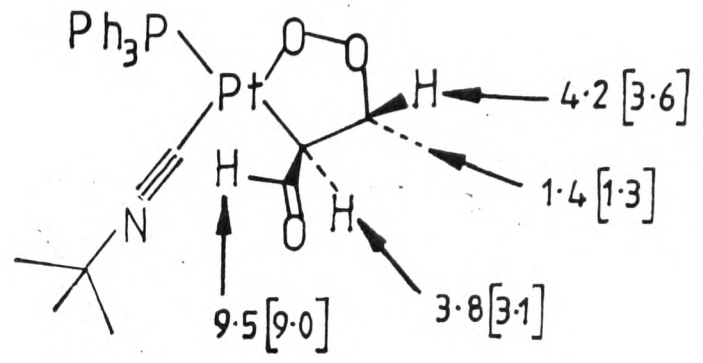


Fig. 37 ^{1}H NMR [270 MHz]

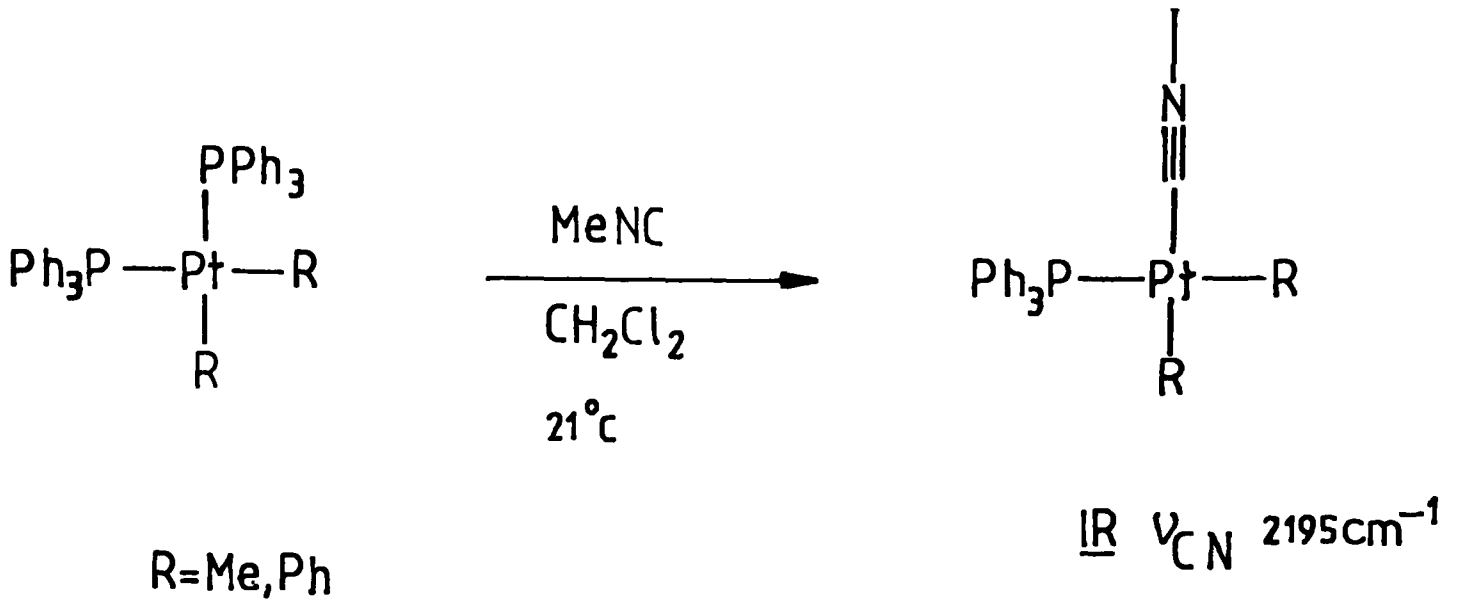
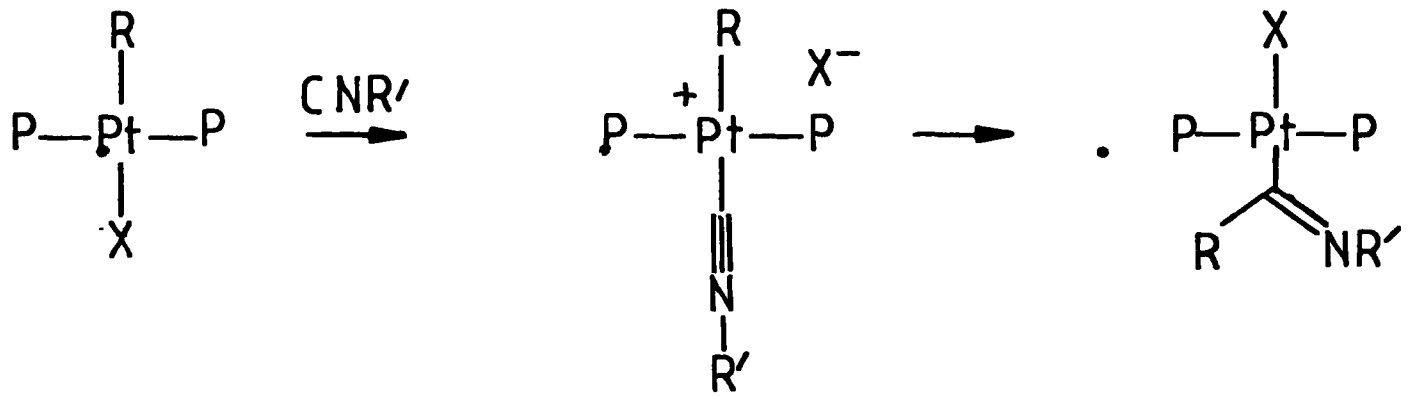


Fig.38

stable isocyanide adduct. However, the complexes trans-[R X bis (triphenylphosphine)platinum] (R = alkyl; X = halide) undergo isocyanide insertion reactions via isolable four-coordinate ionic intermediates (Figure 39).



P = PPh_3

R, R′ = ALKYL , X = HALIDE

Fig.39

The ligand displacement observed here may proceed via a five-coordinate Pt(II) intermediate. This is reasonable in view of the coordinatively unsaturated platinum centre, and indeed such a mechanism has been suggested for addition of carbon monoxide in Pt(II) systems[96]. The selectivity of phosphine displacement implies that (38) rather than (39) is favoured as the necessary intermediate (Figure 40).

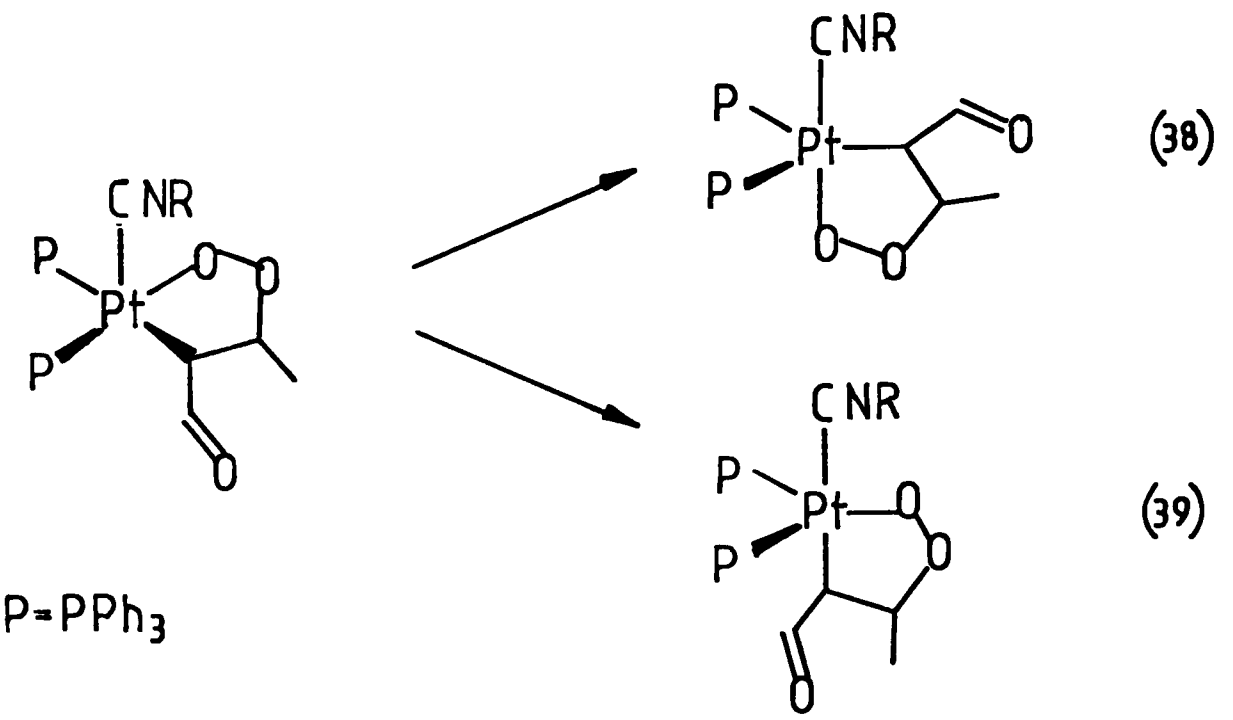
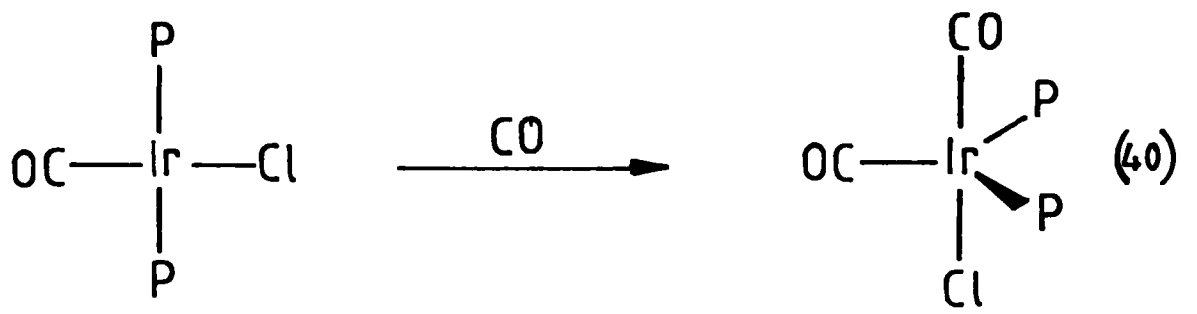


Fig.40

Some support for this comes from the reaction of carbon monoxide with Ir(CO) (PPh_3) Cℓ. Angaletta[97] isolated the five-coordinate iridium complex (40) in which the incoming carbon monoxide is <u>trans</u> to the electronegative Cℓ rather than a phosphine (Figure 41).



P=PPh_3

Fig.41

1.5.5 <u>Phosphine Exchange Reactions of Complex</u> (25)

Addition of a three-fold excess of 1,2-<u>bis</u>(diphenylphosphino)-ethane, DIPHOS, to a solution of (25) in dichloromethane led to a slow displacement of triphenylphosphine. The ^{31}P n.m.r. spectrum (Figure 42) showed predominantly one species, the product of phosphine exchange , (41), (Figure 43), and free triphenyl phosphine.

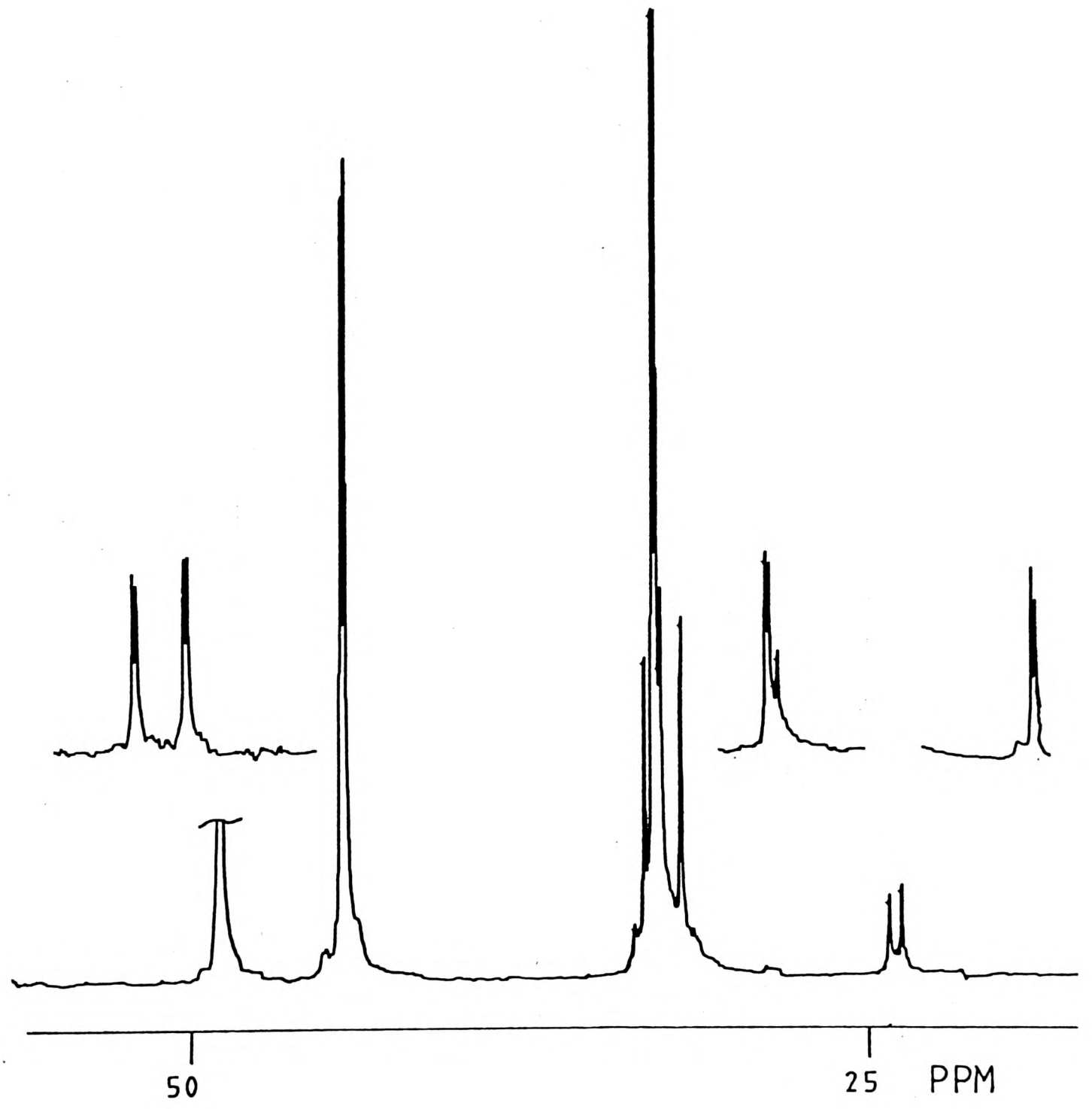
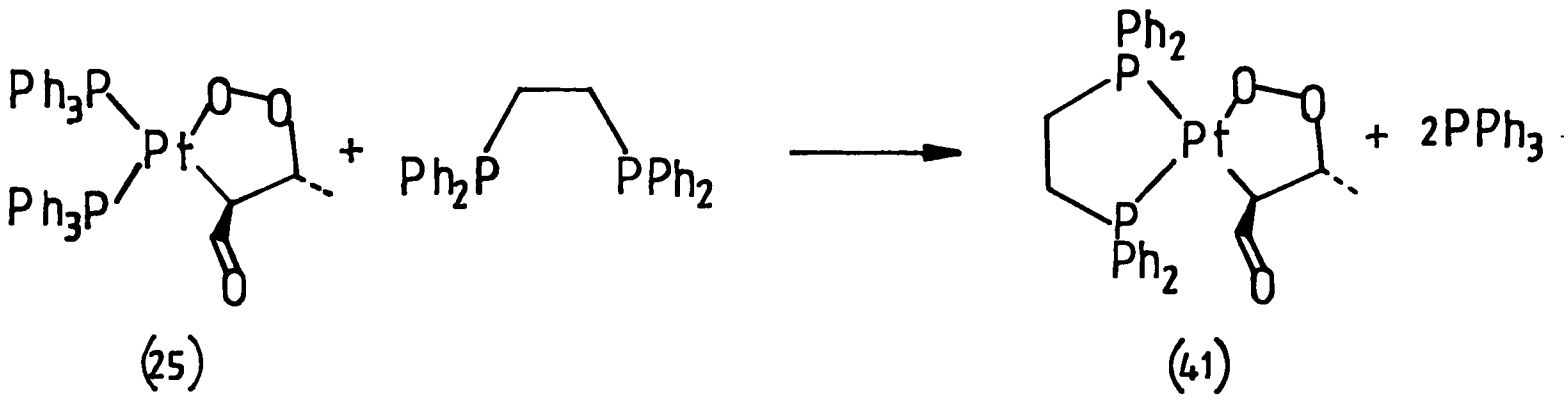


Fig.42 ^{31}P NMR (36·4 MHZ)



(25) (41)

^{31}P n.m.r. data

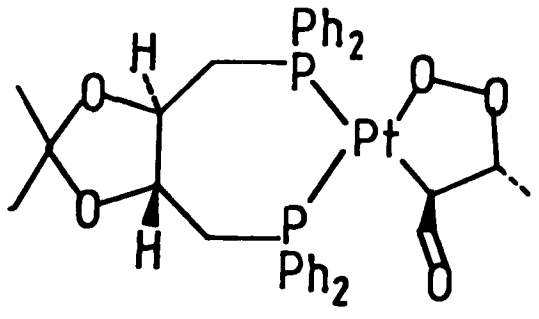
δP^1 44.1 p.p.m. J_{PtP} = 2394 Hz

δP^2 32.4 p.p.m. J_{PtP} = 3096 Hz

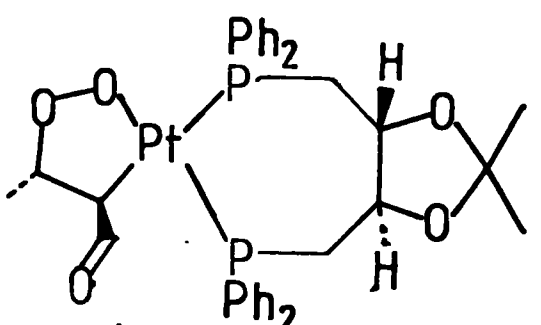
J_{PP} = 5 Hz.

Figure 43. Phosphine Exchange with DIPHOS

The large, 21 p.p.m., downfield shift of the phosphorus resonances relative to those of the initial complex is typical of the deshielding effect found in five-membered ring chelates[98]. In a similar manner, addition of three molar equivalents of the chiral chelating phosphine (4R, 5R)-4,5-(bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan, DIOP, resulted in a quantitative exchange of phosphine. One would expect DIOP, by virtue of its chirality, to form two diastereomeric products of phosphine exchange (Figure 44).



(42)



(43)

Examination of the ^{31}P n.m.r. spectrum (Figure 45) of this exchange process reveals the formation of four sets of doublets each with ^{195}Pt satellites corresponding to the two diastereomers (42) and (43). Integration of peak heights shows they are formed in the ratio 7:3. The ^{31}P n.m.r. spectrum illustrates this and the formation of a minor species, bis(DIOP) Pt, identified by comparison to an authentic sample[99].

Table 7 lists the ^{31}P n.m.r. data for the pair of diastereomers from which it can be seen that again chelation has produced a large change in chemical shift. Here, however, the seven-membered ring of chelated DIOP shields the phosphorus nuclei, moving their resonances upfield by between 16 and 19 p.p.m.[98]

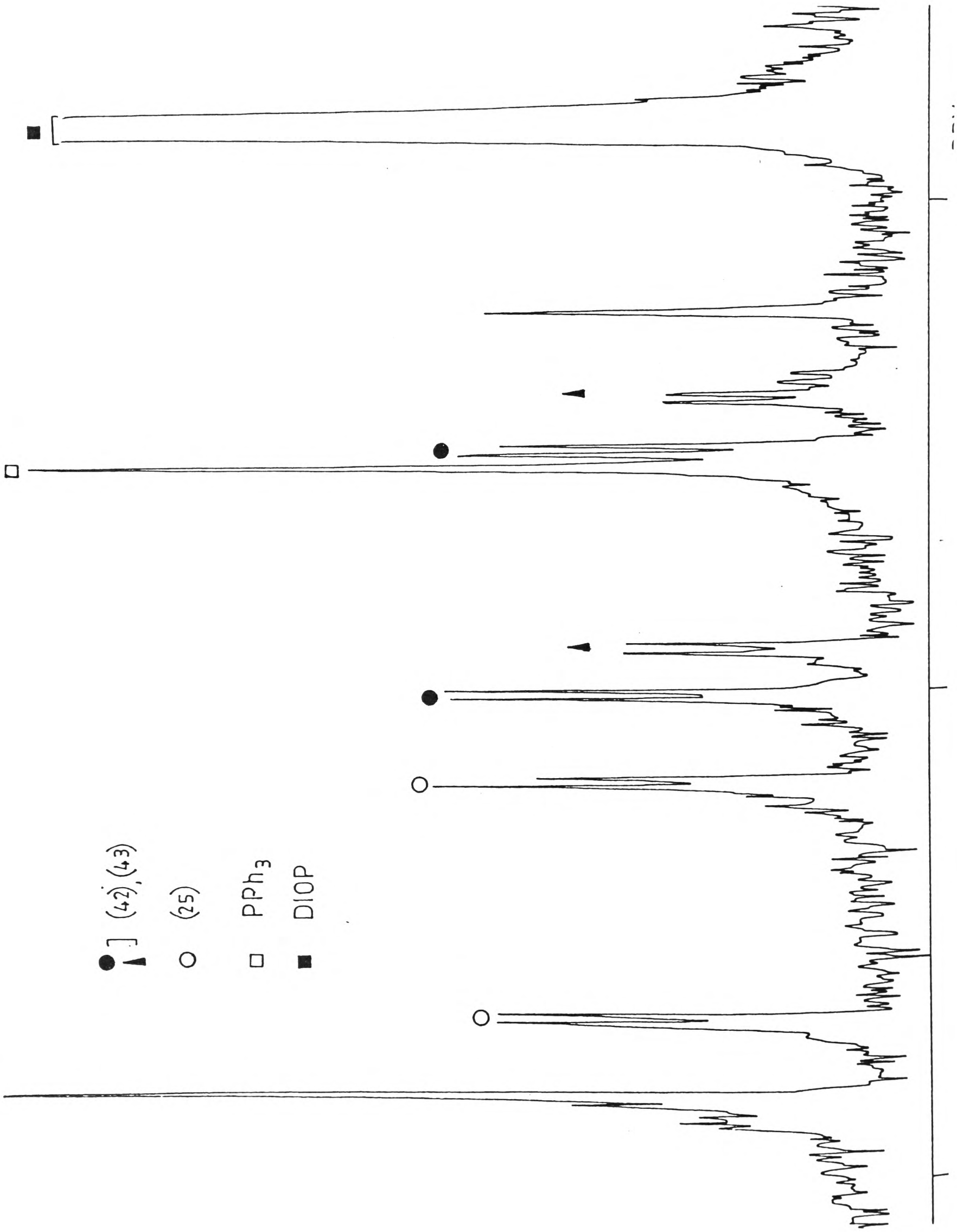
Table 7

^{31}P n.m.r. data for Diastereomers (42) and (43)*

δ p.p.m.	$^{1}J_{PtP}$	$^{2}J_{PP}$
7.1	2780	16
-5.2	3800	16
4.9	2789	16
-7.8	3690	16

*Resonances are not assignable to either (42) or (43).

Fig.45 ^{31}P NMR [36.4 MHZ]



1.5.6 Acid Promoted Cleavage of Complex (25). Epoxide Formation.

The results presented here strongly suggest that acidic cleavage of complex (25) leads to epoxidation within the coordination sphere of the metal.

When approximately one molar equivalent of trifluoroacetic acid was added to a solution of (25) in dichloromethane-d_2 an instantaneous change was observed by ^{1}H n.m.r. (300 MHz) (Figure 46). The major product was trans-2-formyl-3-methyloxirane, (44), (confirmed by GLC analysis against an authentic sample[100]). Smaller quantities of the cis-epoxide and trans but-2-enal were also identified. The cis and trans isomers of the epoxide are readily distinguished by their coupling patterns in the ^{1}H n.m.r. Addition of benzene-d_6, acting as a 'shift-reagent', allowed the resonances of the minor cis epoxide to be analysed. In particular, the difference in size of the vicinal coupling constant, which is 1.5 Hz in the trans isomer and 4.0 Hz in the cis isomer, allowed the correct assignment to be made.

When the reaction was carried out in benzene-d_6 as solvent the yield of olefin was substantially increased, as Table 8 illustrates. In either medium olefin and epoxide were the only products observed by n.m.r. or GLC.

After several hours fine colourless needles crystallised out of the solution. The infra-red spectrum (KBr and $CHCl_3$) of these crystals was identical to an independently prepared sample of cis$[Pt(PPh_3)_2(CF_3CO_2)_2]$, (45)[101].

Fig. 46; ^{1}H NMR(300 MHZ)
Addition of CF_3CO_2H to (25)

B; (25) + CF_3CO_2H

A; (25)

▼ H_2O

inset: ×2·5

10 9 8 7 6 5 4 3 2 1 0 PPM

Table 8. Products of Reaction of (25) with Trifluoroacetic Acid*

Solvent	%but-2-enal	%cis-epoxide	%trans-epoxide	stereoselectivity
$CD_2C\ell_2$	4	8.5	87.5	93 ± 1
C_6D_6	40	3	57	95 ± 1

*% products estimated by peak area integration of ^1H n.m.r.

We envisage the initial step to be protonation of the oxygen adjacent to platinum. Collapse of this metallacycle leads to olefin and dioxygen formation, a competitive pathway in non-polar benzene (Figure 47).

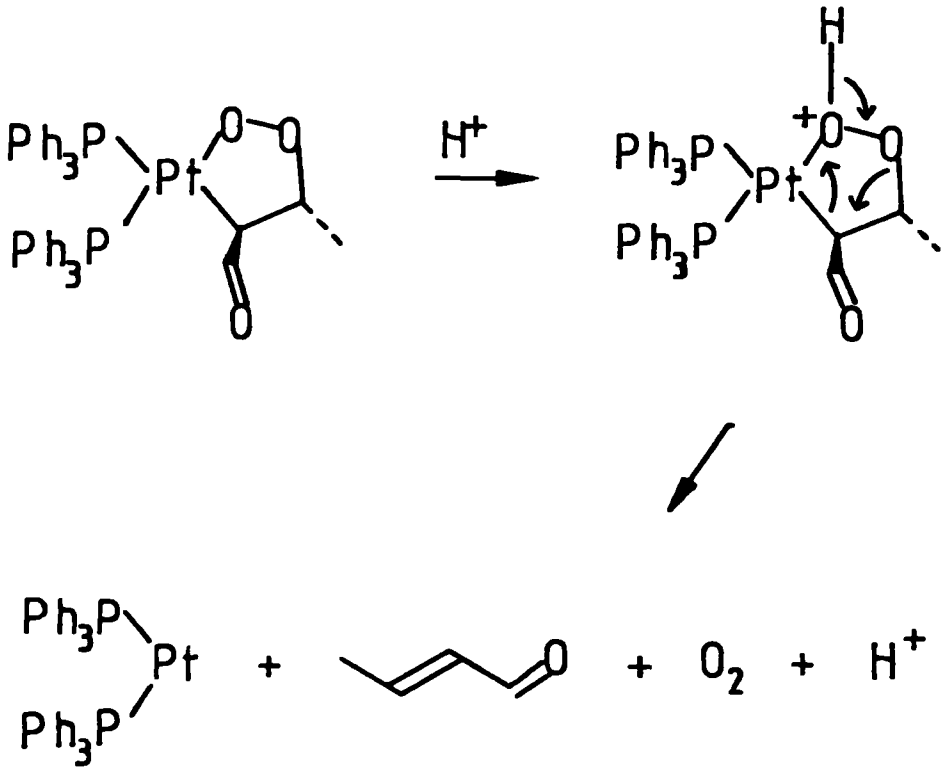
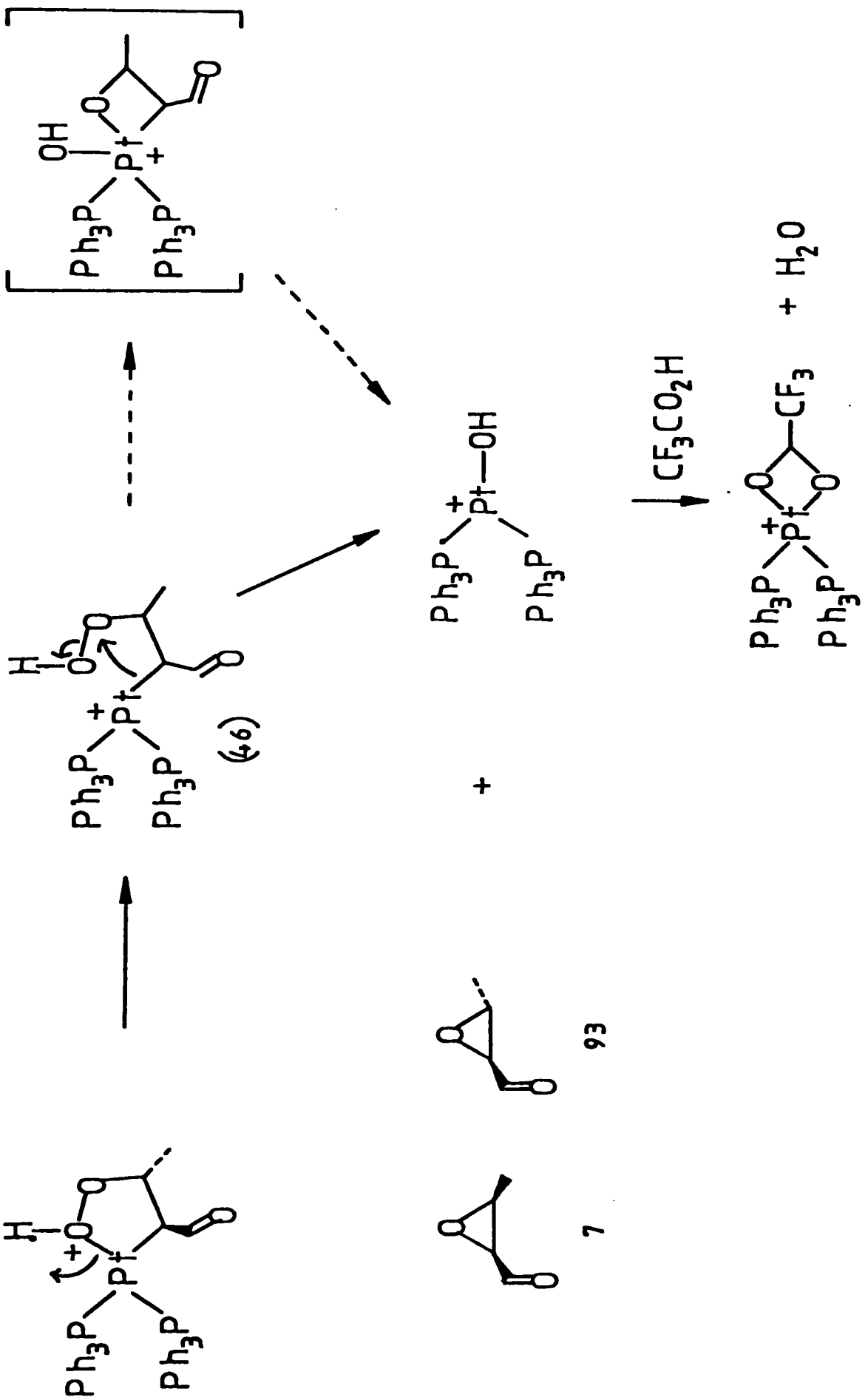


Fig. 47

The data presented here suggests this is a minor process in dichloromethane, epoxide formation becoming predominant. Enhancement of the epoxide pathway in a polar solvent is consistent with the intermediacy of some rather polar species, such as the hydroperoxide, (46), shown in Figure 48. This may then collapse

Fig. 48

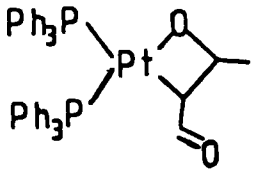


to epoxide directly by hydroxide displacement or *via* a metalla-oxacyclobutane*.

The presence of five molar equivalents of triphenylphosphine in the reaction medium before the addition of trifluoroacetic acid had no effect upon the yield of epoxide or distribution of products. Under various reaction conditions triphenylphosphine oxide was not detected as a co-oxidation product (absence of characteristic IR stretch at 1100 cm^{-1}).

It is known[104] that acyclic α,β-unsaturated carbonyl compounds may be epoxidised by hydrogen peroxide under mildly basic conditions. The electrophilic nature of their double bond allows nucleophilic attack by HO_2^- which is followed by hydroxide ion displacement from the stabilised enolate anion. The process is highly stereo-selective favouring the epoxide product in which the keto function

*There is some support for such a metallacycle. We have observed that $[Pt(PPh_3)_3]$ displaces phosphine in the presence of a large excess of 2-formyl-3-methyloxirane to form a species, (47), observable by ^{31}P n.m.r. but not isolated. A widely-spaced pair of doublets exhibiting very different Pt-P coupling suggested carbon and oxygen moieties *trans* to the phosphines. ^{31}P n.m.r. (36.43 MHz), 20.7 p.p.m. (d, J(PtP) 3746 Hz, J(PP) 15 Hz), 11.3 p.p.m. (d, J(PtP) 2054 Hz, J(PP) 15 Hz). Such species have also been invoked as intermediates in the palladium catalysed conversion of 2,3-epoxyketones to β-diketones (Ref. 102) and in the 1,2-bond shift of epoxides on platinum surfaces (Ref. 103).



(47)

is trans to the bulkier group on the β-carbon atom. Although the epoxidation of trans but-2-enal by peroxide anion has been described[100] the stereoselectivity was not stated. We have found consistently that base catalysed epoxidation of trans but-2-enal by hydrogen peroxide is 85% stereoselective (^{1}H n.m.r. integration) favouring the trans isomer at 0°C in methanol. In dichloromethane and benzene at least, solvents of rather differing polarity, the stereoselectivity observed when epoxide is formed by protolysis of the metalladioxacyclopentane is higher.

Halpern[105] has implicated free peroxide anion as the active oxidising species in the oxidation of triphenylphosphine by $[Pt(PPh_3)_2\ O_2]$, (1). He supposes that nucleophilic attack by triphenylphosphine onto the dioxygen complex releases O_2^{2-} which is then protonated. It is therefore important to distinguish between epoxidation at the metal centre and epoxidation subsequent to formation of free hydroperoxide anion. In general triphenylphosphine would be anticipated to react much faster than trans but-2-enal with free hydrogen peroxide. The results presented here indicate that phosphine neither quenches the epoxidation step nor is a co-oxidation product and so strongly suggest that free peroxide is not generated as the active oxidising species. The differing stereoselectivity observed in the hydrolysis of the metalladioxacyclopentane, to some extent, is consistent with epoxidation taking place on the metal.

In the course of presenting structural evidence Sheldon[78] reports that the metalladioxacyclopentane complex synthesised from complex (1) and the electrophilic olefin 1,1-dicyano-2-methylpropene (complex (19a)) yields up to 50% epoxide upon treatment with trifluoroacetic acid under certain conditions. He states that olefin and epoxide are formed in equimolar quantity in chloroform solution at ambient temperature. In the presence of triphenylphosphine olefin is the sole product of hydrolysis. Assuming that in Sheldon's system free hydroperoxide is not generated by, for instance, trace impurities, then the quenching effect of triphenylphosphine may arise by its competitive reaction with the peroxidic intermediate, (46), as shown in Figure 48.

Phosphines are known to react rapidly with alkyl hydroperoxides by nucleophilic attack at the oxygen bearing hydrogen[106] (Figure 49).

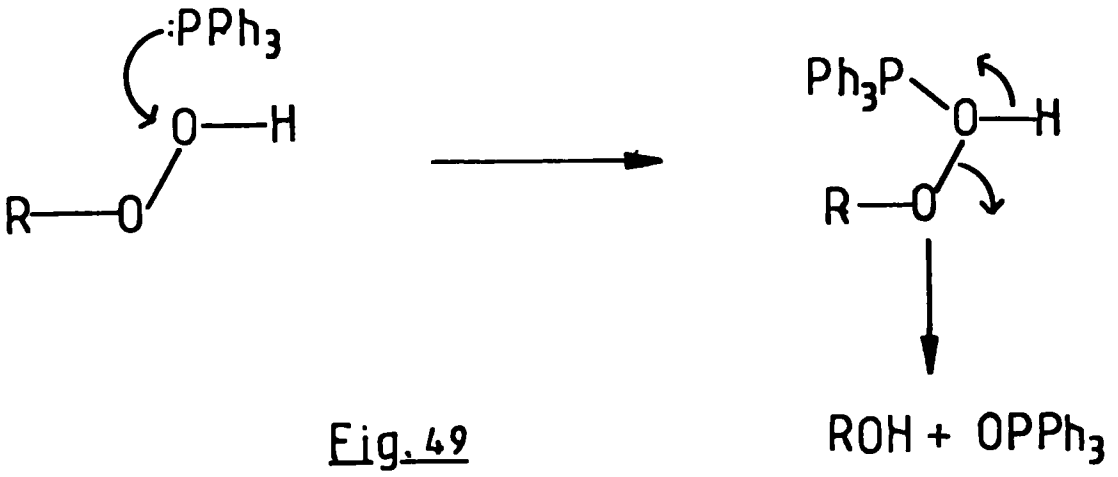


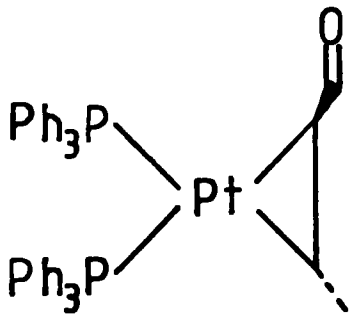
Fig. 49

The acid promoted epoxidation of trans-but-2-enal via the metalladioxacyclopentane, (25), represents the transfer of oxygen from dioxygen to an olefinic double bond. It proceeds with high yield and selectivity, at the metal centre.

1.6 Aspects of the Reaction of Tris-(triphenylphosphine) platinum (0), (47), with Trans-but-2-enal at Low Temperature

The reaction of tris-(triphenylphosphine)platinum (0),[112] (47) with symmetrical olefins such as ethylene has been studied[107]. In order to extend our knowledge of the chemistry of trans but-2-enal with platinum (0) complexes a study of the reaction of this unsymmetrical olefin with (47) was undertaken.

At room temperature only a very broad ^{31}P n.m.r. resonance was observed for a dichloromethane solution of $[Pt(PPh_3)_3]$. Cooling the solution to $-76^{o}C$ resulted in a sharpening of the resonances to give the characteristic line due to $[Pt(PPh_3)_3]$ (δ 47.0 p.p.m.) together with two ^{195}Pt satellites ($^{1}J_{PtP}$ = 4420 Hz). Addition of one molar equivalent of trans but-2-enal resulted in the formation of an equimolar mixture of two new complexes (Figure 50). The structures of these species were unequivocally assigned by independent synthesis. The singlet at δ 6.35 p.p.m. with ^{195}Pt satellites ($^{1}J_{PtP}$ = 3810 Hz) ascribed to $[Pt(PPh_3)_4]$,[111] (48), while the apparent quartet centred at 27.3 p.p.m. was due to the monoolefin complex (49)[114].



(49)

In a separate experiment, the addition of 2 molar equivalents of trans but-2-enal resulted in the complete disappearance of

$[Pt(PPh_3)_3]$ and the mixture of $[Pt(PPh_3)_4]$ and (49) (Figure 51), while a large excess (10 molar equivalents) gave resonances corresponding to (49) and free PPh_3 with only a little $[Pt(PPh_3)_4]$ (Figure 52).

These observations are consistent with reactions 53.1 and 53.2 in Figure 53.

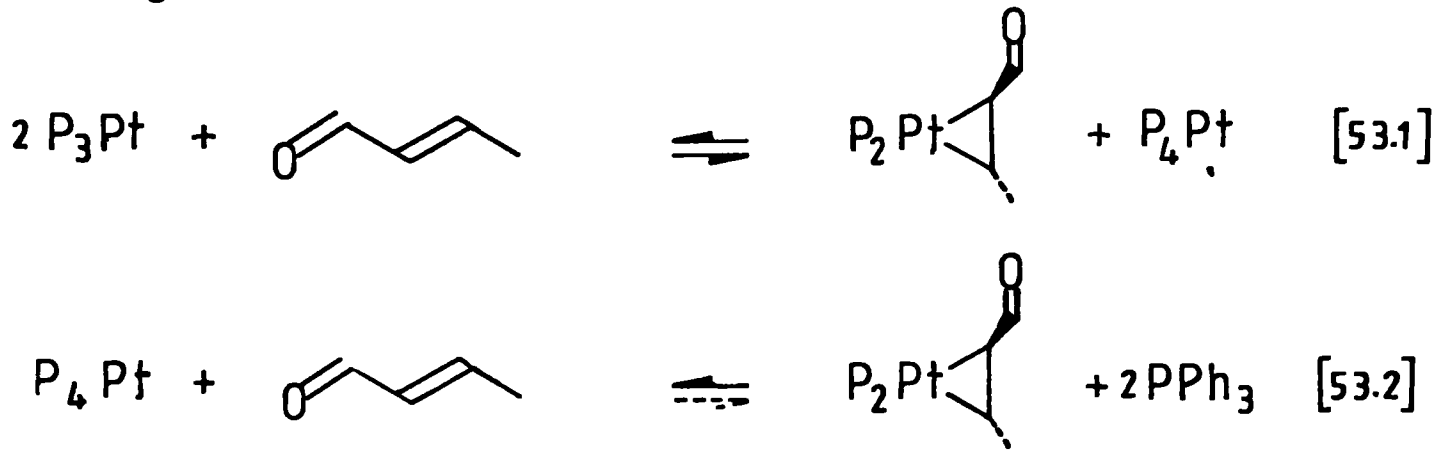


Fig. 53

Tolman[108] has shown that displacement of phosphine from $[Pt(PPh_3)_3]$ by ethene is unfavourable at 25°C, the equilibrium constant for Reaction 53.3 being 0.12. The driving force for this reaction and Reaction 53.1 at -76°C may be attributed partly to the 'scavenging' of the released PPh_3 by $[Pt(PPh_3)_3]$ - forming the complex $[Pt(PPh_3)_4]$ which is stabilized by low temperature. A large excess of olefin drives the equilibrium of Reaction 53.2 towards release of free PPh_3.

Dynamic Behaviour of (49): A dichloromethane solution of (49)

Fig.50 ^{31}P NMR[36.4 MHZ] -76°C

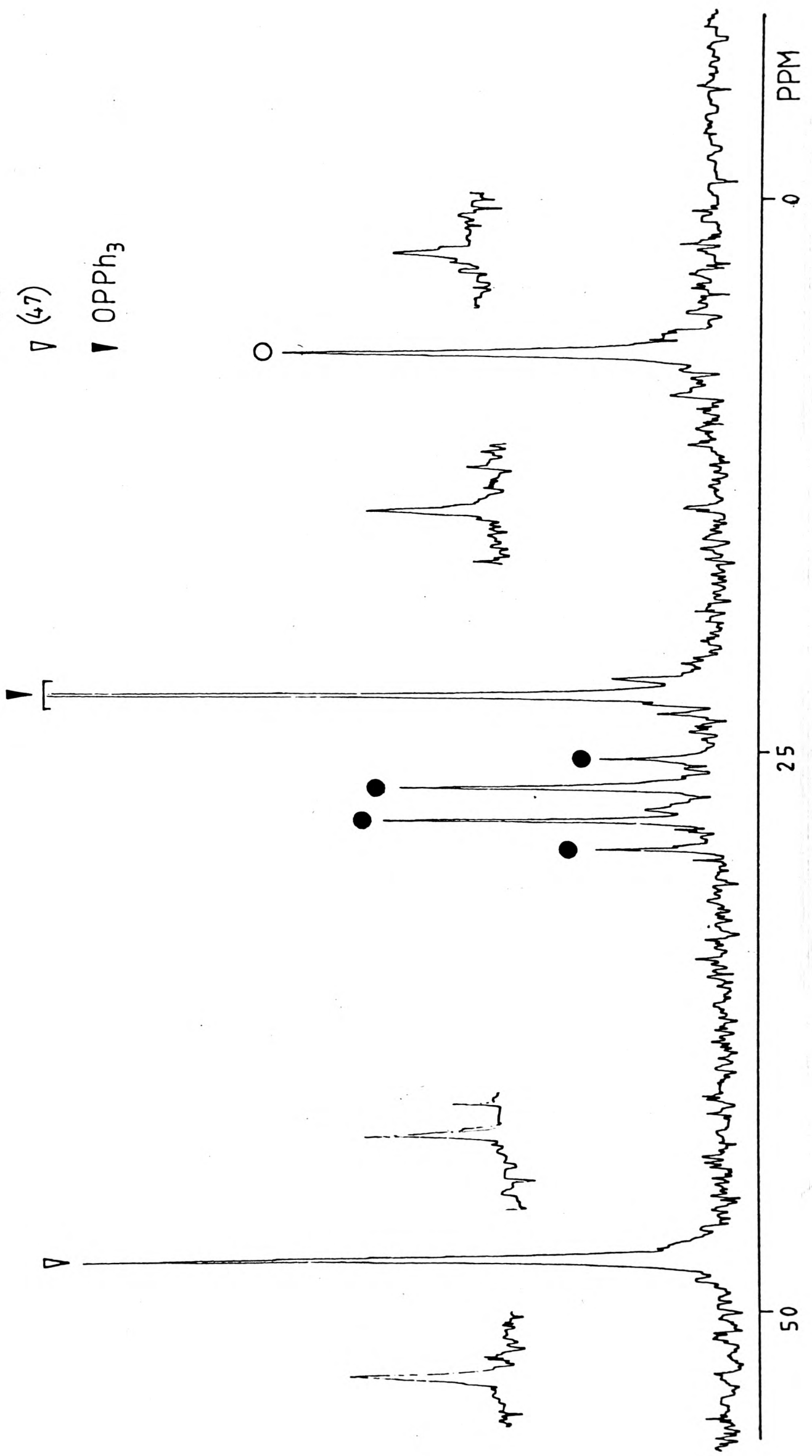
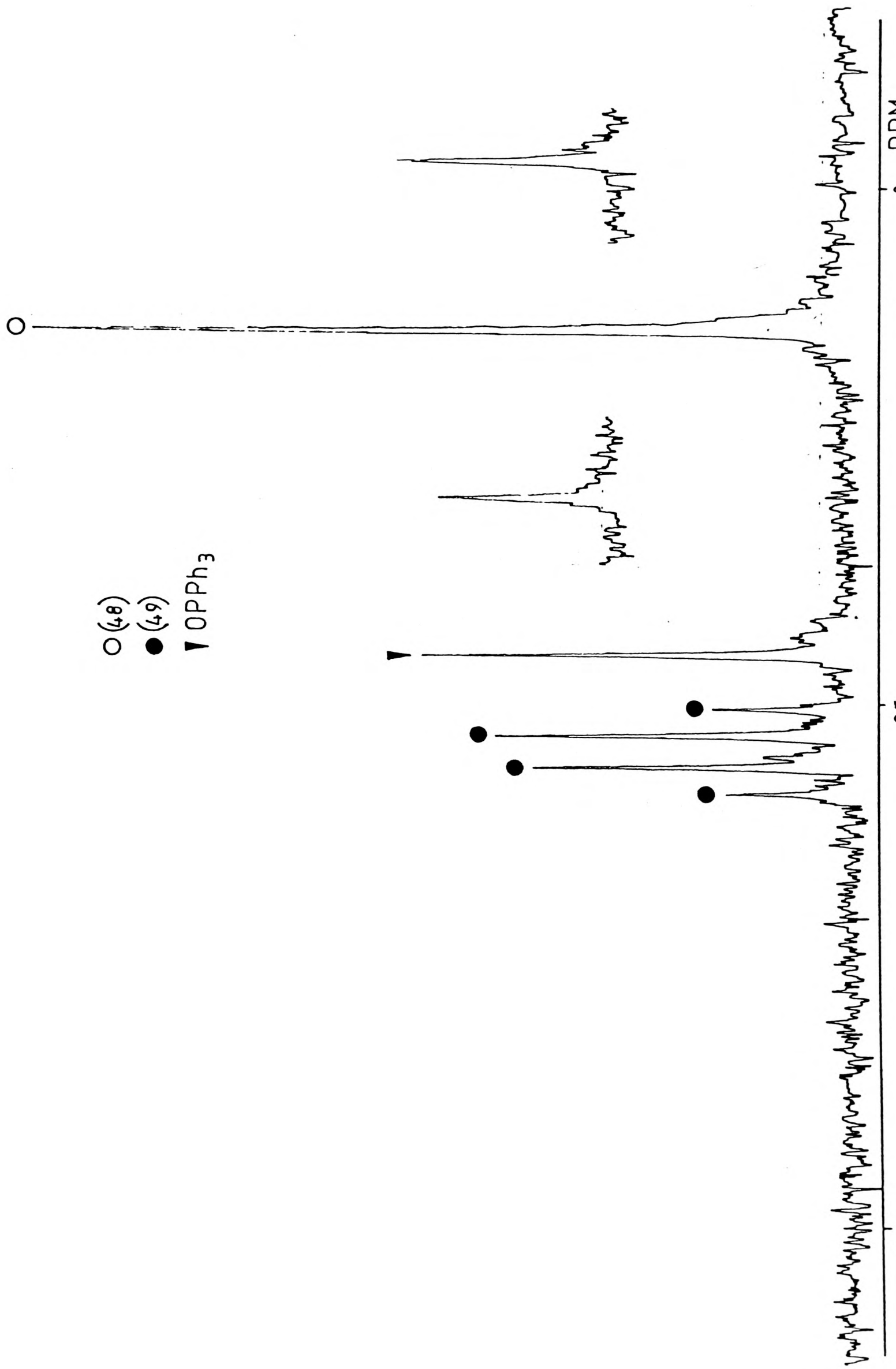


Fig.51 ^{31}P NMR[36·4 MHZ] -76°C



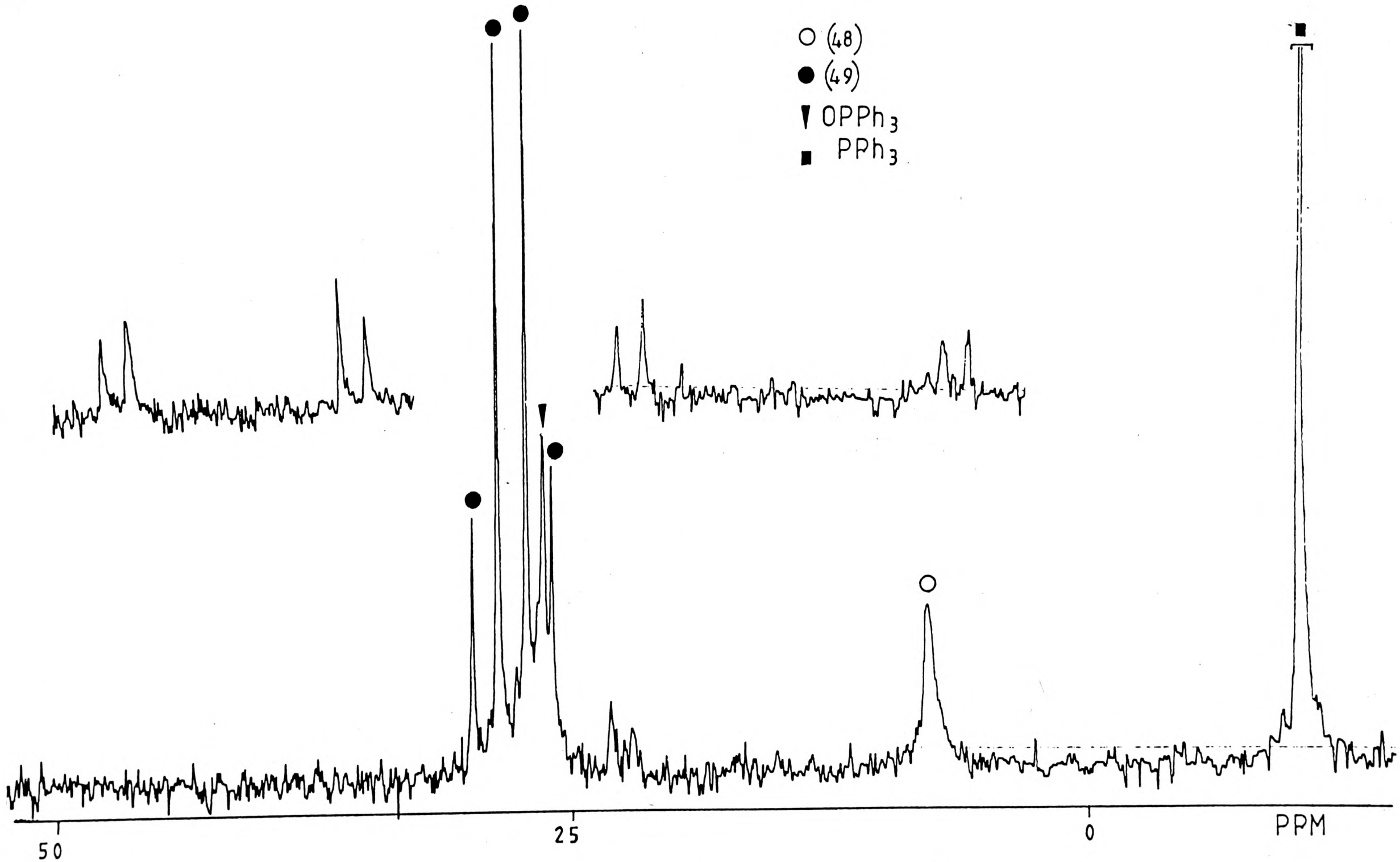


Fig. 52 ^{31}P NMR [36.4 MHZ] -76°C

prepared by independent synthesis or _in situ_ by reactions 53.1 and 53.2 showed unusual dynamic behaviour over a range of temperatures. Figures 54 (i) - (viii) show the central resonances, with their ^{195}Pt satellites as insets, over the temperature range $-76^{o}C$ to $+70^{o}C$. Figures 54 (i) - (v) represent one dynamic process while Figures 54 (vi) and (viii) a second, independent, exchange mechanism. Most striking in the first dynamic process is the persistence of P-P coupling. Although this may not be visible in _all_ signals it nevertheless provides evidence that phosphine displacement does _not_ take place. We envisage an exchange mechanism brought about by interconversion of the two rotamers* _A_ and _B_ (Figure 55), which have identical P_2 and closely similar P_1 chemical shifts.

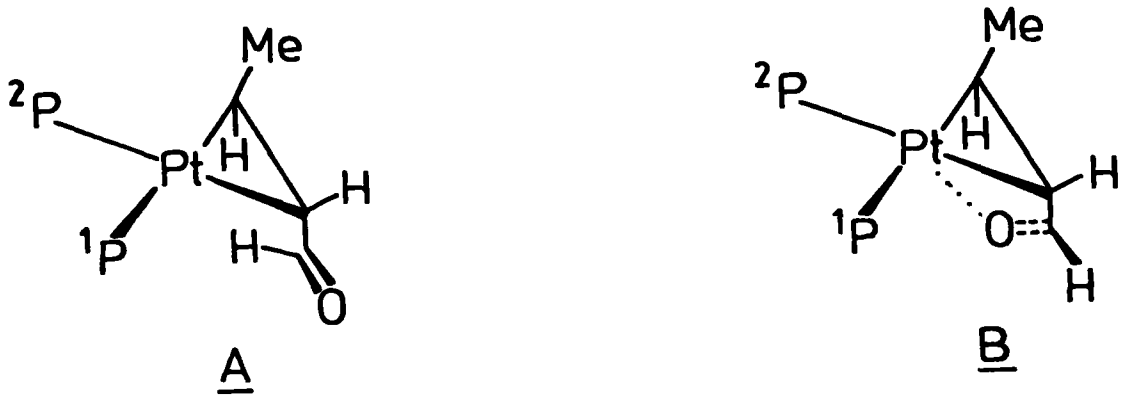


Figure 55. Rotamers of Complex (49)

Rotation of the highly anisotropic carbonyl group was observed indirectly by its small perturbation of only one phosphorus resonance, probably P1.

At $-76^{o}C$ the complex existed largely as its s-_trans_ isomer, any exchange between _A_ and _B_ being too slow to cause broadening of

*In _trans_ but-2-enal steric and electronic requirements favour two rotamers analogous to _A_ and _B_, s-_trans_ and s-_cis_, respectively. But-2-enal exists as 91% s-_trans_ in solution. See Ref. 109.

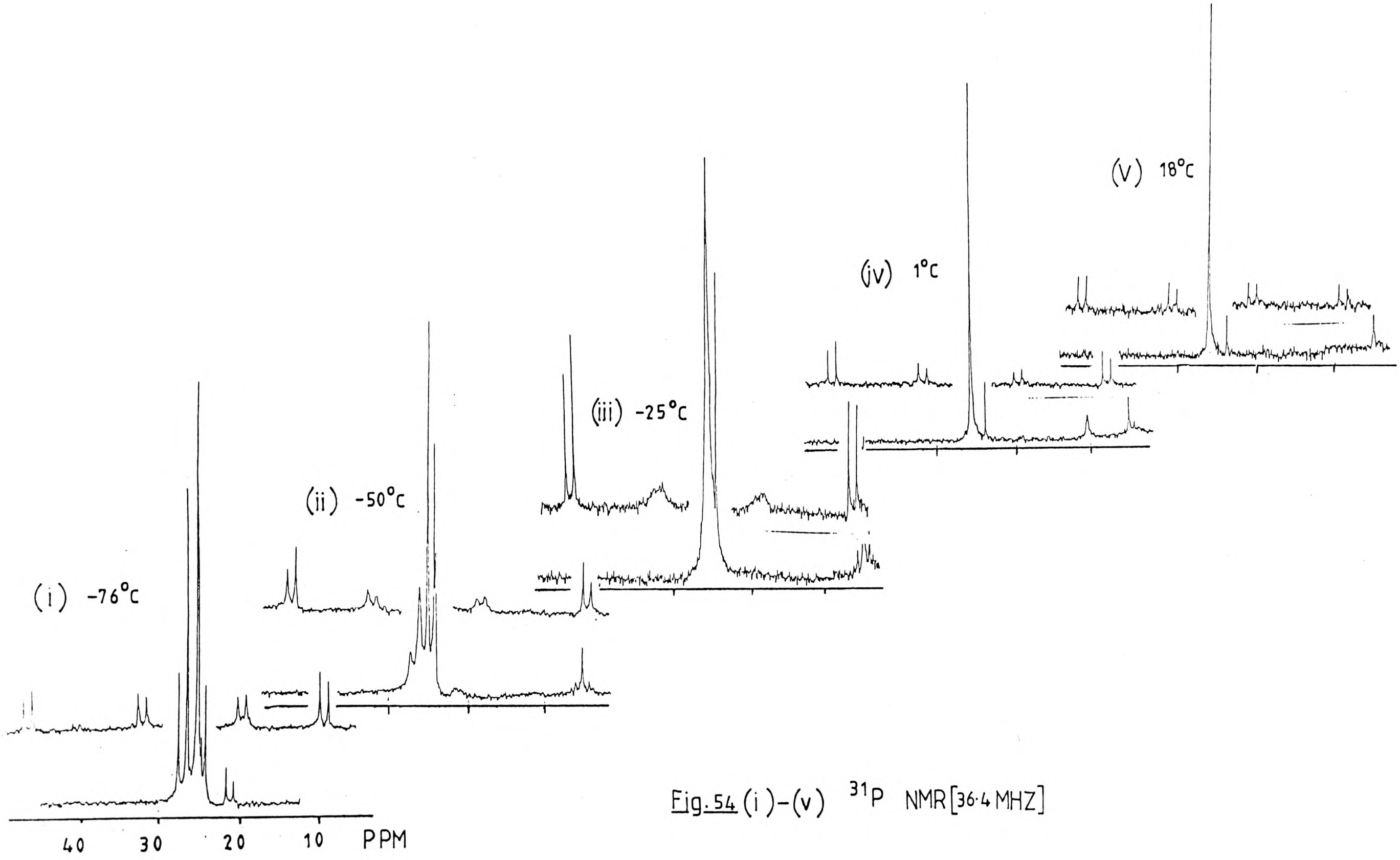


Fig. 54 (i)-(v) ^{31}P NMR [36·4 MHZ]

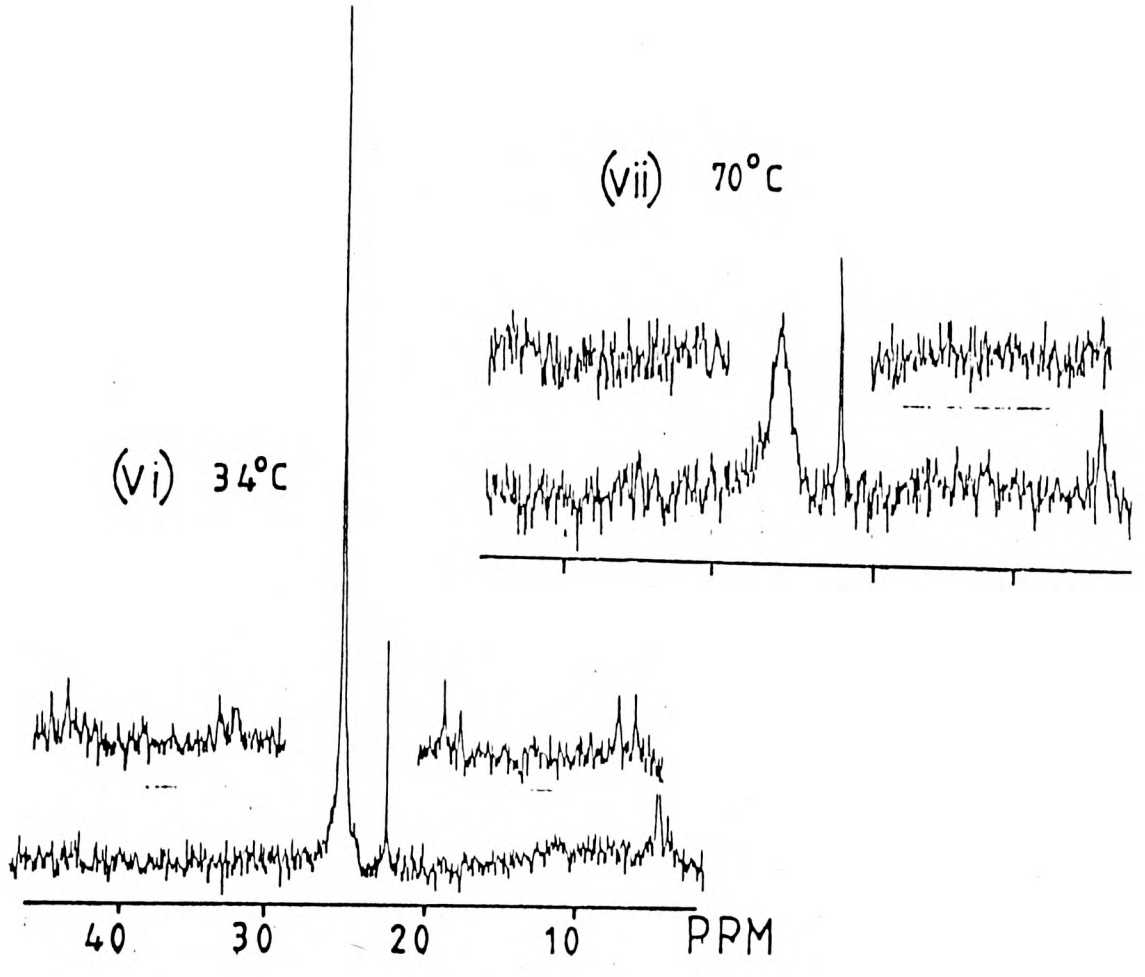


Fig. 54 (vi), (vii)

the P1 resonance. Upon warming to -50°C the rotamers began to exchange at an intermediate rate on the n.m.r. time-scale causing a relaxation of the P1 resonances. At -25°C a complicating factor actually simplified the structure of the central resonances, which appeared as a broad singlet; the rise in temperature affected the relative chemical shifts of P1 and P2, bringing the central peaks closer together and so causing a collapse of the doublet line shape. Above 1°C the central resonance and satellites of P1 sharpened. Exchange of A and B has become a process too fast to observe on the n.m.r. time-scale and a 'time-averaged' resonance was seen. The population of states of B was always so small that it was not directly observed under the experimental conditions.

The second dynamic process came into effect upon heating the solution to 34° C. At 70°C (Figure 54 (vii)) the whole spectrum collapsed. This may be explained by equivalencing of P1 and P2 by rotation of the olefinic bond as illustrated in Figure 56.

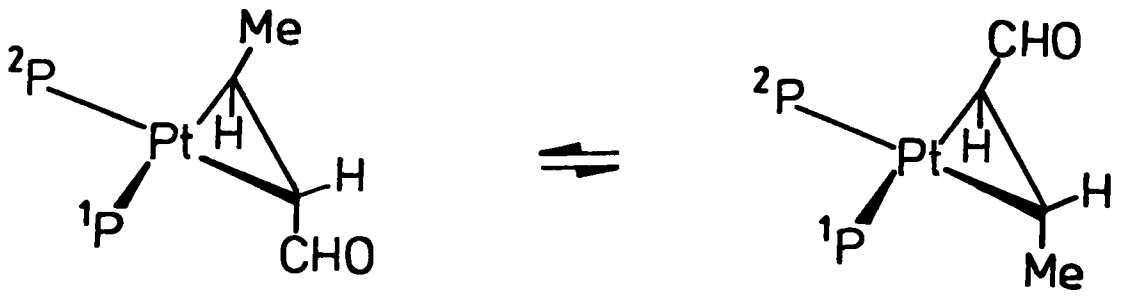


Figure 56. Rotation of Olefinic Bond

The carbonyl stretching absorbance, ν_{CO}, at 1655 cm^{-1} in the infra-red spectrum of complex (49) was not sufficiently well resolved to observe the rotamers A and B.

CHAPTER I

EXPERIMENTAL

E1.1 Instrumentation

^{1}H Nuclear magnetic resonance spectra were obtained on either a Hitachi-Perkin-Elmer R24 (60 MHz), a Perkin-Elmer R32 (90 MHz), a Bruker WH270 (270 MHz) or a Bruker WH300 (300.13 MHz) instrument. Chemical shifts are expressed as parts per million (p.p.m.) downfield from tetramethylsilane. ^{31}P n.m.r. spectra were also recorded on the Bruker WH90 (36.43 MHz) and Bruker WH300 (121.4 MHz) and chemical shifts are quoted in p.p.m. downfield from external phosphoric acid (85%). ^{2}H n.m.r. spectra were recorded on the Bruker WH300 (46.07 MHz), unlocked, with chemical shifts quoted relative to benzene-d_6 (7.27 p.p.m.) All coupling constants are expressed in Hertz (Hz) and the following abbreviations are used in spectral analysis:- s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Infra-red spectra were recorded on potassium bromide discs using a Perkin-Elmer 257 or Unicam SP 1000 spectrometer. The following abbreviations are used:- vs = very strong, s = strong, m = medium, w = weak.

Mass spectra were obtained from a Micromass ZAB 2F using the Field Desorption technique. Melting points were determined on a Reichert-Kofler block and are uncorrected. Microanalyses were performed by Dr. F.B. Strauss and his staff.

Materials

All reactions were carried out under a controlled atmosphere using standard vacuum-line techniques and Schlenk glassware

Argon was prepurified by passage through liquid paraffin, concentrated sulphuric acid, potassium hydroxide pellets and glass wool. Oxygen was used directly from a cylinder (BOC Ltd).

Commercial solvents were distilled prior to use from an appropriate drying agent according to standard procedures[110]. Dichloromethane was distilled from phosphorus pentoxide, methanol from magnesium turnings. Diethyl ether and tetrahydrofuran distilled from sodium wire using benzophenone ketyl as indicator.

Cyclohex-2-en-1-one was used as obtained from Aldrich. *trans* But-2-enal and propenal were freshly distilled before use. All precious metal salts were used as obtained *gratis* from Johnson-Matthey Ltd.

E1.2 Experimental Details

Perketyl Adducts

Typically, perketyl adducts were prepared in an 8 mm n.m.r. tube, under an argon atmosphere. Bis(triphenylphosphine)dioxygen-platinum (0) (50 mg, 64 μmol) was dissolved in 2.5 ml dichloromethane, to which three molar equivalents of the carbonyl compound were added by syringe. The course of perketyl formation and any subsequent reaction was monitored by ^{31}P n.m.r. (36.43 MHz). Perketyl adducts could be isolated by reducing the volume of dichloromethane by evaporation at reduced pressure and adding the resulting solution to 10 ml hexane. The crude white solid was washed with hexane, and dried in vacuo.

^{1}H and ^{2}H n.m.r. Studies using trans But-2-enal-d_3

Samples for ^{1}H n.m.r. measurement were made up as follows: i) (31) (5 mg, 6.1 μmol) in 0.25 ml $CDC\ell_3$ adding 2.5 μl but-2-enal (18 μmol; 3 molar equivalents) ii) (31) (5 mg, 6.1 μmol) on 0.25 ml $CDC\ell_3$, adding 8 μl trans but-2-enal (61 μmol, 10 molar equivalents). Each sample was duplicated and kept in a temperature regulated oil-bath at 40°C. Samples were taken at 0, 3, 6 and 8.5 hr and their ^{1}H n.m.r. spectra obtained. In such cases that it was not possible to run spectra immediately, samples were frozen at -30°C. The %extent exchange in perketyl complex and product as well as %extent of product formation were estimated by integration of the spectral signals, on a suitably expanded frequency scale. They are listed in Table 6 (Chapter 1).

Samples (i) to (vi) for ^{2}H n.m.r. spectra were made up as follows:-

(i) (20) (20 mg, 24 μmol), but-2-enal-d_3 (10 μl, 72 μmol)

(ii) (31) (20 mg, 24 μmol), but-2-enal (10 μl, 72 μmol)

(iii) (20) (20 mg, 24 μmol), but-2-enal-d_3 (25 μl, 240 μmol)

(iv) (31) (20 mg, 24 μmol), but-2-enal (25 μl, 240 μmol)

(v) (20)-d_3 (20 mg, 24 μmol) (vi) (25) (20 mg, 24 μmol), trans but-2-enal-d_3 (10 μl, 72 μmol). All were made up in 2.0 ml $CH_2C\ell_2$ adding 50 μl C_6D_6. Samples were sealed and kept at 39°C.

^{2}H n.m.r. spectra were obtained after 8.5, 26.5 and 47.5 hr. The spectra obtained confirmed that the perketyl complex exchanged with free trans but-2-enal and that the metalladioxacyclopentane product was not labile to exchange even far outside the normal experimental conditions. However no quantitative data could be formulated.

The Chemistry of Complex (25)

i) Reaction of (25) with Sodium Borohydride

To a solution of (25) (10 mg, 1.2 mmol) in chloroform-d (0.2 ml) was added sodium borohydride (2.4 mg, 1.5 mmol) in methanol-d_4 (ca. 0.05 ml). The colourless solution turned brown immediately. The ^{1}H n.m.r. (300 MHz) revealed the quantitative reduction of (25) to butan-2-ol. ^{1}H n.m.r. ($CDC\ell_3$) 3.65 p.p.m. (m, 1H), 1.5 p.p.m. (m, 2H), 1.2 p.p.m. (d, 3H), 0.9 p.p.m. (t, 3H). GLC (5% Hi-eff 1 AP, Adipate, on WHP 100-200 mesh; 62°C Retention time 8.2 min)

showed a single peak which corresponded to an authentic sample of butan-2-ol (obtained from B.D.H. Ltd).

Reaction of Complex (20) with Sodium Borohydride

A solution of sodium borohydride (0.05 ml, 2.4 mg, 1.5 mmol) in methanol was added to a solution of complex (20) in dichloromethane (0.2 ml, 10 mg, 1.2 mmol). The colourless solution turned brown immediately.

Analysis of the solution by GLC (15% OV17 on diatonite C-4W 100-200 mesh 80°C) revealed a single volatile prøduct (Retention time 3.7 min), but-2-en-1-ol, identical to an authentically prepared sample (vide infra).

The Reaction of trans But-2 enal with Sodium Borohydride[90]

Following the method of Johnson and Rickborn, trans but-2-enal (1.4 g, 0.02 mol) was added through a dropping funnel to sodium borohydride (0.37 g, 0.01 mol) in 25 ml water and 25 ml ethanol at 0°C. After stirring at room temperature dor 3 h , the mixture was saturated with salt, extracted with diethyl ether (2 x 50 ml), dried (anhydrous sodium sulphate). The resulting oil was distilled at atmospheric pressure through a 20 cm Vigreux column and the fraction boiling at 120°C collected to give 1.0 g clear colourless liquid. Analysis by GLC (15% OV17 on diatonite C-4W 100-200 mesh, 80°C, retention time 3.7 min) showed a single product, trans but-2-en-1-ol.

ii) Reaction of (25) with Carbon Monoxide

Carbon monoxide was bubbled through a solution of (25) (50 mg, 61 mmol) in dichloromethane in an n.m.r. tube. The ^{31}P n.m.r. spectrum was observed to collapse at room temperature, but sharpened on cooling to $-70^{o}C$: ^{31}P n.m.r. (36.43 MHz) 7.7 p.p.m. (s, with ^{195}Pt satellites J_{PtP} = 3232 Hz), corresponding to $[Pt(PPh_3)_2(CO)_2]$[92]. ^{1}H n.m.r. (300 MHz) revealed trans but-2-enal as sole product.

iii) Reaction of (25) with t-Butylisocyanide

A solution of complex (25) (50 mg, 61 mmol) in dichloromethane (2.5 ml) was added to t-butylisocyanide (5 mg, 61 mmol) in an n.m.r. tube. The resulting solution showed broad signals in ^{31}P n.m.r. at room temperature but cooling to $-50^{o}C$ caused their sharpening. The solvent was reduced to half volume and a fine white precipitate was obtained by adding hexane dropwise. The white solid was analysed by ^{1}H n.m.r., IR and mass spectrometry. ^{31}P n.m.r. (36.43 MHz) 14.9 p.p.m. (s, ^{195}Pt satellites, J_{PtP} 2270 Hz), -10.9 p.p.m. (s, free PPh_3). ^{1}H n.m.r. (300 MHz, $CD_2C\ell_2$) 9.54 p.p.m. (d, 1H, J 4 Hz), 7.5-7.0 p.p.m. (m, 15H, aromatic), 4.15 p.p.m. (m, 1H), 3.84 p.p.m. (m, 1H, J_{PtH} 88 Hz), 1.4 p.p.m. (d, 3H, J 6 Hz), 1.10 p.p.m. (s, 9H). IR (KBr) 2182 (vs), 1660 (vs), 1480 (m), 1435 (s), 1370 (w), 1190 (m), 1090 (s), 749 (m), 695 (s). Mass Spectrum (Field Desorption) Parent Ion, m/e 642/3/4/6 (Pt isotopes).

Reaction of (25) with Chelating Phosphines

Typically, (25) (50 mg, 61 mmol) was dissolved in dichloromethane (2.5 ml) in an n.m.r. tube, under argon to which 3 molar equivalents of chelating phosphine, DIPHOS or DIOP, were added. The tubes were sealed and set aside for several days. The ^{31}P n.m.r. spectra were recorded and data is tabulated in Section 1.5.5.

Reaction of (25) with Trifluoroacetic Acid

Complex (25) (5 mg, 6.1 mmol) was dissolved in dichloromethane-d_2 (250 µl). Trifluoroacetic acid (0.5 µl, 10 mmol) was added and the ^{1}H n.m.r. (300 MHz) obtained immediately. Careful evaporation of about half the dichloromethane-d_2 and addition of benzene-d_6 (as shift reagent) allowed accurate integration of the sole organic products: trans but-2-ene (4%), cis-2-formyl-3-methyloxirane (8.5%), trans-2-formyl-3-methyloxirane (87.5%). GLC (15% OV17 on diatonite C-4W 100-120 mesh, 82°C) confirmed the formation of epoxide by comparison with an authentic sample[100]. The reaction was repeated using benzene-d_6 as solvent to reveal a different distribution of products by ^{1}H n.m.r: 40%, 3%, 57% respectively.

The reaction was further repeated in the presence and absence

of triphenylphosphine (8 mg, 30 mmol). The reaction was followed by GLC which revealed neither an effective difference in formation of epoxide, nor in the relative distribution of products.

Low Temperature Chemistry of Tris(triphenylphospine)platinum (0) with trans But-2-enal

In 8 mm n.m.r. tubes containing 2.5 ml dichloromethane under argon were added; $[Pt(PPh_3)_3]$ (50 mg, 5.1 mmol). To these were added but-2-ene, 4 µl (5.1 mmol), 8 µl (10.2 mmol) and 40 µl (51 mmol) respectively. The tubes were sealed under argon and ^{31}P n.m.r. spectra obtained at various temperatures. The stated temperatures were obtained from a methanol-thermometer calibration curve.

E1.3 Synthesis of Organometallic Complexes

Tetrakis(triphenylphosphine)platinum[111]

A solution of triphenylphosphine (650 mg, 0.5 mmol) and potassium hydroxide (60 mg, 0.25 mmol) in ethanol (20 ml) was stirred in a Schlenk tube, under argon, just below its reflux temperature. To this was added dropwise a solution of potassium tetrachloroplatinum (II) ($K_2PtCl_4 \cdot xH_2O$) in a minimum of hot water. A yellow precipitate of tetrakis(triphenylphosphine)-platinum (0) formed within minutes and was collected under argon by filtration. The crude solid was washed with ethanol (5 ml), water (10 ml), ethanol (20 ml) and dried *in vacuo* 370 mg (57% based on Pt). m.p. 118-121°C. ^{31}P n.m.r. (CH_2Cl_2) -13.3 p.p.m. (s with ^{195}Pt satellites J_{PtP} 1905 Hz). IR (KBr) 1432 (vs), 1302 (w), 1162 (m), 1147 (m), 1077 (vs), 1022 (s), 992 (s), 837 (w), 737 (vs), 700 (vs).

Tris(triphenylphosphine)platinum (0)[112]

A suspension of tetrakis(tristriphenylphosphine)platinum (0) (580 mg, 2.13 mmol) in ethanol (25 ml) was boiled and stirred under argon for 2 hr. The temperature was not allowed to rise above 95°C. The supernatant liquid was then pipetted off and the dark orange product washed with 3 ml ethanol. The solid was collected by filtration and dried *in vacuo* 300 mg (65%). ^{31}P n.m.r. (toluene, -76°C) 47.0 p.p.m. (s with ^{195}Pt satellites

J_{PtP} 3820 Hz). IR (KBr) 1430 (vs), 1300 (w), 1177 (m), 1150 (m), 1078 (vs), 1023 (s), 997 (s), 840 (w), 742 (vs), 700 (s).

Bis(triphenylphosphine)dioxygenplatinum (O)

Tris(triphenylphosphine)platinum (O) (200 mg, 0.20 mmol) was dissolved in 10 ml dry toluene under argon. The bright orange solution was saturated with dioxygen by freeze-thaw degassing (x 3). After several minutes pale buff coloured crystals appeared. These were collected by filtration and washed with argon-saturated toluene (5 ml) and hexane (2 x 10 ml). The solid was dried in vacuo giving 107 mg (70%) of (1). m.p. 123-125°C. ^{31}P n.m.r. ($CH_2C\ell_2$) 17.4 p.p.m. (s with ^{195}Pt satellites J_{PtP} 4034 Hz). IR (KBr) 1485 (vs), 1440 (vs), 1325 (w), 1190 (w), 1160 (w), 1100 (vs), 1030 (m), 1000 (m), 830 (vs) (ν_{O-O}), 750 (vs), 710 (vs).

Cis[4-trans(prop-2-enyl)-1,1-Bis(triphenylphosphine)platina-2,3,5-trioxacyclopentane], (20)

trans But-2-enal (16 µl, 0.26 mmol) was added to a suspension of bis(triphenylphosphine)platinum (O) (100 mg, 0.13 mmol) in toluene (0.5 ml). Within minutes the pale yellow suspension became a clear straw-coloured solution. Stirring for 12 hr , produced some white solid. Concentration of the solution at low pressure followed by addition of hexane dropwise effected full precipitation of a white solid, which was collected by filtration and washed with hexane (x2 5 ml). The crude product was recrystallised by dissolving in the minimum volume of dichloromethane followed

by addition of 0.5 ml toluene. On standing at 4°C the filtered solution produced a white microcrystalline solid (20) 53 mg (50%) m.p. 130° (dec). ^{1}H n.m.r. ($CDC\ell_3$, 300 MHz) 7.1-7.7 p.p.m. (m, 30H, aromatic), 5.65 p.p.m. (m, 2H, H^b, H^c), 5.40 p.p.m. (d, 1H, H^a, J_{ab} 4 Hz), 1.60 p.p.m. (d, 3H, H^d, J_{cd} 3 Hz). ^{31}P n.m.r. ($CH_2C\ell_2$) 13.7 p.p.m. (d, with ^{195}Pt satellites, J_{PtP} 3567 Hz, J_{PP} 16 Hz), 10.9 p.p.m. (d, with ^{195} satellites, J_{PtP} 3353 Hz, J_{PP} 16 Hz). IR (KBr) 1480 (m), 1430 (s), 1180 (m), 1090 (s), 740 (m), 690 (s).

The 4-(prop-2-enyl-$3d_3$) analogue (31) was similarly prepared on the same scale. m.p. 130°C (dec). ^{1}H n.m.r. (300 MHz, $CDC\ell_3$) 7.1-7.7 p.p.m. (m, 30H, aromatic), 5.65 p.p.m. (d, 2H, H^b, H^c), 5.40 p.p.m. (d, 1H, H^a). IR (KBr) 1480 (m), 1430 (s), 1180 (m), 1090 (s), 740 (m), 690 (s).

Cis[trans(5-formyl-4-methyl)-1,1-bis(triphenylphosphine)platina-2,3-dioxacyclopentane], (25)

A solution of bis(triphenylphosphine)dioxygenplatinum (0) (100 mg, 0.13 mmol) and but-2-enal (100 µl, 1.63 mmol) in toluene (0.1 ml) was stirred under argon for 4 days. The yellow solution deposited a white solid which was collected by filtration, washed with toluene (2 x 5 ml) and hexane (2 x 5 ml) and dried in vacuo. The crude solid was recrystallised by dissolving in the minimum volume of dichloromethane, adding 1 ml toluene followed by hexane dropwise to the point of cloudiness. On standing, white crystalline rosettes, (25), were collected, 64 mg (60%). ^{31}P n.m.r. ($CH_2C\ell_2$):

23.38 p.p.m. (d, with ^{195}Pt satellites, J_{PtP} 2426 Hz, J_{PP} 17 Hz), 21.08 p.p.m. (d with ^{195}Pt satellites, J_{PtP} 3400, J_{PP} 17 Hz). ^{1}H n.m.r. ($CD_2C\ell_2$, 300 MHz) 9.0 p.p.m. (d, 1H, H^a, $^{3}J_{ab}$ 3 Hz), 7.2-7.6 (m, 30H, aromatic), 3.6 p.p.m. (m, 1H, H^c, J_{dc} 6 Hz, J_{bc} 12 Hz, $^{4}J_{PH}$ 1.5 Hz), 3.1 p.p.m. (m, 1H, H^b, J_{ab} 3 Hz, J_{bc} 12 Hz, J_{PtH} 79 Hz, $^{3}J_{PH}$ 6 Hz), 1.3 (d, 3H, J_{cd} 6 Hz). IR (KBr) 1665 (vs), 1480 (m), 1435 (s), 1095 (s), 745 (m), 700 (vs). m.p. 145°C (dec). Analysis: Found C (58.0%); H (4.6%); P (7.5%); Calculated C (58.5%), H (4.4%), P (7.5%).

Cis[bis(triphenylphosphine)-η^2-(ethylene)platinum (0)][89]

Tetrakis(triphenylphosphine)platinum (0) (2 g, 1.6 mmol) was dissolved in 60 ml toluene through which dioxygen was bubbled while solid carbon dioxide was added, over 30 min. A pale yellow solid was collected. This was a mixture of carbonate and peroxycarbonate complexes. Complete conversion to the carbonate was ensured by dissolving the crude solid in 35 ml dichloromethane with 2g triphenylphosphine. The solution was refluxed for 6 hr. Upon evaporation of solvent and tritriation of the resulting oil with toluene a white crystalline solid appeared which was washed with diethyl ether (2 x 20 ml). 700 mg (59%) IR (KBr) $\nu_{C=O}$ 1680 (vs). Bis(triphenylphosphine)(carbonato)platinum (0) (700 mg, 0.9 mmol) was stirred in 40 ml ethanol in a three-necked flask. ca. 12 ml 0.1 M ethanolic solution of sodium borohydride was added dropwise while ethylene was bubbled slowly through the solution. After 30 min , there was no apparent change in the white suspension.

The white solid was collected by filtration and washed with ethanol (5 ml), water (5 ml) and finally ethanol (5 ml), 400 mg (59%) m.p. 126-128°C. ^{31}P n.m.r. ($CH_2C\ell_2$) 33.9 p.p.m. (s with ^{195}Pt satellites J_{PtP} 3704 Hz). ^{1}H n.m.r. (C_6D_6, 300 MHz) 7.6-6.9 p.p.m. (m, 30H, aromatic), 2.6 p.p.m. (t, 4H, J_{PtH} 60 Hz).

Cis[bis(triphenylphosphine)-trans(but-2-enal)platinum (0)][114]

A suspension of bis(triphenylphosphine)platinum (0) (100 mg, 0.14 mmol) and but-2-enal (100 µl, 1 mmol) in 5 ml hexane was stirred for 12 hr. The white solid was collected by filtration and washed with hexane (10 x 2 ml) 90 mg (82%). m.p. 124-125°C. IR (KBr) 1655 (vs, $\nu_{C=O}$), 1475 (m), 1430 (m), 1090 (s), 740 (s), 695 (s). ^{31}P n.m.r. ($CH_2C\ell_2$, -76°C) 26.0 p.p.m. (d, with ^{195}Pt satellites J_{PtP} 4360, J_{PP} 44 Hz), 28.7 p.p.m. (d, with ^{195}Pt satellites, J_{PtP} 338 Hz, J_{PP} 44 Hz). ^{1}H n.m.r. ($CDC\ell_3$, 300 MHz) 8.45 p.p.m. (d, 1H), 7.3 p.p.m. (m, 30H, aromatic), 3.4 p.p.m. (m, J_{PtH} 60 Hz), 2.85 p.p.m. (m, J_{PtH} 55 Hz), 1.1 p.p.m. (m, 3H).

Cis[bis(triphenylphosphine)bis(trifluoroacetato)platinum (0)]

This preparation was adapted from the analogous acetate preparation[115].

A solution of trifluoroacetic acid (25 µl, 500 mmol) and tetrakis(triphenylphosphine)platinum (0) (40 mg, 32 mmol) in 1.5 ml toluene was stirred in air for 1 hr. The solution was evaporated under reduced pressure to half volume. Addition of light petroleum ether induced precipitation. The white solid

was collected and recrystallised from dichloromethane by addition of hot petroleum ether, giving fine white needles, m.p. 234-237°C. IR (KBr) 1730 (vs, ν_{OCO}), 1705 (vs, ν_{OCO}), 1490 (m), 1440 (m), 1406 (m, ν_{OCO}), 1190 (vs), 1145 (m), 1105 (m), 1005 (m), 850 (w), 790 (w), 750 (w), 735 (w), 715 (m), 700 (m).

Dicarbonylbis(triphenylphosphine)platinum (0)[92]

Carbon monoxide was bubbled through a solution of tris-(triphenylphosphine)platinum (0) (50 mg, 51 mmol) in toluene at ca. -60°C. The orange solution became colourless and was poured into cold hexane with agitation. An off-white solid was collected, 20 mg (50%). ^{31}P n.m.r. (toluene, -70°C) 7.7 p.p.m. (s, with ^{195}Pt satellites J_{PtP} 3232 Hz). IR (KBr) 1983 (s), 1948 (s) ($\nu_{C=O}$).

E1.4 Synthesis of Organic Compounds

trans But-2-enal-d_3

(i) Methyl-d_3-methanesulphonate:

Methanol-d_4 (4.8 g, 0.13 mol) and triethylamine (15.0 g, 0.15 mol) were stirred at 0°C in 150 ml diethyl ether. Methanesulphonyl chloride (19.5 g, 0.13 mol) was added dropwise over 30 min. The mixture was stirred for 5 hr at room temperature before the ether was evaporated at reduced pressure. The sludge was taken up in dichloromethane (50 ml) and water (50 ml) and the organic layer dried over sodium sulphate and evaporated under reduced pressure to yield 30 g of a light red oil. The crude product was distilled through a 15 cm Vigreux column. The fraction boiling at 50°C (0.6 mm) afforded 10 g of a clear colourless oil (66%), methyl-d_3-methanesulphonate. ^{1}H n.m.r. ($CDC\ell_3$ 90 MHz) 3.0 p.p.m. (s).

(ii) 1,3-bis(methylthio)allyllithium[86]

A solution of sodium hydroxide (22 g, 0.55 mol) in 150 ml methanol was stirred vigourously at 0°C. Methanethiol (28 ml, 0.52 mol) was distilled into the reaction flask at such a rate that the temperature was maintained below 20°C. Epichlorohydrin (19 ml, 0.24 mol) was then added dropwise, maintaining a temperature below 50°C. The reaction was stirred at 25°C for 1 hr , diluted with 250 ml water and extracted with ether (2 x 100 ml). The combined extracts were washed with water (5 x 50 ml) and brine

(50 ml) then dried over anhydrous sodium sulphate. Solvent was removed under reduced pressure and the resulting liquid distilled on a 20 cm Vigreux fractionating column. The fraction boiling at 110°C (7 mm) afforded 26.2 g (71%) of 1,3-bis(methylthio)-propan-2-ol. ^{1}H n.m.r. ($CDC\ell_3$, 90 MHz) 3.86 p.p.m. (m, 1H), 3.78 p.p.m. (s, 1H), 2.63 (d, 4H), 2.12 (s, 6H).

Sodium hydride (7.4 g, 0.17 mol) washed free of mineral oil with hexane was vigourously stirred in 250 ml dry tetrahydrofuran. 1,3-bis(methylthio)propan-2-ol (17 g, 0.11 mol) was added dropwise over 15 minutes, with evolution of hydrogen. The reaction was cooled to 20°C and methyl iodide (7.5 ml, 0.12 mol) added dropwise. The reaction was stirred for 24 hr , at room temperature. The mixture was concentrated to 100 ml under reduced pressure diluted with 100 ml ether and washed with brine (50 ml), 0.5 M aqueous ammonium chloride (2 x 50 ml) and brine (50 ml). The ethereal extract was dried over sodium sulphate, evaporated at reduced pressure and the remaining oil distilled on a 20 cm Vigreux column. The fraction boiling at 95°C (10 mm) afforded 12.0 g (60%) of 1,3-bis(methylthio)-2-methoxypropane. ^{1}H n.m.r. ($CDC\ell_3$ 90 MHz) 3.5 p.p.m. (m, 1H), 3.5 p.p.m. (s, 3H), 2.7 p.p.m. (d, 4H), 2.1 p.p.m. (s, 6H).

Under dry conditions, diisopropylamine (6 g, 0.05 mol) and 90 ml tetrahydrofuran were stirred under argon.

The solution was stirred at -76°C while 38 ml (0.055 mol) of 1.45 M solution of n-butyllithium in hexane was added dropwise. While the resulting solution of lithium diisopropylamide

was maintained at -76°C, 1,3-bis(methylthio)-2-methoxypropane (4.1 g, 0.025 mol) was added dropwise. The solution was allowed to warm up to 0°C during which time the deep purple 1,3-bis-(methylthio)allyllithium was generated.

(iii) 1,3-bis(methylthio)-4,4,4-[$^2H_3$]-but-1-ene

To the solution of 1,3-bis(methylthio)allyllithium at -76°C was added methyl-d_3-methanesulphonate (3.73 g, 38 mmol) dropwise. The solution was allowed to warm to 20°C for 30 min. The solution was diluted with 120 ml ether and washed with 5 M aqueous ammonium chloride (2 x 50 ml), water (2 x 50 ml), brine (50 ml). Each aqueous layer was washed with a little ether. The combined ethereal layers were dried over anhydrous sodium sulphate and evaporated under reduced pressure to yield a black oil. The crude product was distilled 'trap-to-bucket' to afford 3.2 g (85%) of a clear colourless oil with repugnant odour, which was pure by ^1H n.m.r. ^1H n.m.r. ($CDC\ell_3$, 60 MHz) 5.0 - 5.6 p.p.m. (m, 1H), 6.0 - 6.3 (m, 1H), 3.1 - 3.3 (m, 1H), 2.3 (s, 3H), 2.0, 2.05, 2.1 (s, 3H). The presence of multiplets in the olefinic region suggested a mixture of cis and trans, diastereomers.

(iv) But-2-enal-d_3

1,3-bis(methylthio)-4,4,4-[$^2H_3$]-but-1-ene (1 g, 6.6 mmol) in 5 ml tetrahydrofuran was added to a suspension of 5 g mercury(II)-chloride (16 mmol) and 600 µl water in 5 ml tetrahydrofuran. The reaction was followed by ^1H n.m.r. in the aldehydic region where product formation could be monitored. The mixture was stirred for 1 hr. Mercuric salts were removed by 'trap-to-bucket' distillation at low pressure. A small Vigreux column was used to carefully reduce the solvent volume to 2 ml. The resulting mixture of product and solvent was subjected to preparative GLC (15 foot column Diatonite C 15% PEG 20M; 100°C)

The yield of the product, collected and stored in dichloromethane, was estimated by ^1H n.m.r. (100 µl, 15%). ^1H n.m.r. (90 MHz, $CDC\ell_3$) 9.5 p.p.m. (d, 1H), 7.1 p.p.m. (m, 1H), 6.1 p.p.m. (m, 1H).

t-Butylisocyanide

A procedure modified from Ref. 115

A solution of t-butylamine (36 ml, 0.34 mol), trichloromethane (21 g, 0.17 mol) and 18 Crown 6 (ca. 20 mg) in dichloromethane (53 ml) was added dropwise to a vigourously stirred solution of potassium hydroxide (74 g, 1.32 mol) in 74 ml water at 45°C. The mixture was refluxed for 4 hr., during which time a copious white precipitate of potassium chloride formed. Water (140 ml) was added and the organic layer extracted and washed with water (50 ml) and finally brine (50 ml). The organic

layer was dried over anhydrous magnesium sulphate to give a pale yellow solution. Product was collected as the fraction boiling at 92-93°C when the solution was distilled through a 20 cm Vigreux column at atmospheric pressure. 5.3 g (25% of t-butyl-isocyanide which was pure by ^{1}H n.m.r. was collected as a clear and colourless liquid with strong odour. ^{1}H n.m.r. ($CDC\ell_3$, 90 MHz) 1.45 p.p.m. (t, $^3J_{NH}$ 2 Hz).

2-Methylenecyclohexan-1-one

2-(N,N-dimethylaminomethyl)cyclohexan-1-one was prepared by the method of Mannich[116]. Cyclohexanone (123 g, 1.25 mol), formaldehyde (20.5 ml 40% aqueous, 0.5 mol) and dimethylamine hydrochloride (20.4 g, 0.25 mol) were stirred together. Initiation of an exotherm by the careful application of a small flame to the reaction vessel led to refluxing. The mixture became yellow and homogenous. After heating for 1 hr., the solution was cooled and 125 ml water added. Excess cyclohexanone was extracted with ether. Evaporation of the aqueous layer gave 32 g brown oil. The free base was released by addition of sufficient aqueous potassium hydroxide and extracted with ether. The ether was dried using anhydrous sodium sulphate and evaporated to give a brown oil. Distillation through a 20 cm Vigreux column gave a clear, colourless oil boiling at 82°C (9 mm) 10 g (13%). 2-(N,N-dimethylaminomethyl)cyclohexan-1-one (1.7 g, 11.3 mmol) was dissolved in 15 ml dichloromethane at 0°C. Methyl iodide (2.0 g, 13.6 mmol) was added slowly dropwise. A white solid formed which was dissolved in 25 ml dichloromethane

and 25 ml sodium hydrogen carbonate (aqueous 5%) at 0°C. After 1 hr , the dichloromethane layer was extracted and dried over anhydrous sodium sulphate. The solvent was evaporated at 0°C at reduced pressure to afford a colourless oil, 0.53 g (60%) ^{1}H n.m.r. ($CDC\ell_3$, 90 MHz), 5.8 p.p.m. (m, 1H), 5.1 (m, 1H), 1.5-2.5 p.p.m. (m, 8H). The product was unstable at room temperature and was stored at -30°C.

2-Formyl-3-methyloxirane[100]

A solution of trans but-2-enal (5 g, 63 mmol) and hydrogen peroxide (10 ml, 30%, 65 mmol) in methanol (50 ml) were added dropwise to 50 ml of aqueous saturated sodium bicarbonate. The temperature was not allowed to rise above 5°C. After stirring for 1 hr., the epoxide was extracted with dichloromethane (5 x 25 ml). The combined organic layers were dried over sodium sulphate and solvent removed by evaporation at 0°C under reduced pressure. Polymeric products were removed by 'trap-to-bucket' distillation to afford a clear colourless liquid 2.1 g (49%), pure by ^{1}H n.m.r. (300 MHz). ^{1}H n.m.r. (C_6D_6 as shift reagent) revealed that the isomeric epoxides were present in 85 (trans): 15 (cis) ratio. ^{1}H n.m.r. (C_6D_6, 300 MHz) ($H^aCO)CH^b(O)CH^c(CH_3{}^d$) (trans isomer) 8.6 p.p.m. (d, 1H, H^a, J_{ab} 6 Hz), 2.6 p.p.m. (dd, 1H, H^b, J_{ab} 6 Hz, J_{bc} 1.5 Hz), 2.4 p.p.m. (qd, 1H, H^c, J_{bc} 1.5 Hz, J_{cd} 4 Hz), 1.6 p.p.m. (d, 3H, H^d, J_{cd} 4 Hz); (cis-isomer) 9.0 p.p.m. (d, 1H, H^a, J_{ab} 4 Hz), 2.8 p.p.m. (t, 1H, H^b, J_{ab} 4 Hz, J_{bc} 4 Hz), 2.5 p.p.m. (pentet, 1H, H^c, J_{bc} 4 Hz, J_{cd} 4 Hz), 1.8 p.p.m. (d, 3H, H^d, J_{cd} 4 Hz).

CHAPTER II

2.1 Introduction

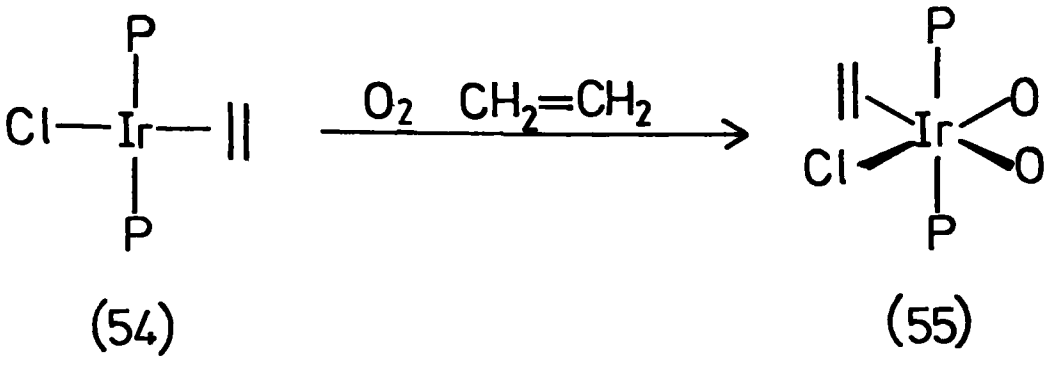
It was reported by Read[69,70] that Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, (16), in the presence of triphenylphosphine and dioxygen catalyzed the co-oxidation of oct-1-ene and triphenylphosphine (vide supra). Under optimum conditions, and in the presence of a free radical inhibitor up to 7 moles of octan-2-one per mole of complex were formed. On the basis of GLC analysis Read identifies a rapid initial phase of oxidation followed by the catalytic cycle involving different reactive intermediates.

The analogous complexes (50), (51) and (52) are similarly active catalysts in the presence of triphenylphosphine[117].

In order to explain these observations Read, supported by others[71] suggested the formation of the metallacycle (53) which subsequently broke down to yield the oxidation products. This metallacycle or its immediate precursor, a complex coordinating both olefin and dioxygen, have not been isolated nor identified. Although the reaction is carried out under conditions where Rh(III) peroxo complexes may form[118] it has not been demonstrated that they are involved in the oxidation.

In the course of studying the hydrogenation and isomerisation of olefins, van der Ent[119] prepared the square planar complex (54). He found that this coordinatively unsaturated Ir(I) complex added dioxygen in the presence of ethylene to form the stable peroxo complex (55) as shown in Figure 57. Although the configuration of complex (55) has not been defined by X-ray crystallographic analysis, the molecular geometry of the analogous complex $[Ir(PPh_3)_2(CO)Cl(O_2)]$, (27), and similar complexes has been determined[6] (vide supra).

Van der Ent further showed that the ethylene ligand in complex (55) was labile to substitution by triphenylphosphine and pyridine giving the stable complexes (56) and (57) respectively. The complex (55) was noted

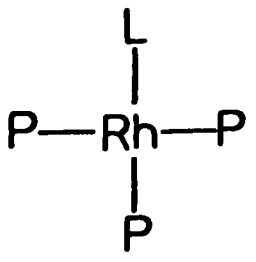


(54) (55)

Figure 57

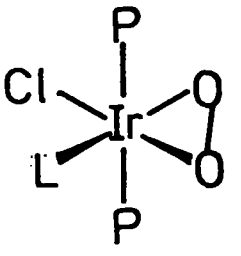
by van der Ent to be unique in coordinating both an olefin and dioxygen at the same metal centre.

It was the intention of this work to investigate the ability of complex (55) and its analogues to oxidize terminal olefins. Also an attempt has been made to prepare and characterize neutral and cationic iridium (I) olefin complexes and explore their reactivity towards dioxygen.



L= Cl (16)
CN (50)
OCN (51)
SCN (52)

P=Ph3P



L= CO (2)
CH2=CH2 (55)
P (56)
N (57)

2.2 The Preparation of trans-[$Ir(PPh_3)_2(CH_2{=}CH_2)Cl$], (51), and its Analogues

Complex (54) was synthesised by the method of van der Ent[120] from the freshly prepared dimer (58) by addition of triphenylphosphine, as shown in Figure 58.

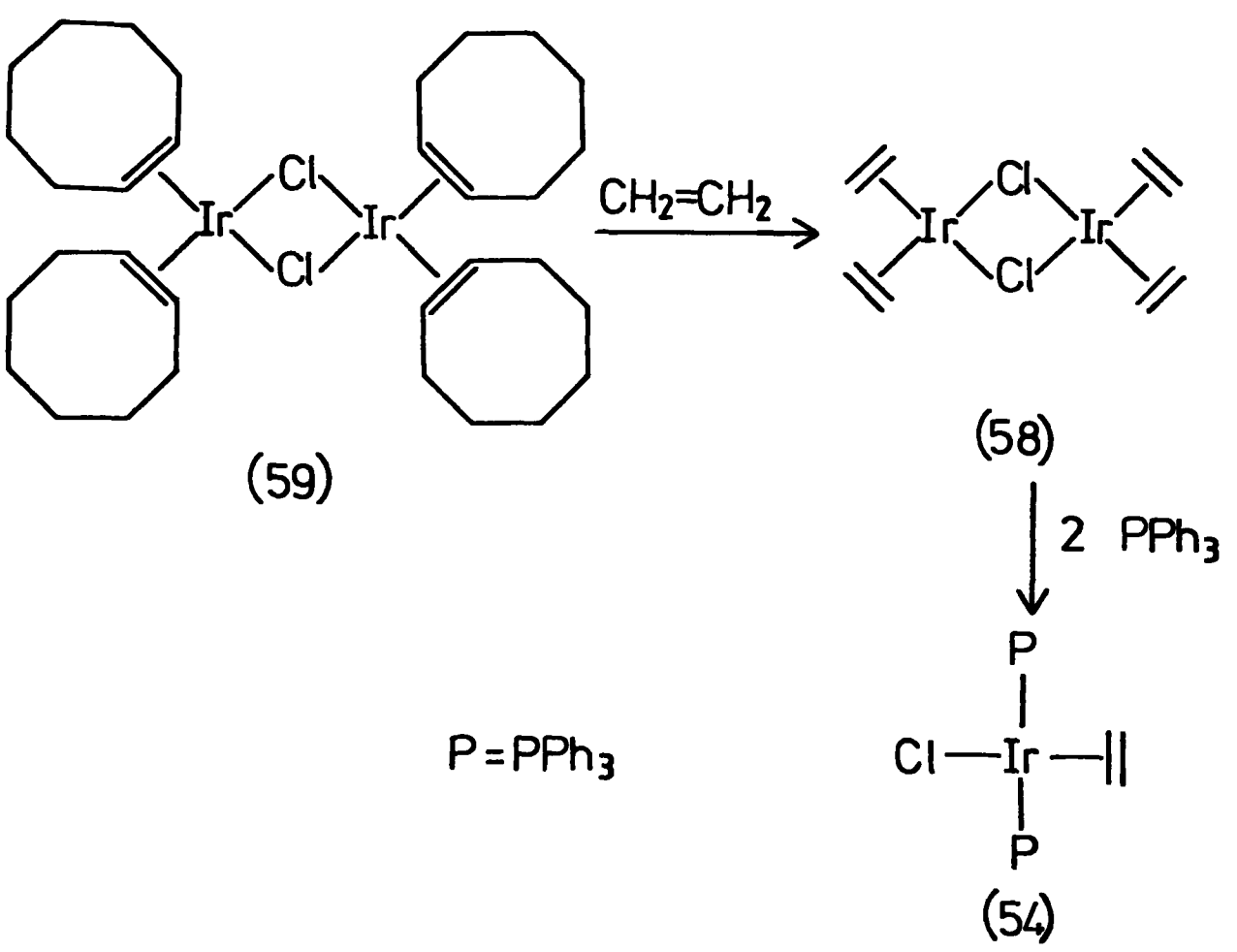
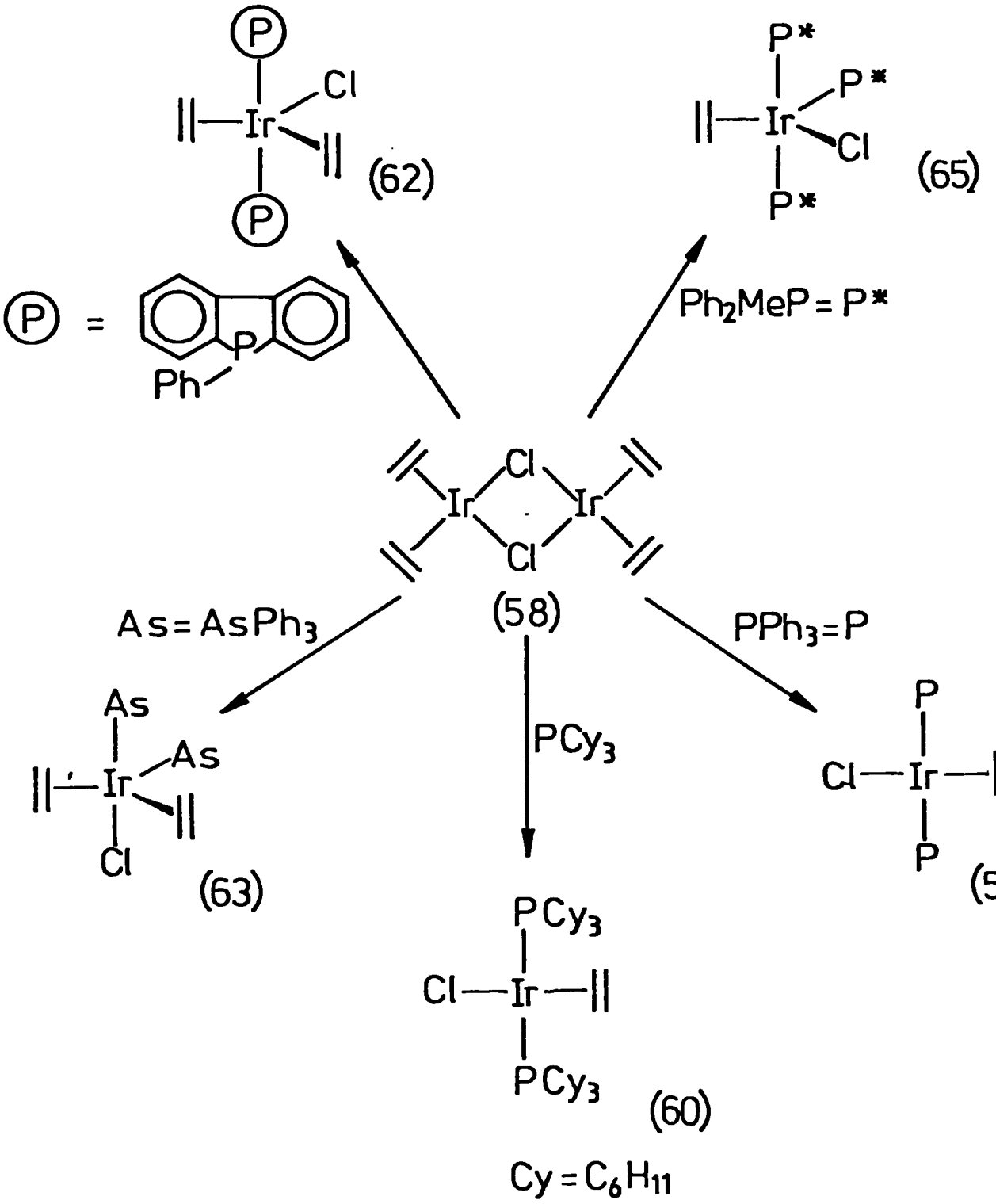


Figure 58

The ^{31}P n.m.r. (36.43 MHz) spectrum of complex (54) displays a singlet at 27.0 p.p.m. as would be anticipated for the magnetically equivalent phosphorus atoms. The ^{1}H n.m.r. (300 MHz) spectrum reveals broad resonances at 5.4 p.p.m. and 1.1 p.p.m. indicating a dynamic exchange of free and bound ethylene at ambient temperature.

Similarly the addition of 2 molar equivalents of tricyclohexylphosphine (Pcy_3) to (58) results in the formation of the previously unknown stable ethylene complex, (60) as shown in Figure 59. This complex exhibits, as expected, a singlet in its ^{31}P n.m.r. spectrum (9.4 p.p.m.). The ^{1}H n.m.r. (300 MHz) spectrum of complex (60) (Figure 60) shows the ethylene protons

Figure 59


P
Cl
Ir
(62)
P
P = P
Ph
P*
P*
Ir
Cl
(65)
P*
Ph2MeP = P*
Cl
Ir
Ir
Cl
(58)
As = AsPh3
PCy3
PPh3 = P
As
As
Ir
Cl
(63)
PCy3
Cl
Ir
PCy3
(60)
P
Cl
Ir
P
(54)
Cy = C6H11

resonating at 1.5 p.p.m. The coupling to the two equivalent phosphorus nuclei is clearly seen in the triplet structure (J_{PH} 4 Hz) of the signal. Unlike complex (54) exchange with free ethylene is not occurring at ambient temperature, which may be a consequence of the very bulky phosphine employed.

The addition of 5-phenyl-5H-dibenzophosphole[121] (61), to complex (58) resulted in the formation of the 5-coordinate bis(ethylene) complex, (62) (Figure 59), which could be isolated as a stable off-white solid giving satisfactory elemental analysis. The ^{31}P n.m.r. spectrum (36.43 MHz) of this complex (Figure 61) indicates that the phosphorus nuclei are in magnetically inequivalent environments and coupled to each other. This defines a cis configuration of the phosphole ligands. The ^{31}P n.m.r. spectrum does not distinguish, however, the two possible configurational isomers A and B shown in Figure 62.

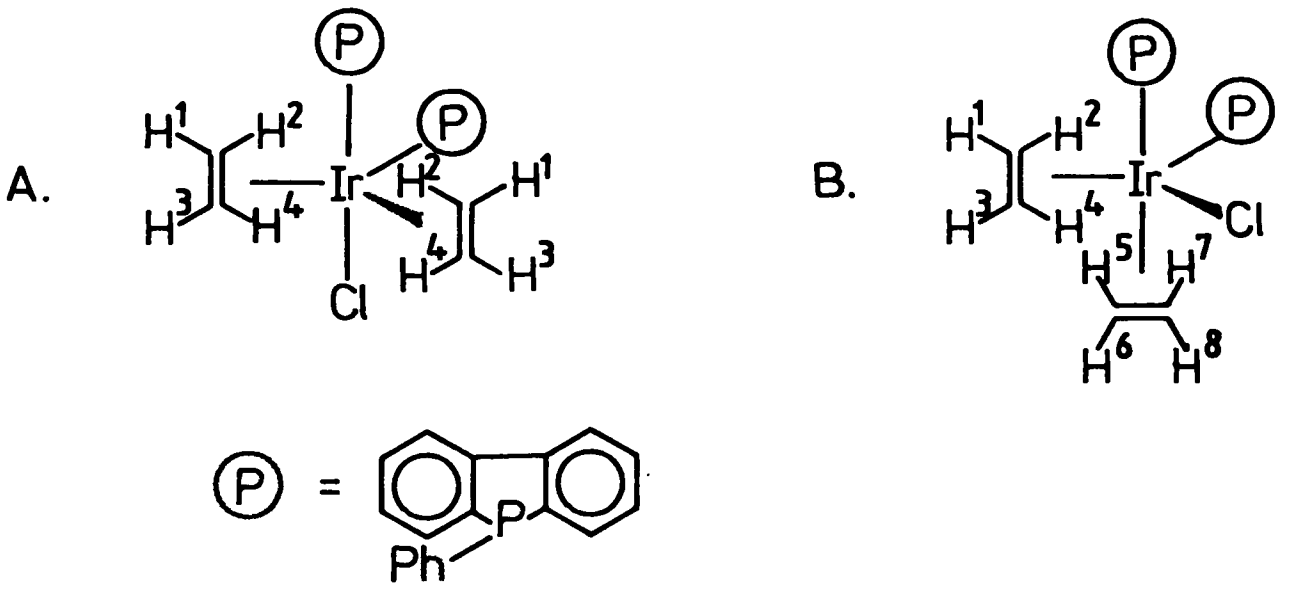


Figure 62

The ^{1}H n.m.r. spectrum (300 MHz) of complex (62) shown in Figures 63a and 63b suggests four distinct proton environments in the olefinic region (2.5 - 3.- p.p.m.) each resonance possessing complex quartet structure. At -80°C the spectral line shape in this region is essentially unaltered. Isomer A possesses four pairs of inequivalent protons, rotation of the

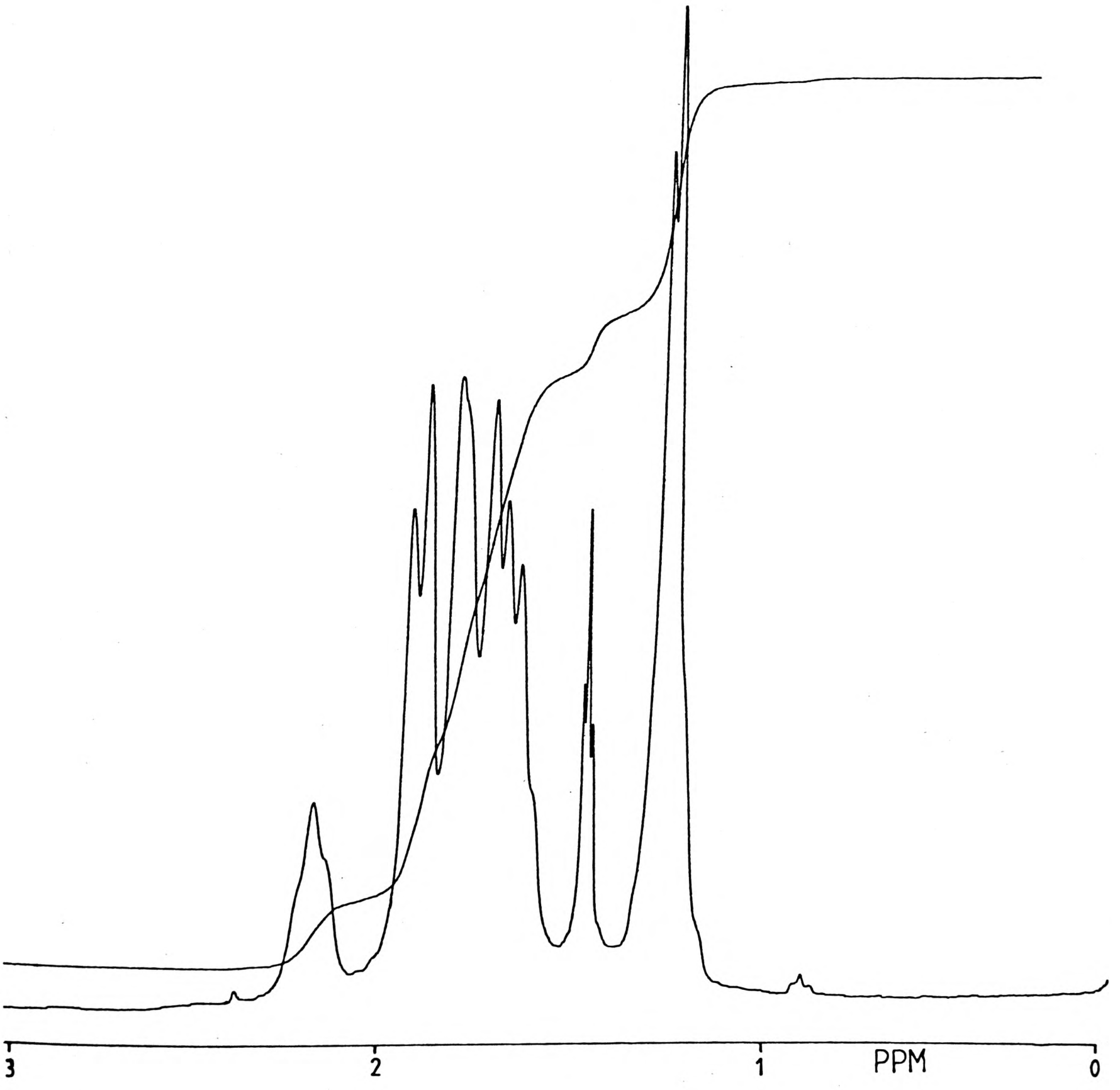
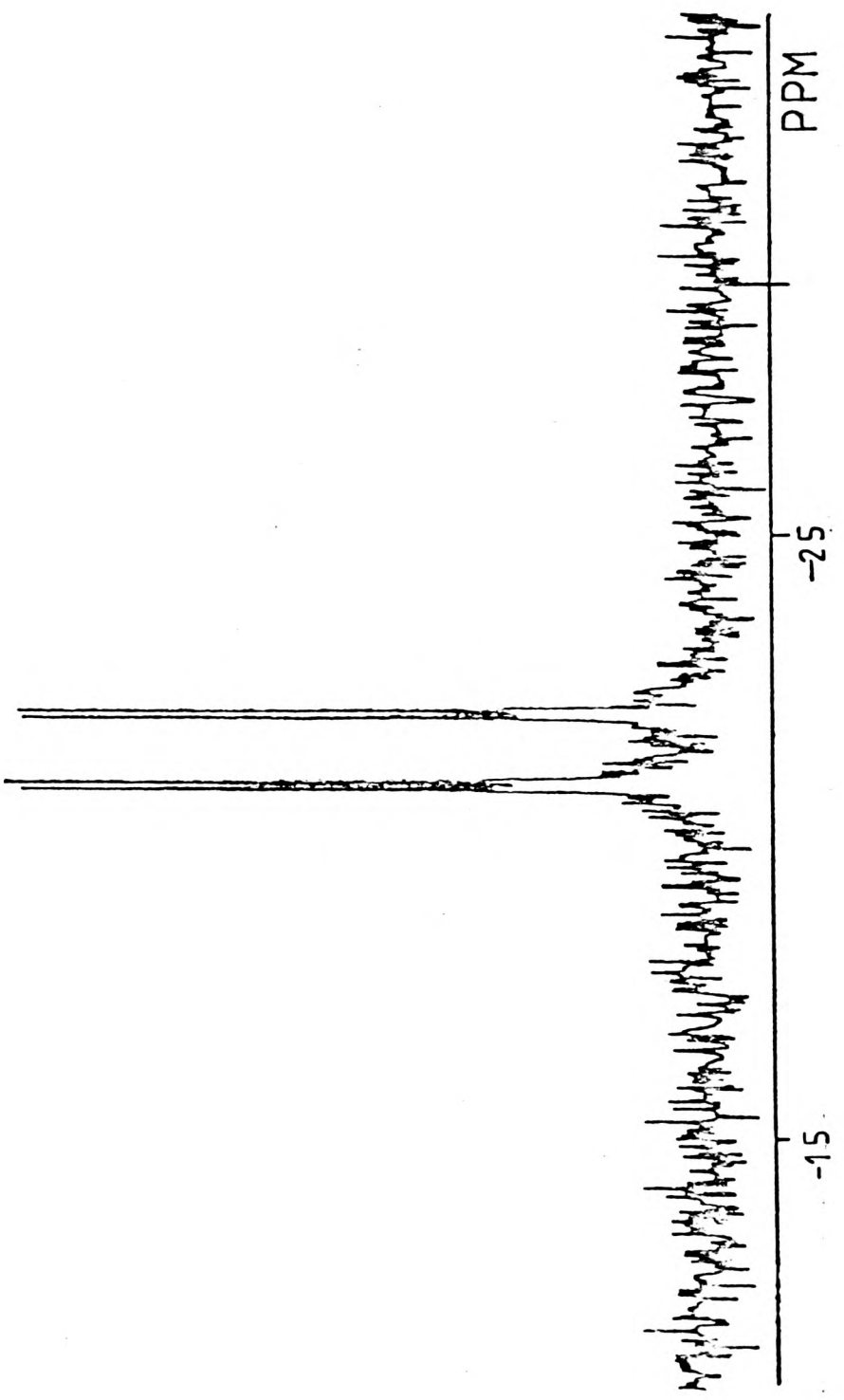


Fig. 60 ^{1}H NMR [300 MHZ]

Fig. 61 ^{31}P NMR [36.4 MHZ]

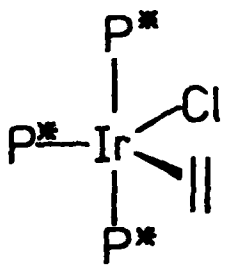


double bond would equivalence diagonal pairs. Isomer B has eight proton environments which would become four inequivalent pairs by olefin rotation. The observations, particularly the absence of line change at low temperature, favour the assignment of isomer A in which the double bond does not rotate at ambient temperature or below.

The analogous triphenylarsine complex, (63), formed by addition of triphenylarsine to (58) (Figure 59) could not be isolated in pure form. The complex is unstable in the absence of ethylene and probably disproportionates to the tris(triphenylarsine) complex (64). The ^{1}H n.m.r. spectrum (300 MHz) of the olefinic region in (63) (Figure 64) suggests that the complex exists as a mixture of (ax,ax) and (ax,eq) isomers. Flushing the solution with either argon or oxygen leads to the simultaneous decrease in intensity of signals from these isomers, and formation of a species which, by n.m.r. integration, contains $3(AsPh_3)$ per $CH_2{=}CH_2$ (complex (64)).

The addition of four molar equivalents of diphenylmethylphosphine to a solution of complex (58) led to formation of the tris(diphenylmethylphosphine) complex (65) (Figure 65), as suggested by the ^{31}P n.m.r. spectrum which exhibited a triplet resonance corresponding to the equatorial phosphine, and a doublet resonance arising from the two equivalent axial phosphines. The two sets of phosphorus nuclei are inequivalent and couple to each other (J_{PP} = 14 Hz).

Fig.65



P* = Ph_2MeP

(65)

Fig.63a ^{1}H NMR [300 MHZ]

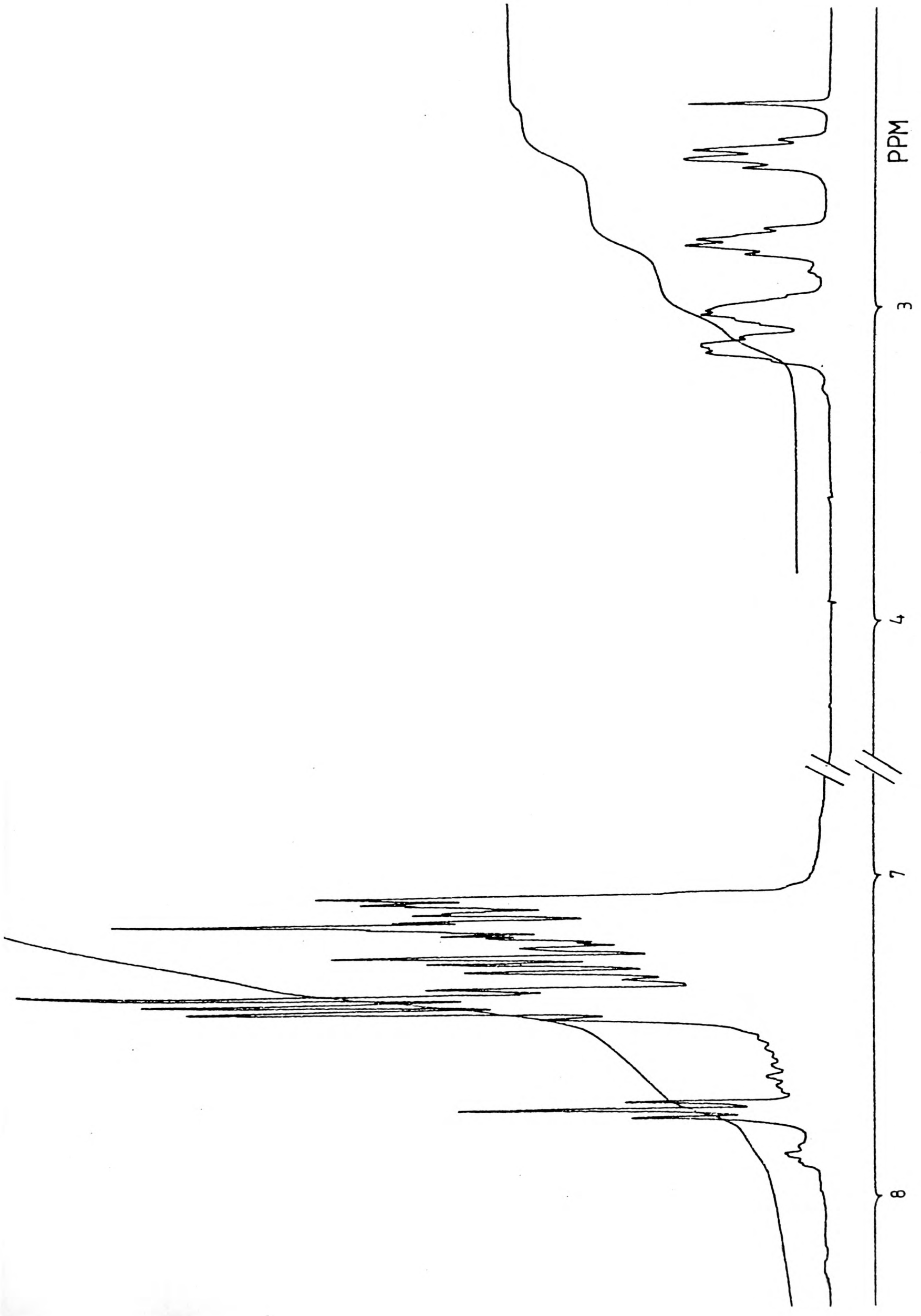


Fig 63b ^{1}H NMR[300MHZ]

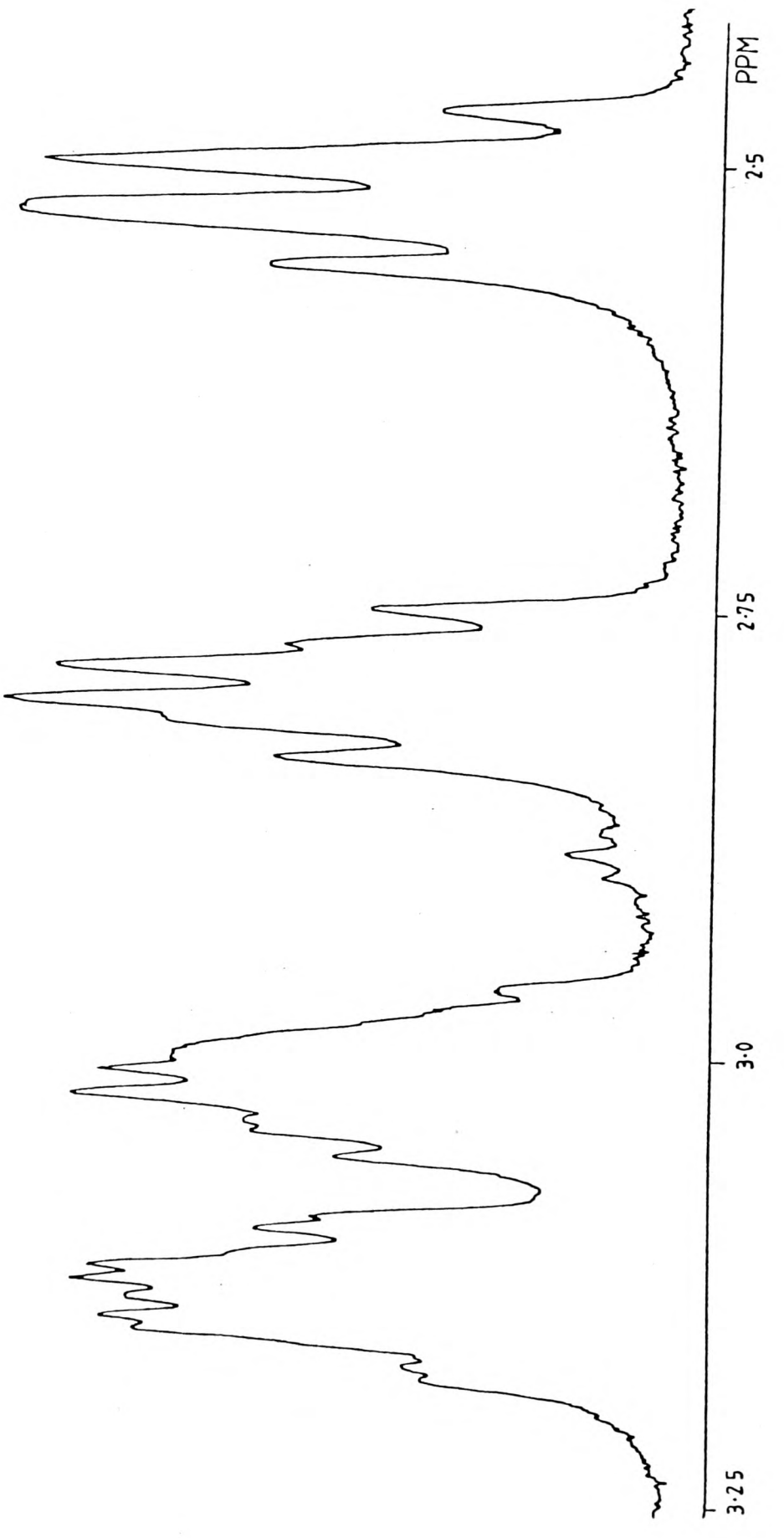
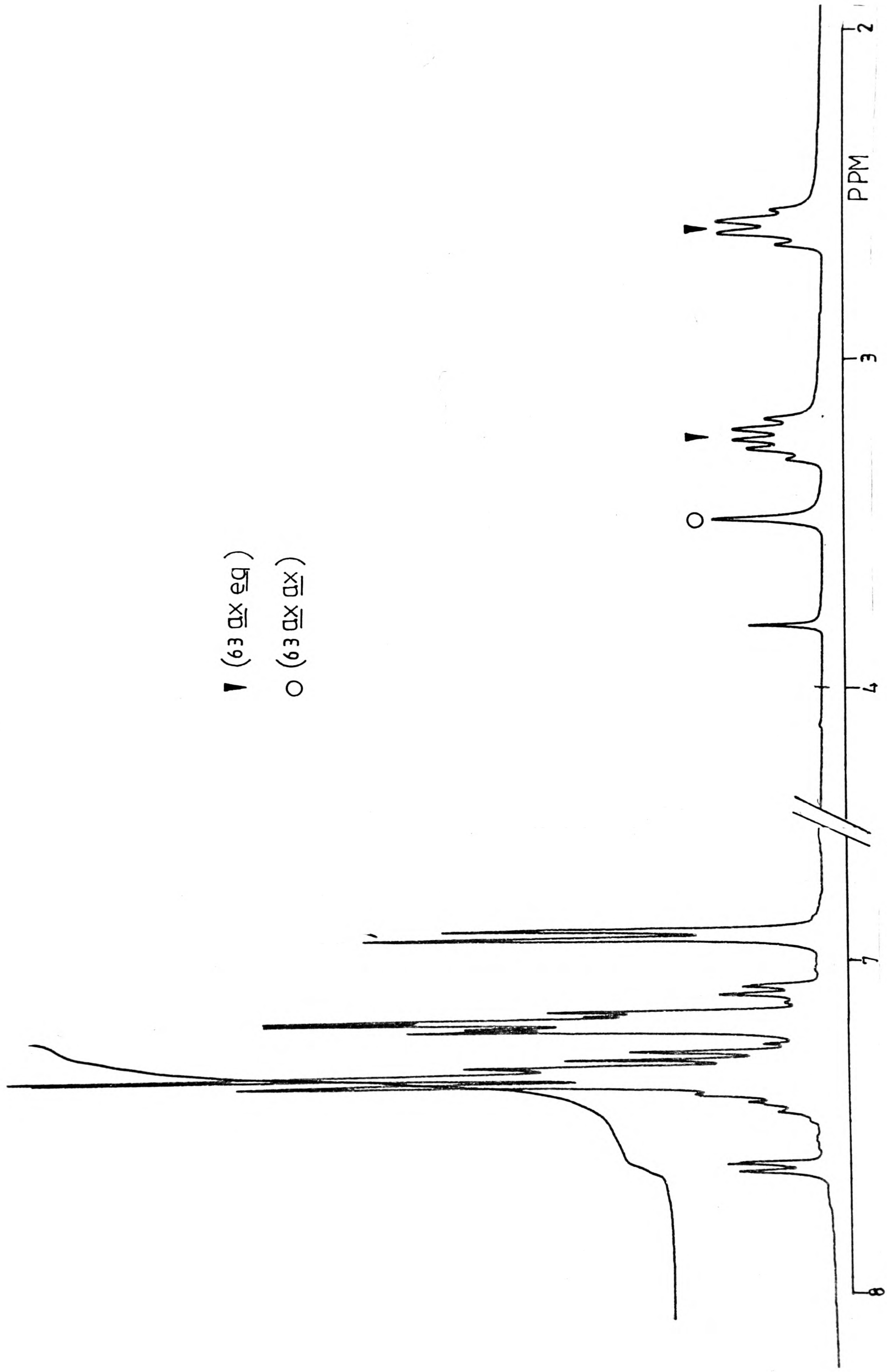


Fig. 64 ^{1}H NMR[300MHZ]



2.3.1 Attempted Preparation of Substituted Olefin Complexes

An attempt was made to synthesise complexes of the type $[Ir(PPh_3)_2Cl(CH_2CHR)]$ where R = Me, Ph, by means of the ethylene complexes (54) and (58). Addition of a 20 molar excess of styrene to complex (54) in dichloromethane solution led to little significant change in the ^{31}P n.m.r. spectrum after 2 days. Warming the solution to 40°C produced only numerous products of decomposition. Similarly, complex (54) dissolved in propylene-saturated dichloromethane gave rise to recovered starting material. Products of propylene addition were not identified by ^{31}P or ^{1}H n.m.r. spectroscopy. In view of this unreactivity of ethylene displacement by other simple olefins in complex (54), an attempt was made to add these olefins to the ethylene dimer, complex (58), followed by addition of phosphine. It was found, however, that when either an excess of styrene or propylene was added to the dimer (58) no changes in the deep red colour were observed. Addition of triphenylphosphine to these solutions resulted only in recovery of the ethylene complex (54). In these cases it was not possible to displace ethylene by either propylene or styrene.

2.3.2 The Reaction of trans but-2-enal with trans$[Ir(PPh_3)_2Cl(CH_2{=}CH_2)]$.

The reaction of trans but-2-enal with some Pt(0) complexes had been investigated (Chapter I). Unlike these reactions, the addition of this unsaturated aldehyde to the iridium (I) complex (54) resulted in its quantitative decarbonylation.

The addition of two molar equivalents of trans but-2-enal to a solution of complex (54) in dichloromethane at ambient temperature led to a change in colour of the solution from orange to canary yellow over 30

minutes. After two hours fine yellow needle-like crystals began to appear. The ^{31}P n.m.r. and IR spectra of these crystals were identical to an independently synthesised sample of trans[Ir(PPh_3)(CO)Cl], (66)[6]. The absorbance at 1960 cm^{-1} was particularly diagnostic of the carbonyl group. It was reasonable to suppose that the unsaturated aldehyde had been decarbonylated, but the formation of the resulting propylene could not be established because of its volatility. Consequently the reaction was repeated using 3-phenylpropenal as substrate. After five hours the orange solution had become yellow. Analysis of this resulting solution by gas chromatography showed the quantitative formation of styrene. Crystals of the Vaska complex (66) were also isolated from the solution, and identified by infra-red spectroscopy. A number of transition metal complexes are known to function as decarbonylation agents and they are subject to a recent review[122]. The mechanism presumably involves oxidative addition of the aldehyde function as the first step, shown in Figure 66. An alkyl

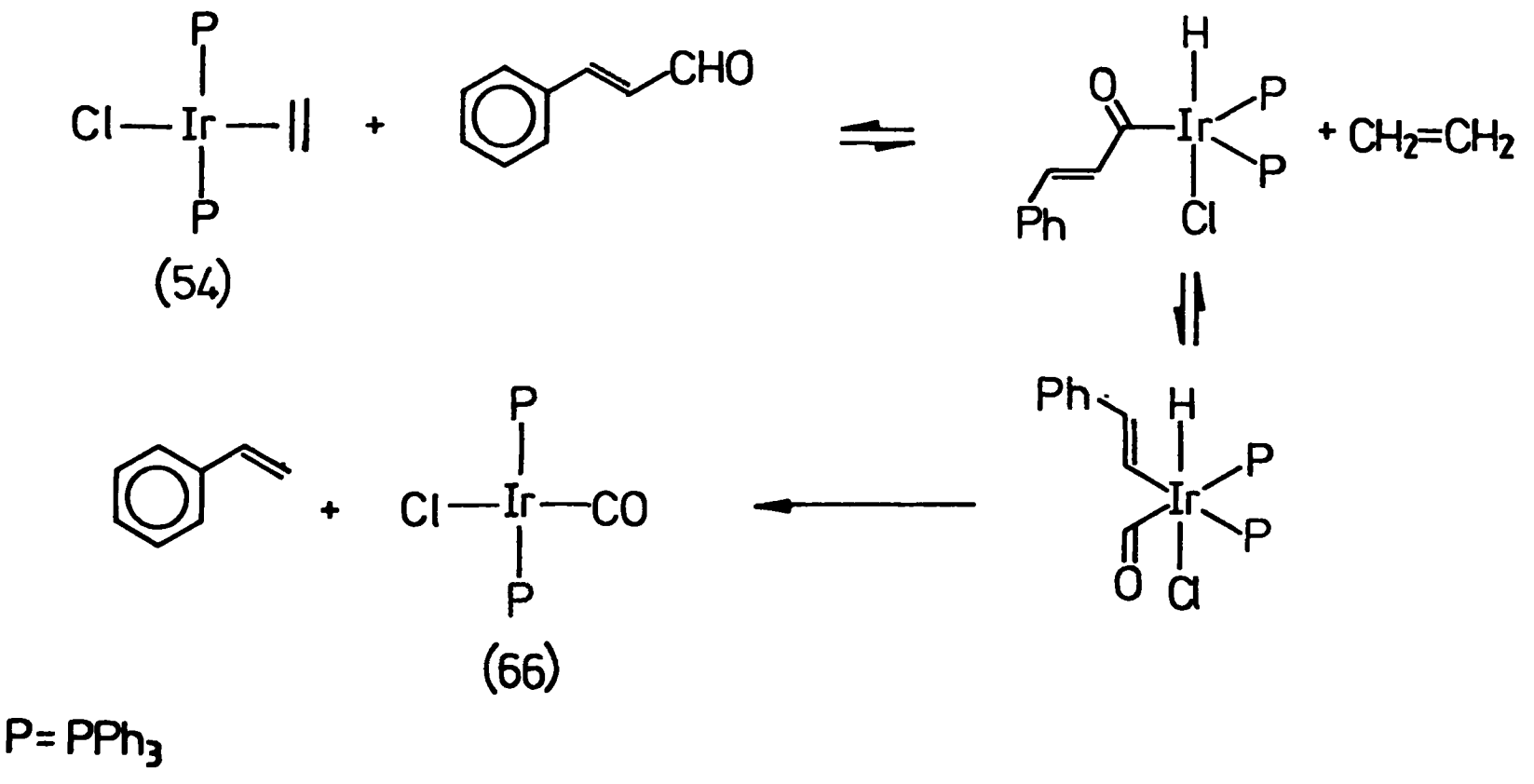


Figure 66

migration to the metal followed by reductive elimination of styrene completes

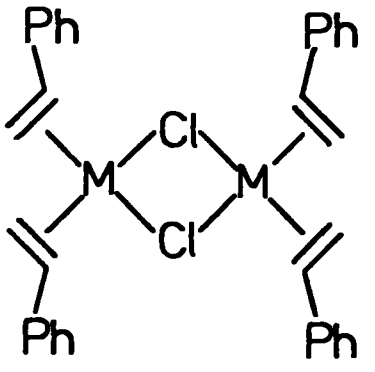
the sequence.

2.3.3 The Preparation of Iridium(I) Styrene Complexes

Although styrene was not able to displace ethylene from complex (54) (vide supra), it very readily displaces cyclooctene from complex (59). The reaction of an excess of styrene with a suspension of complex (59) in isopentane results in the formation of the stable, deep red styrene dimer, (67), in high yield. The structure was confirmed by satisfactory analytical and mass spectromeric data, and by ^{1}H n.m.r. The analogous rhodium complex, (68), has been described by Milner and co-workers in a synthetic route starting from $RhCl_3$[123]. Nucleophilic attack by triphenylphosphine upon (67) in the presence of excess styrene resulted in a complex and uninterpretable ^{31}P n.m.r. spectrum, thereby differing significantly from the ethylene dimer, (58), where attack of the bridging chloride ligands proceeds in a selective manner (vide supra).

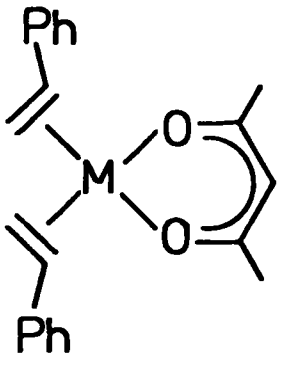
Attack of complex (67) in tetrahydrofuran by the nucleophilic acetylacetonate anion, however, gives the acetylacetato complex (69) in good yield. The rhodium complex (70) has been described[124]. It was hoped that protonation of (69) followed by reaction with triphenylphosphine would result in a styrene-containing phosphine complex[125]. Addition of one equivalent of 40% fluoroboric acid and triphenylphosphine, in the presence of styrene, gave several unidentifiable products. IR spectra showed the presence of coordinated H_2O in the solid isolated from the reaction (ν_{OH} 3400 cm^{-1}).

Over a period of days, complex (54) dissolves in styrene to give a pale orange solution. An off-white solid can be isolated, by treatment with isopentane, which contains no phosphine. The ^{1}H n.m.r. spectrum (300



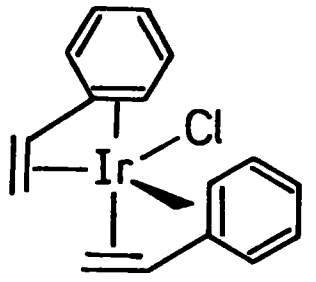
M=Ir (67)

Rh (68)

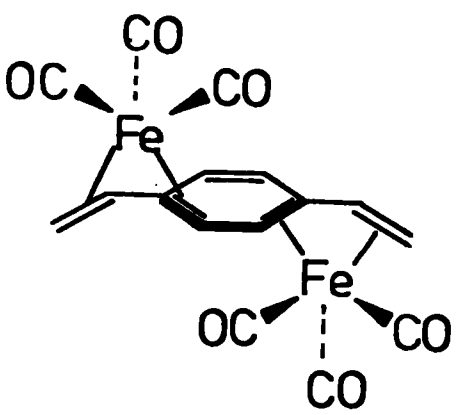


M=Rh (69)

Ir (70)



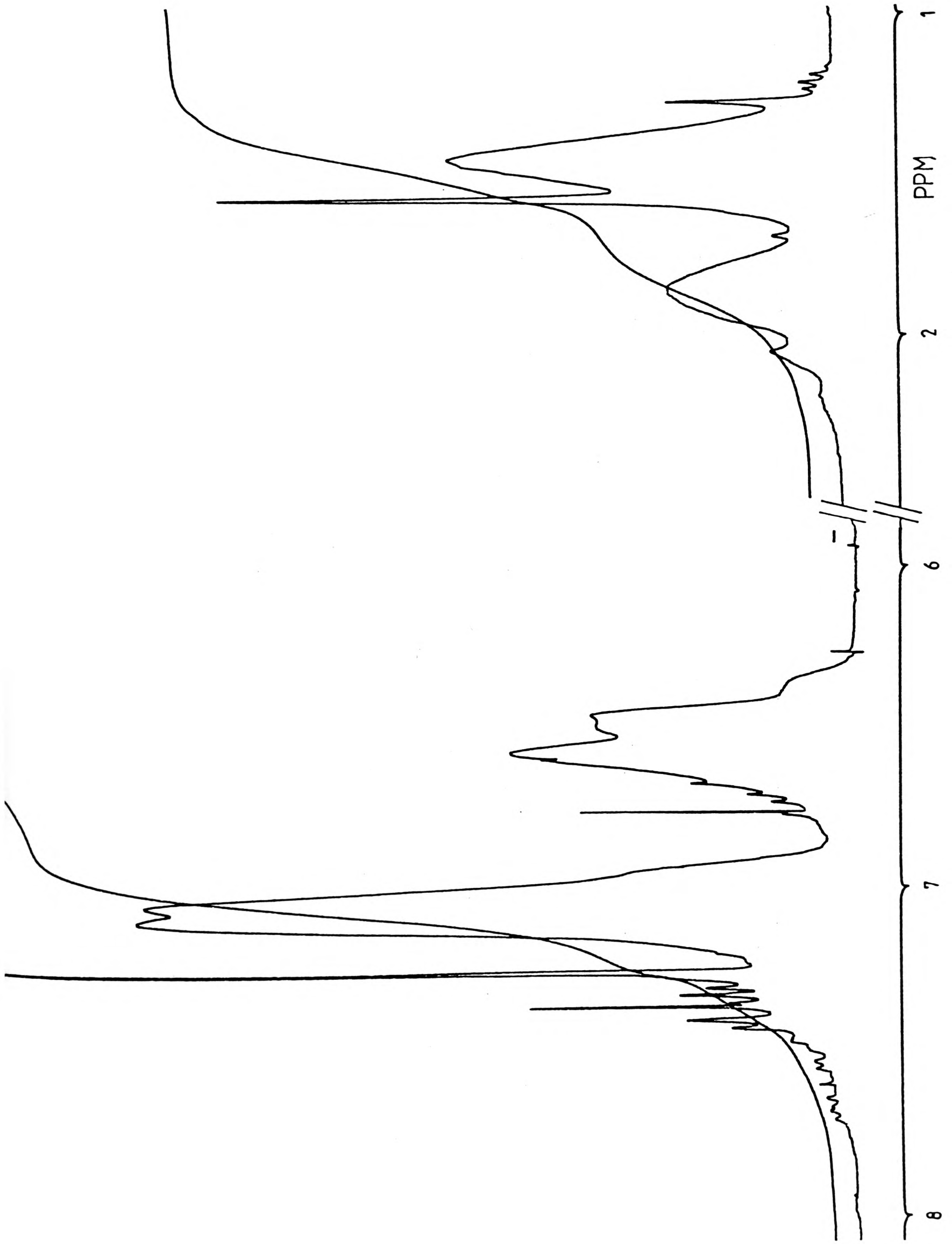
(71)



(72)

MHz) of this dichloromethane-soluble solid (Figure 67) shows the presence of coordinated styrene, its resonances broadened by some dynamic process. The structure (71) was considered in which each styrene acts as an η-4 (dihapto) ligand in accord with the upfield chemical shift observed for the ortho-phenyl and olefinic protons. The related complex (72) has been structurally characterised[126]. Complex (71) is rather inert in solution, displaying no reactivity with triphenylphosphine as observed by ^{1}H n.m.r. spectroscopy.

Fig. 67 ^{1}H NMR [300 MHZ]



2.4 Preparation of Iridium(I) Cations

A white solid can be isolated from the reaction of complex (62) with silver tetrafluoroborate in ethylene-saturated dichloromethane solution. The ^{31}P n.m.r. (36.43 MHz) spectrum of this solid, complex (73), shown in Figure 68 is predominantly a singlet, indicating equivalent phosphorus environments. The ^{1}H n.m.r. (300 MHz) spectrum of this complex in the region where coordinated olefins resonate shows a sharp triplet with J_{PH} 4 Hz. This evidence, together with ^{1}H n.m.r. integration, suggested the structure shown. The complex is very moisture-sensitive, displacing one ethylene in favour of coordinated water, to give the aquo complex (74). The addition of H_2O also brings about a change in relative geometry of the phosphole ligands, from trans to cis. This is suggested by the effect of one molar equivalent of added water on the ^{31}P and ^{1}H n.m.r. spectra (Figures 68/9and 70 respectively). In the ^{1}H n.m.r. spectrum the coordinated H_2O resonates at 2.4 p.p.m., the signal broadened by exchange with free water (1.7 p.p.m.). As expected this signal for coordinated H_2O disappears on addition of D_2O. The cis relationship of the phosphole ligands is consistent with the AB structure of the ^{31}P n.m.r. spectrum. It was not possible to displace coordinated ethylene in (73) by addition of styrene as observed by ^{1}H n.m.r. Similarly, the aquo complex, (74), was not substitutionally labile to styrene.

Complex (75) was observed by ^{31}P n.m.r. spectroscopy when a solution of (54) in ethylene-saturated dichloromethane was treated with silver tetrafluoroborate and the resulting precipitate of silver chloride removed by filtration. In the presence of ethylene a solution of this complex is colourless and exhibits a singlet in the ^{31}P n.m.r. spectrum at -2.9 p.p.m. Flushing the solution with argon results in an orange colouration and a complex and uninterpretable spectrum. Re-addition of ethylene results in

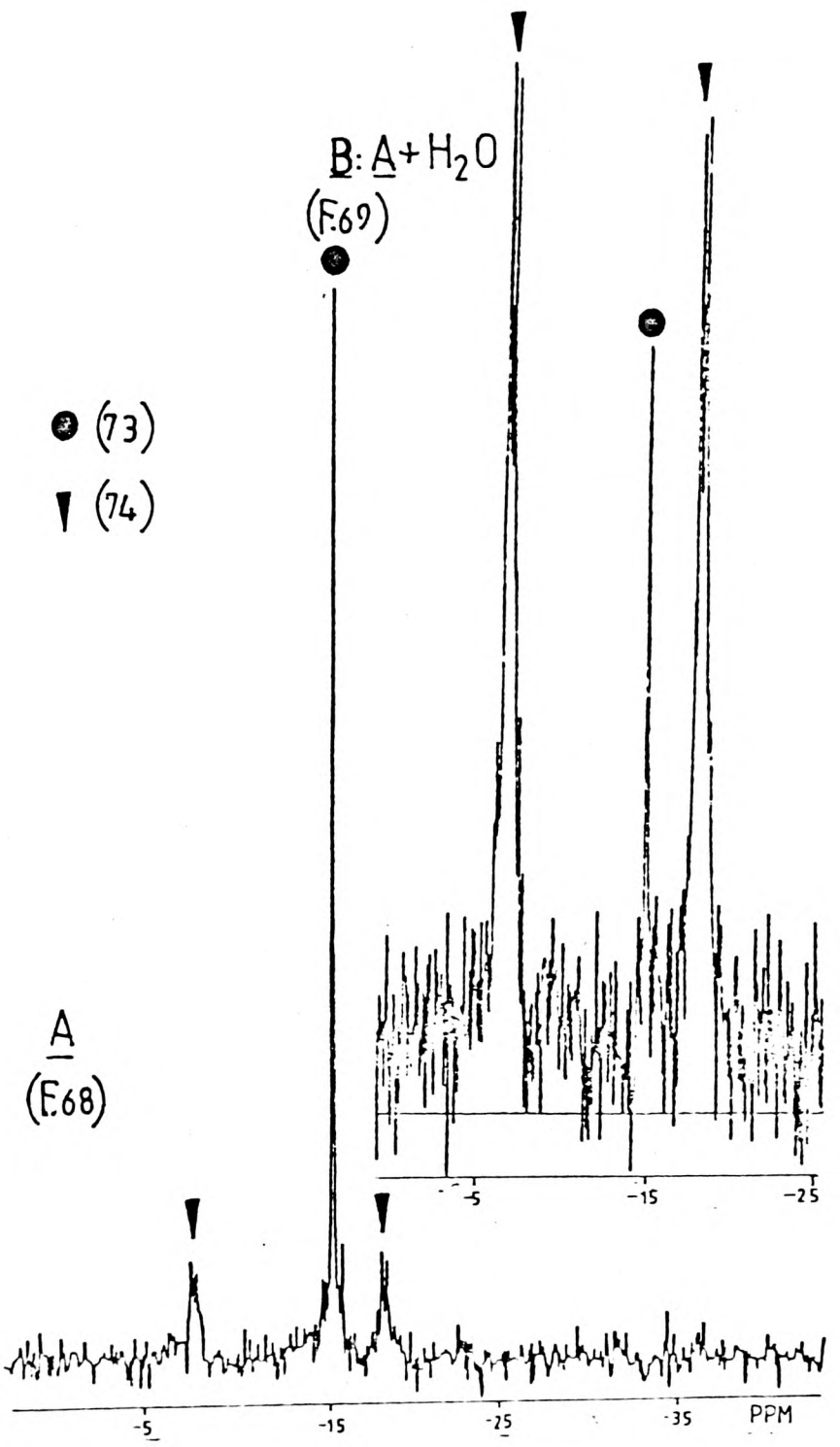


Fig. 68/9 ^{31}P NMR [36.4 MHZ]

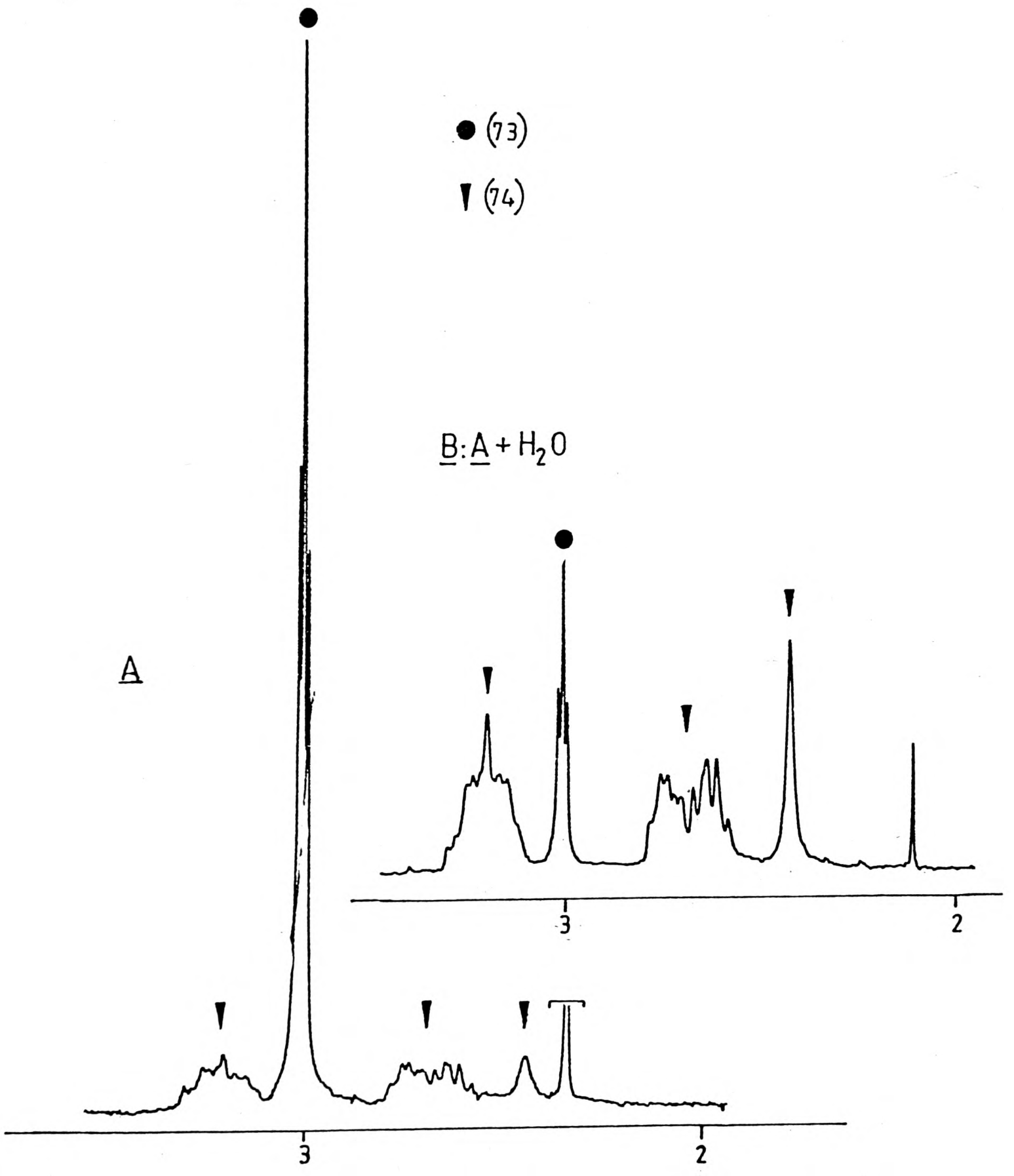
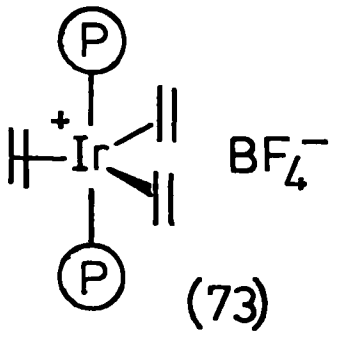
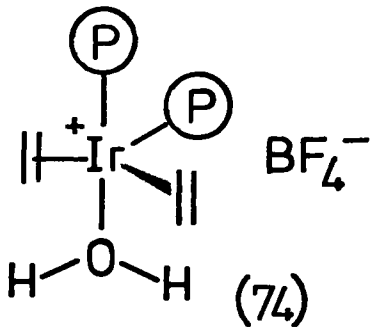


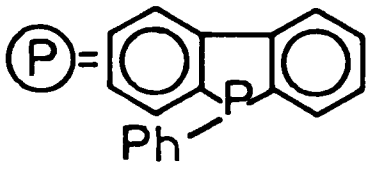
Fig.70 ^{1}H NMR[300 MHZ]

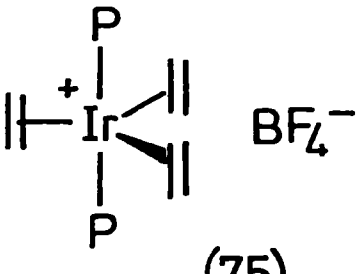


(73)



(74)





(75)

P= PPh_3

the original colourless solution and the recurrence of some signal intensity at -2.9 p.p.m. This process can be repeated over two or three cycles before the solution decomposes. The colour change, in particular, suggests that the tris(ethylene) complex, (75), disproportionates to coloured square planar species in the absence of free ethylene, in a partially reversible manner.

2.5 Oxygenation of Iridium(I) Complexes

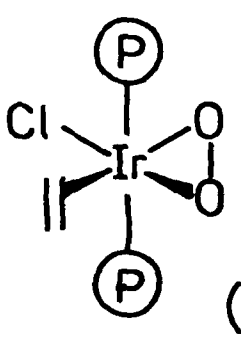
The addition of dioxygen to a toluene suspension of trans-$[Ir(PPh_3)_2Cl(C_2H_4)]$, (54), leads only to phosphine oxide-containing products. In the presence of free ethylene, however, the dioxygen complex, (55)[120], is formed (Figure 57), and may be isolated as an off-white solid, which decomposes slowly in air at ambient temperature but which is stable indefinitely under argon at -30°C. The solid is soluble in chlorinated solvents in which it decomposes rapidly in the absence of ethylene. The ^{31}P n.m.r. spectrum of (55) exhibits a singlet at -5.3 p.p.m. At ambient temperature the ^{1}H n.m.r. spectrum of the dioxygen complex shows a sharp triplet at 3.35 p.p.m. The ethylene protons are equivalenced by rotation of the C=C bond and coupled to the two equivalent phosphorus nuclei (J_{PH} 4 Hz). When the spectrum is obtained at -30°C the olefinic resonance becomes broad because rotation of the C=C bond becomes slow on the n.m.r. timescale.

The requirement for free ethylene may suggest that a five-coordinate bis(ethylene) complex is the true precursor of the oxidative addition of dioxygen to complex (54). Indeed, van der Ent[127] has isolated, at low temperatures, the ethylene adduct of complex (54) with an analysis conforming to the molecular formula $[Ir(PPh_3)_2(C_2H_4)_2Cl]$. The oxidative addition of dioxygen to this 18-electron complex may then proceed by dissociation of an ethylene ligand[128,129]. Some recent kinetic evidence suggests, however, that addition of dioxygen may take place by a direct 'end-on' process in five coordinate Ir(I) complexes[130].

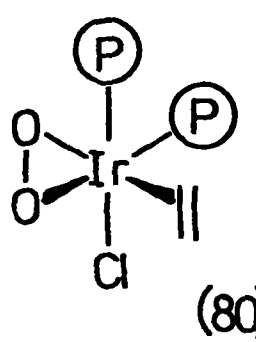
Addition of dioxygen to the tricyclohexylphosphine complex (60) in dichloromethane results only in a slow decomposition to phosphine oxide-containing mixtures, in the presence or absence of free ethylene. The dioxygen complex $[IrCl(PCy_3)_2O_2]$, (76), has been described recently by

James and co-workers[131]. Their synthesis involves oxygenation of solutions containing $[HIr(OH)(CH_3CN)Cl(PCy_3)_2]$, (78).

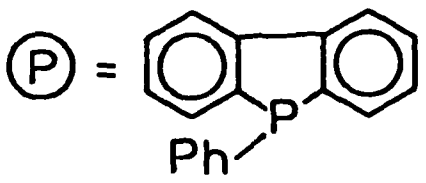
The oxygenation of the five-coordinate phosphole complex (62) may be followed conveniently by ^{31}P and ^{1}H n.m.r. (Figures 71 and 72 respectively). In dichloromethane solution the ^{31}P n.m.r. spectra show the formation of two new species possessing singlet and AB quartet line structure respectively, with concomitant decrease in the resonances of the initial complex. Similarly, in dichloromethane-d_2 the ^{1}H n.m.r. spectra (300 MHz) in the olefinic region show the growth of these new complexes with disappearance of the starting material. The isomers (79) and (80) were first



(79)



(80)



considered. The singlet resonance in the ^{31}P n.m.r. spectrum (-20.3 p.p.m.) and sharp triplet in the ^{1}H n.m.r. spectrum (2.9 p.p.m.) are consistent with complex (79) because the equivalent phosphorus nuclei each couple to the magnetically equivalent protons of the rotating ethylene. In complex (80) the cis orientation of phosphole ligands puts them into inequivalent environments giving rise to the AB pattern. The broad resonances at 3.95 p.p.m. and 3.50 p.p.m. in the ^{1}H n.m.r. spectrum arise because of an intermediate rotation on the n.m.r. timescale, of the olefin in complex (80). In the absence of rotation the four protons are magnetically inequivalent. Rotation about the C-C bond makes vicinally trans protons equivalent, thereby

Fig. 71 ^{31}P NMR[36·4 MHZ]

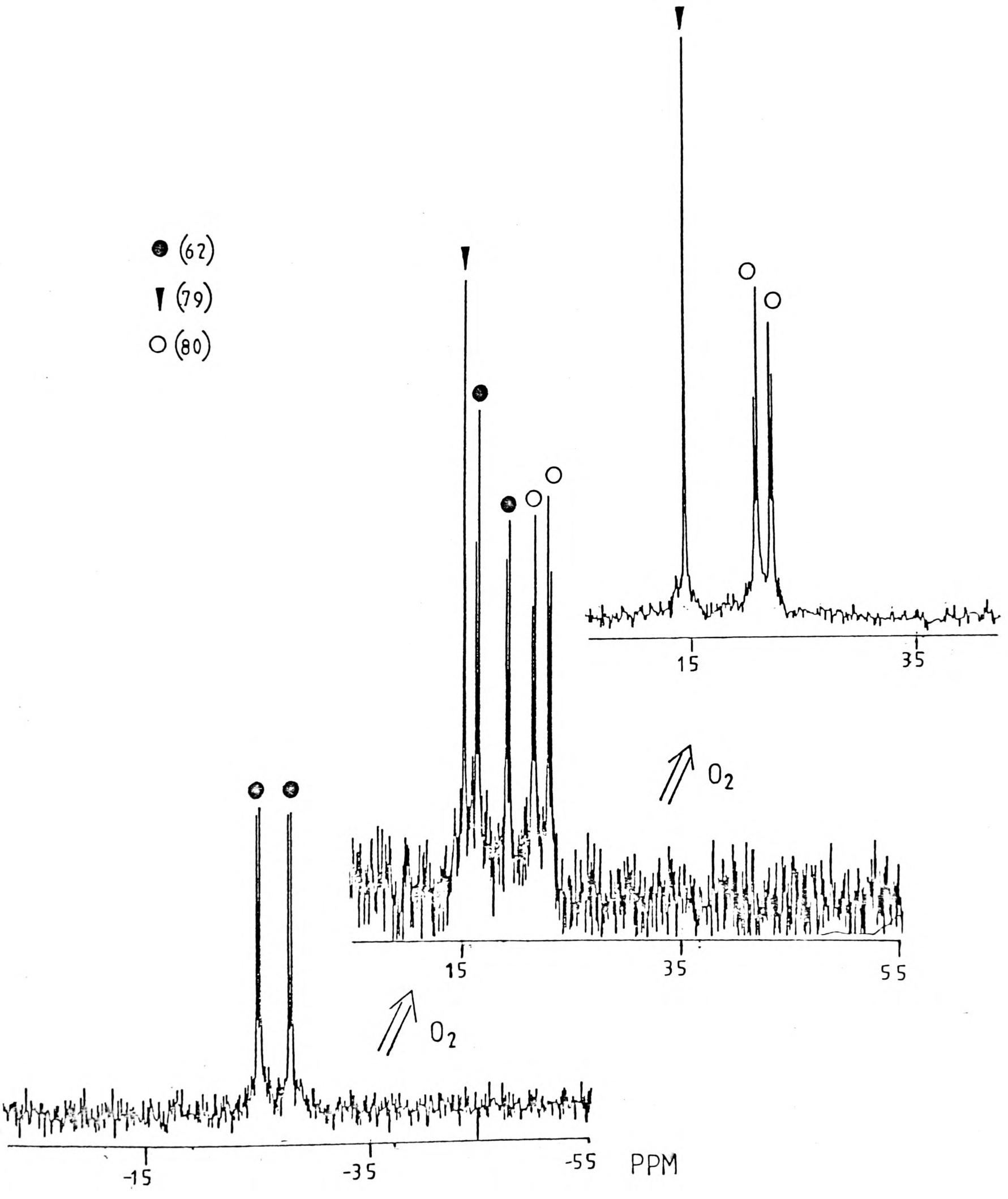
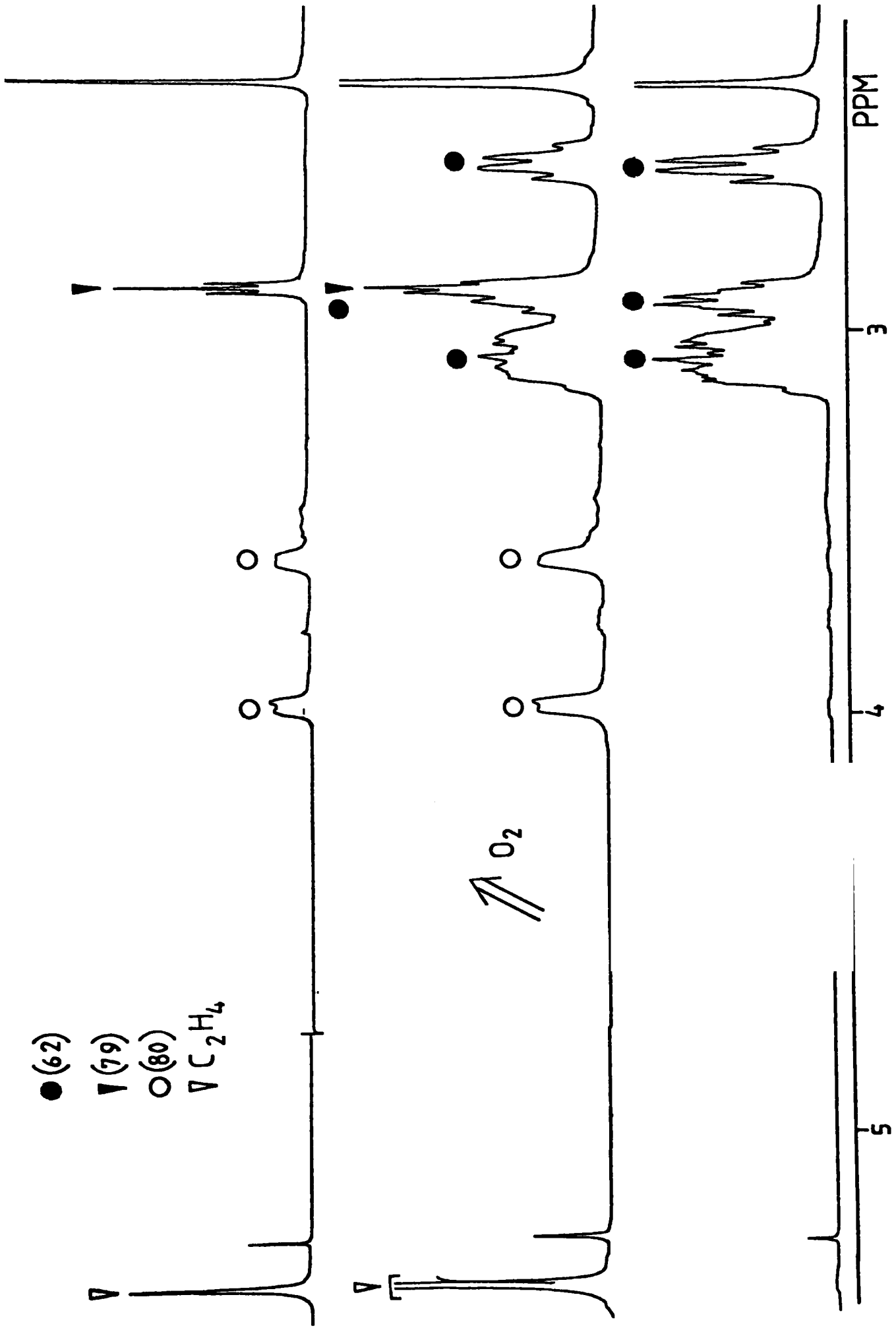


Fig.72 ^1H NMR[300MHZ]



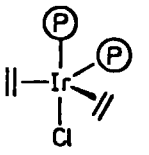
creating only two proton environments. The formation of the oxygenated complexes proceeds with release of ethylene as evidenced by the growth of its resonance at 5.5 p.p.m. in the ^{1}H n.m.r. spectrum. The mixture of isomeric complexes (79) and (80) can be isolated as an off-white solid which gives an IR absorbance at 870 cm^{-1} indicative of the O-O stretching vibration. In dichloromethane the isomers (79) and (80) form in a ratio 1:2, and in 1,2-dichloroethane 1:4, respectively. On standing in solution these ratios are not observed to change with time.

The cationic complexes (73) and (74) failed to react with dioxygen in dichloromethane solution.

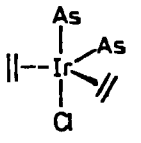
The known oxygen complexes (56) and (57) were prepared by direct addition of triphenylphosphine and pyridine, respectively, to (55)[127] and gave characteristic absorbances in their IR spectra arising from the O-O stretching vibration at 850 cm^{-1} and 840 cm^{-1}, respectively. The previously unknown dioxygen complex (81) was similarly prepared by addition of 4-(N',N'-dimethylamino)pyridine to the ethylene complex (55). The ^{31}P n.m.r. spectrum of this complex displayed only a sharp resonance at -8.1 p.p.m. indicating the presence of one isomer, having <u>trans</u> phosphine ligands.

2.6 Olefin Rotation

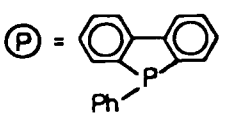
The fluxional nature of coordinated ethylene and other olefins has been studied by numerous workers[132]. Rotational barriers, brought about by variations in bond strength with orientation of the olefin vary between 13 and 20 kcal/mole. The barrier in Ir(I) complexes is generally greater than in the corresponding Rh(I) complexes, so that, for example, the ethylene ligands in $[Ir(C_2H_4)_2(C_5H_5)]$ are static up to 85°C whereas in its rhodium analogue $[Rh(C_2H_4)_2(C_5H_5)]$ olefin rotation is frozen only below 0°C[133]. The ^1H n.m.r. spectra of complexes (62), (63), (74) and (80) have been interpreted in terms of the absence of olefin rotation at ambient temperatures. These structures possess phosphine, phosphole or arsine ligands in the equatorial plane. Two complexes have been identified with rotating ethylene ligands at room temperature, complexes (55) and (79). It has been noted that in (55) this fluxional behaviour can be frozen by cooling the solution to below -25°C.



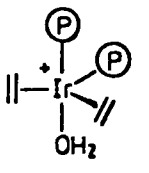
(62)



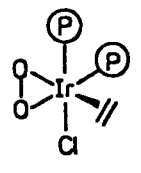
(63)



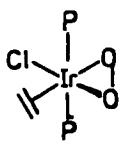
As = $AsPh_3$



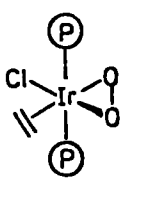
(74)



(80)



(55)

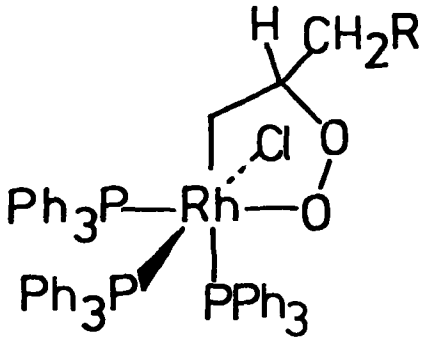


(79)

P = PPh_3

2.7 Oxidation Studies with Iridium(I) Complexes

The conversion of terminal olefins to methyl ketones catalyzed by rhodium(I) complexes[70] is thought to proceed *via* a metallacyclic intermediate, (53) (*vide supra*), which subsequently decomposes directly to



products or *via* a dioxetan (see Scheme 21 (Introduction)). Other mechanisms have been invoked, however, which account for the oxidation. Halpern[104] suggests the true oxidant could be hydrogen peroxide anion produced *in situ* from metal peroxo complexes. Other alternatives include the initial oxidation of triphenylphosphine followed by subsequent reaction of olefin with a transient metal oxo complex (M=O). The iridium(I) complex $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, (55), is unique in coordinating an olefin and dioxygen to the same metal centre. It was therefore an objective to study the reactivity of this and related complexes with olefins.

2.7.1 The Decomposition of $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl$, (55), in solu

Complex (55) dissolves in chlorinated solvents to give a c solution. In air or argon this solution rapidly decomposes with appearance of a green colour. The decomposition may be monitored ^{31}P n.m.r. spectroscopy by measuring the rate of decay of the cha singlet resonance at -5.3 p.p.m. Figure 73 illustrates the rate of this

process in dichloromethane solution, saturated with either argon or ethylene. In the presence of ethylene the decomposition process is considerably retarded.

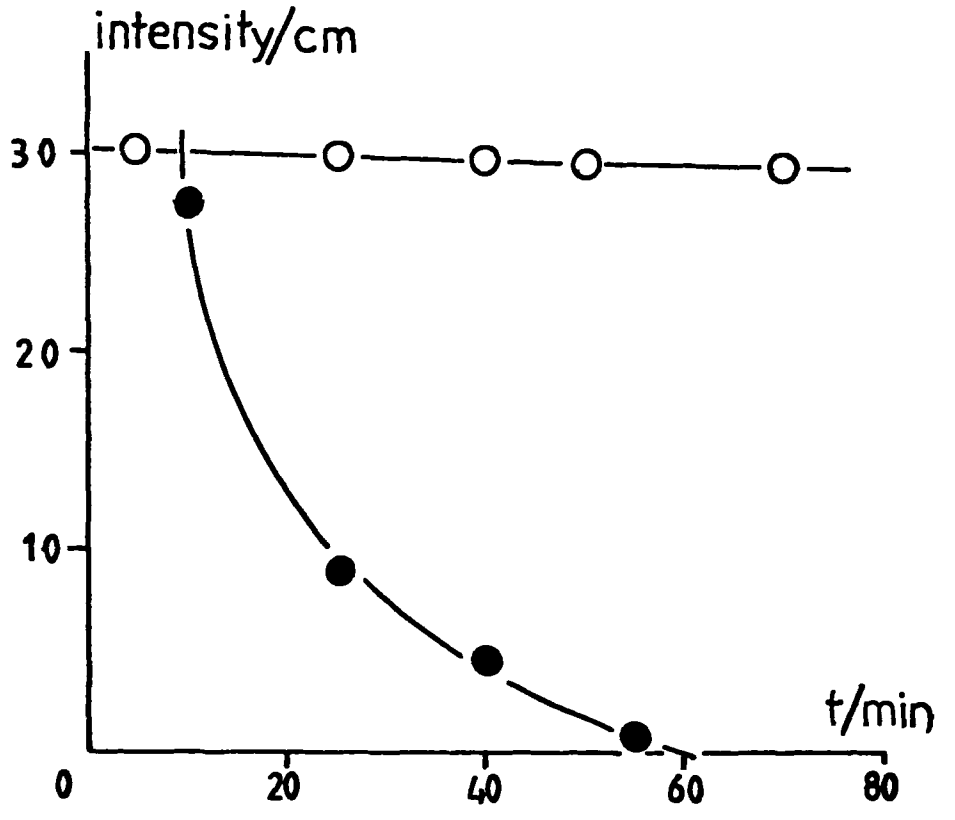


Figure 73: Decomposition of $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, (55), in dichloromethane saturated with argon (•) or ethylene (o) at 38°C.

Concomitant with the decrease in line intensity at -5.3 p.p.m. is the growth of a singlet resonance at 27.0 p.p.m. attributable to triphenylphosphine oxide. The numerous species found in the final spectrum are not identifiable. A broad hump at -27.3 p.p.m. which does not become sharper at lower temperatures (-50°C) accounts for most of the phosphorus intensity.

A pale green solid can be isolated from the decomposition. Its infra-red spectrum shows the absence of the O-O stretching vibration, present as an intense band at 890 cm^{-1} in the parent complex. A new absorbance at 1195 cm^{-1} originating from triphenylphosphine oxide appears but no other significant changes in the spectrum are observed. The addition of Brady's reagent to the final solution results in identification of the 2,4-dinitrophenylhydrazone of ethanal by TLC.

The exchange of ethylene for ligands such as triphenylphosphine has

been noted (vide supra)[120]. When the addition of one molar equivalent of triphenylphosphine to a solution of complex (55) in dichloromethane is followed by ^{31}P n.m.r. the displacement of ethylene appears to be instantaneous.

2.7.2 The Oxidation of Olefins by $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, (55)

When a five molar excess of oct-1-ene is added to an argon-saturated solution of complex (55) in dichloromethane, octan-2-one is identified as the sole volatile product (GLC and TLC-2,4-dinitrophenylhydrazone derivative). Similarly, styrene yields acetophenone (GLC and TLC). It had not been previously noted that a defined iridium(I) peroxo complex was able to promote the oxidation of an olefin to its methyl ketone. Internal olefins, however, remain inert under the reaction conditions. Thus when the reaction is performed using oct-2-ene as substrate no oxidation of the olefin is detected; the complex decomposes as in the absence of added substrate.

The selectivity to terminal olefins is exemplified by the oxidation of penta-1,3-diene. Complex (55) reacts with this diolefin in dichloromethane to yield pent-3-en-2-one as the only observable oxidation product, as determined by GLC. When the reaction was carried out in a sealed n.m.r. tube the growth of peaks attributed to pent-3-en-2-one could be observed in the ^{1}H n.m.r. spectrum (90 MHz).

In these three oxidation reactions the presence of 10% 4-methyl-2,6-di-t-butylphenol in the reaction medium had no effect on the production of methyl ketone. It therefore seems reasonable to discount the possibility of radical-chain processes being involved in the oxidation. Such processes have been shown to be responsible for the oxidation of organic substrates, including olefins, by platinum group metals (vide supra)[139,140,141].

The absolute quantities of methyl ketone produced in these reactions could be measured by using an internal standard, 1,2-dichlorobenzene, in the reaction medium followed by GLC analysis. Initial measurements were made by direct injection of microlitre quantities of the reaction mixture into the gas chromatograph. It was found, however, that this method led to spurious measurements, particularly at early stages of the reaction. A solution of Complex (55) was allowed to react with oct-1-ene for 2 min. The extent of reaction was determined by GLC (against a calibrated internal standard) by direct injection of an aliquot. The remaining solution was immediately quenched in excess isopentane at -30°C. The precipitated solid was removed and the supernatant liquid subjected to GLC analysis. The yield of octan-2-one obtained by direct injection was found to be 15% (based on Ir) while the figure obtained after first precipitating the metal complexes was only 1.5%. It may be concluded that a rapid vapour-phase oxidation takes place after injection into the gas chromatograph inlet. At later stages in the reaction the discrepancy lessens with the reduction of active metal dioxygen species in solution. The method of direct injection in this system would lead to the false conclusion that up to 30% of the final yield of octan-2-one is produced 'instantly'.

In the oxidation of oct-1-ene by $[Rh(PPh_3)_3Cl]$, (16), Read[70], injecting aliquots directly into the gas chromatograph, observes a rapid initial phase which produces a little less than 0.5 mol of ketone per mol of catalyst in the first few minutes, regardless of the rates of subsequent catalytic processes. He concludes that the metal species in the first phase differ from those at later stages of reaction. It is possible that the observations presented here require a re-interpretation of the results obtained with the rhodium catalyst.

The absolute yields of methyl ketone obtained by GLC analysis upon completion of reaction (10 hr at 40°C) are summarised in Table 9.

TABLE 9. Yield (based on Ir) of Methyl Ketone in Oxidation of Olefins by $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, under oxygen and argon atmosphere (10 h; 40°C)

Olefin	Methyl ketone	Yield (argon)	Yield (oxygen)
Oct-1-ene	Octan-2-one	42	72
Styrene	Acetophenone	51	80
Pent-1,3-diene	Pent-3-en-2-one	52	-

The course of the oxidation of oct-1-ene was monitored by ^{31}P n.m.r. (36.43 MHz) spectroscopy (vide supra). Figure 74 illustrates the decay of the singlet resonance assigned to complex (55) in the presence or absence of oct-1-ene under an argon or ethylene atmosphere.

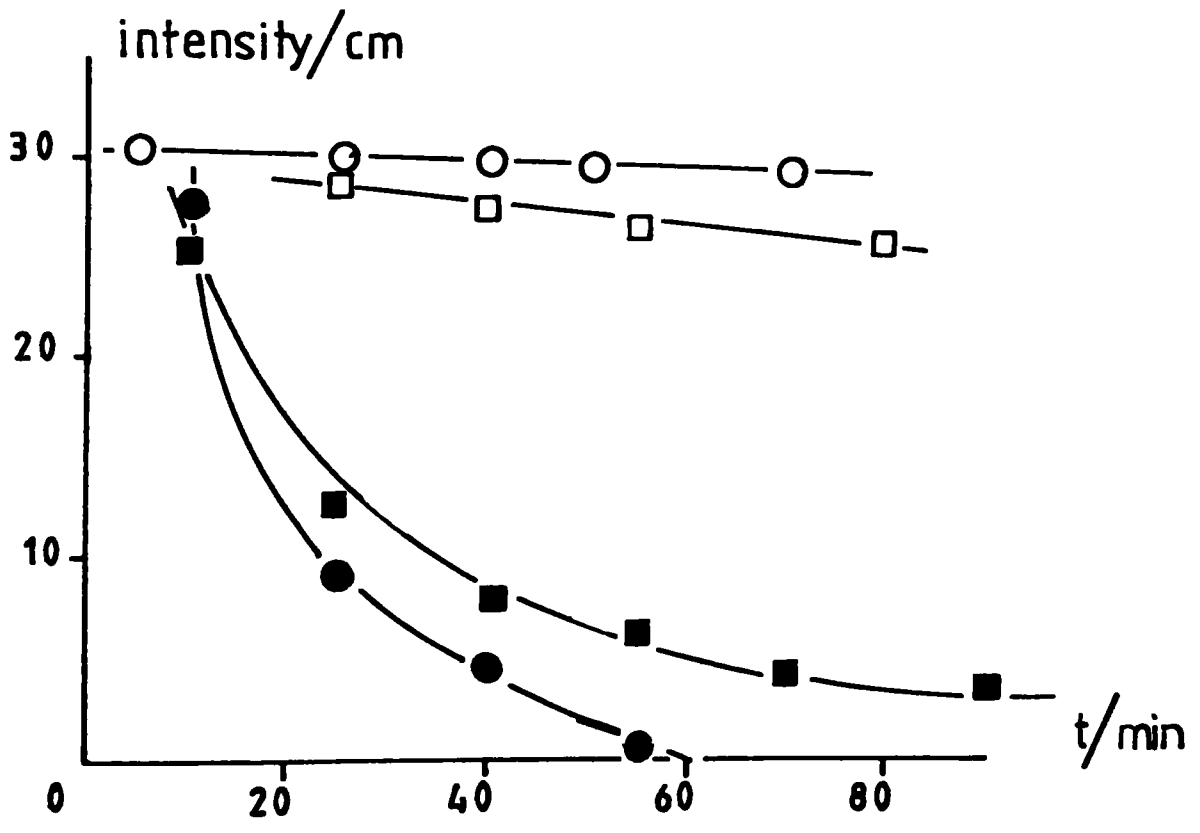


Figure 74: Decay of the ^{31}P n.m.r. singlet (-5.3 p.p.m.) of $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, (55) (50 mM) in dichloromethane solution in the presence of argon only (●); argon, oct-1-ene (250 mM) (■); ethylene only (○); ethylene, oct-1-ene (250 mM) (□). 38°C.

The plots in Figure 74 illustrate the stability of complex (55) in the

presence of ethylene over the time scale of the experiment. Further, oct-1-ene competes to a small extent with ethylene as shown by the rate of decay in the presence of both olefins. An important conclusion is that oct-1-ene effects a mild inhibition of the decomposition of the complex under argon.

The ^{31}P n.m.r. (300 MHz) plots in Figure 75 obtained from the reaction of complex (55) and oct-1-ene under argon illustrate the decay of the parent complex singlet at -5.3 p.p.m. and the concomitant growth of the resonance assigned to phosphine oxide at 27.0 p.p.m. Intermediate species are not observed in the time course of reaction.

Separate experiments have shown that the products obtained from the decomposition of complex (55) in argon-saturated dichloromethane are not effective as oxidants of terminal olefins in the presence of dioxygen.

Results were obtained on the effect on oct-1-ene concentration on the yield of octan-2-one, although before the implications of direct GLC injection were realised, and are illustrated in Figure 76.

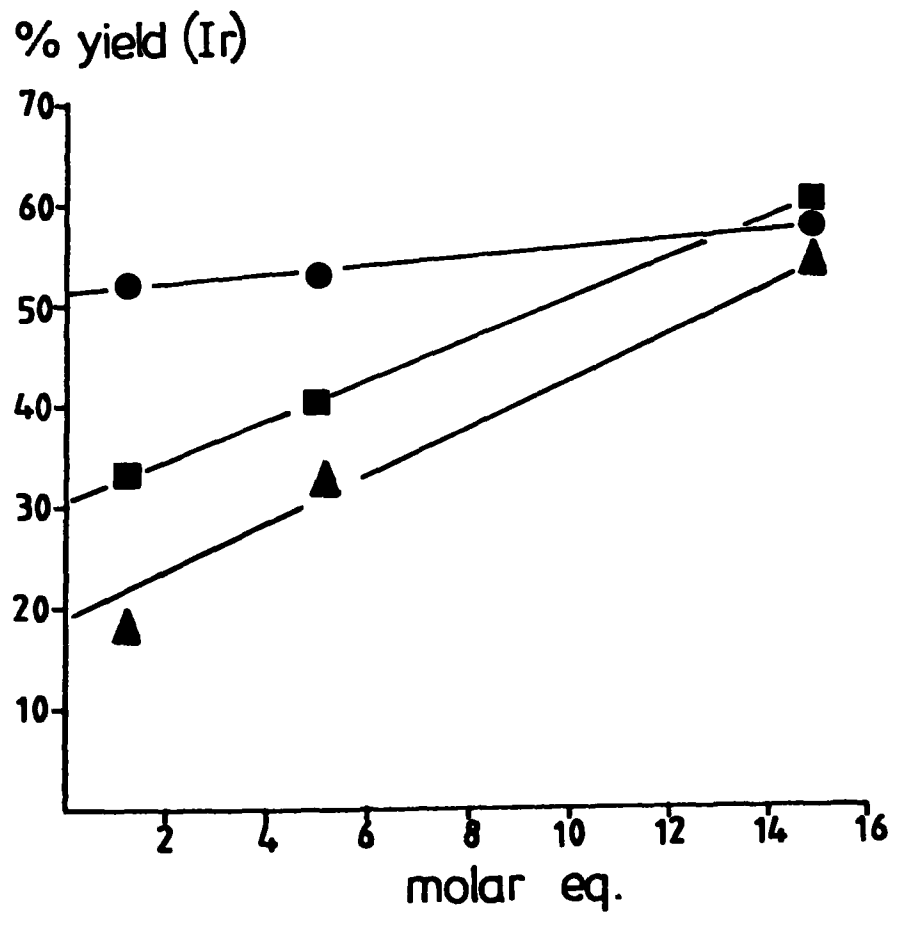


Figure 76: Effect of oct-1-ene concentration of yield of octan-2-one.
3 min (▲); 60 min (■); 19 h (●).
(55) (25 mM); 21°C.

The results presented here favour a prior dissociation of ethylene in both the decomposition and oxidation pathways. The presence of ethylene

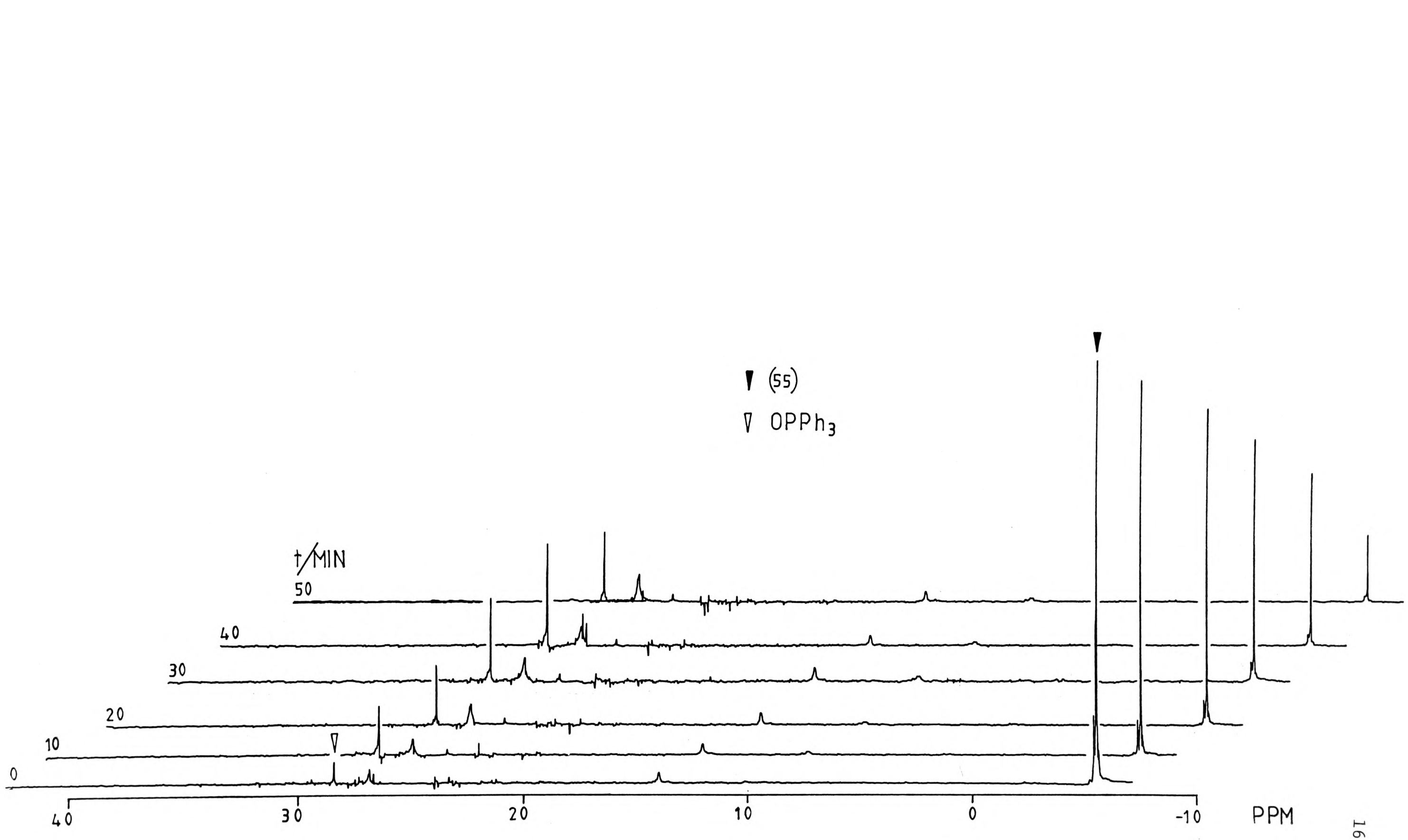


Fig. 75 ^{31}P NMR [121·4 MHZ] 40° C

in high concentration effectively suppresses this first step. Figure 77 illustrates how decomposition or oxidation may proceed via the coordinatively unsaturated 16-electron intermediate (85). James[131] has isolated the analogous but stable complex $[Ir(PCy_3)_2(O_2)Cl]$, (76), employing tricyclohexylphosphine (PCy_3) ligands. When ethylene is replaced by carbon monoxide i.e. $[Ir(PPh_3)_2(CO)(O_2)Cl]$, (2), the complex is not able to oxidise oct-1-ene or styrene[123] presumably because carbon monoxide is more strongly coordinated than ethylene and thus does not allow a dissociative pathway. The hypothesized olefin complex (86) has not been observed and attempts to isolate it by displacement of ethylene in complex (55) were not successful. An attempt to photolyse a mixture of (55) and styrene at -76°C, using a xenon arc lamp, led to no observable reaction.

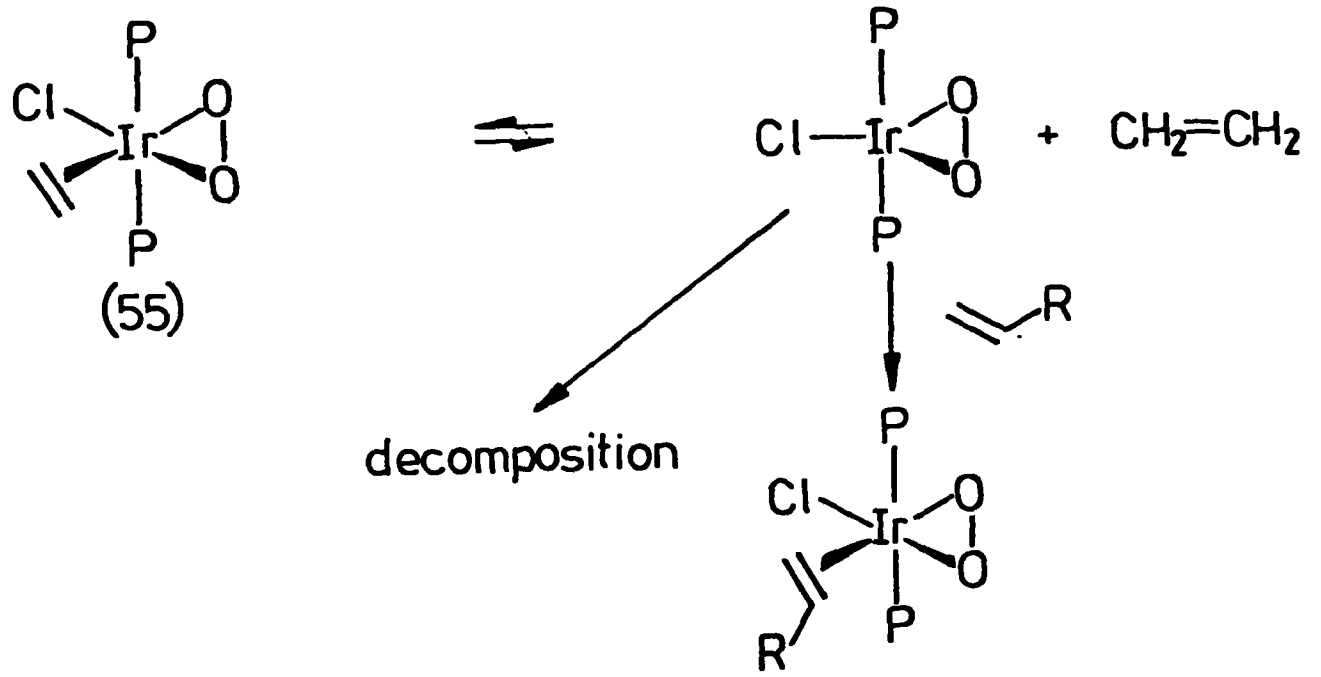


Figure 77: Decomposition and Oxidation Pathways.

2.7.3 The Effect of Triphenylphosphine on the Oxidation of Olefins by Ir(I) complexes

The reaction of triphenylphosphine on $[Ir(PPh_3)_2(O_2)(C_2H_4)Cl]$, (55), produces an instantaneous displacement of ethylene to yield the complex $[Ir(PPh_3)_3(O_2)Cl]$, complex (56) (vide supra). This complex decomposes more slowly than (55) in dichloromethane solution yielding unidentifiable phosphine oxide-containing products, and oxidises terminal olefins with slightly higher efficiency. The ^{31}P n.m.r. spectrum of (56) exhibits the expected doublet and triplet structure (Figure 78).

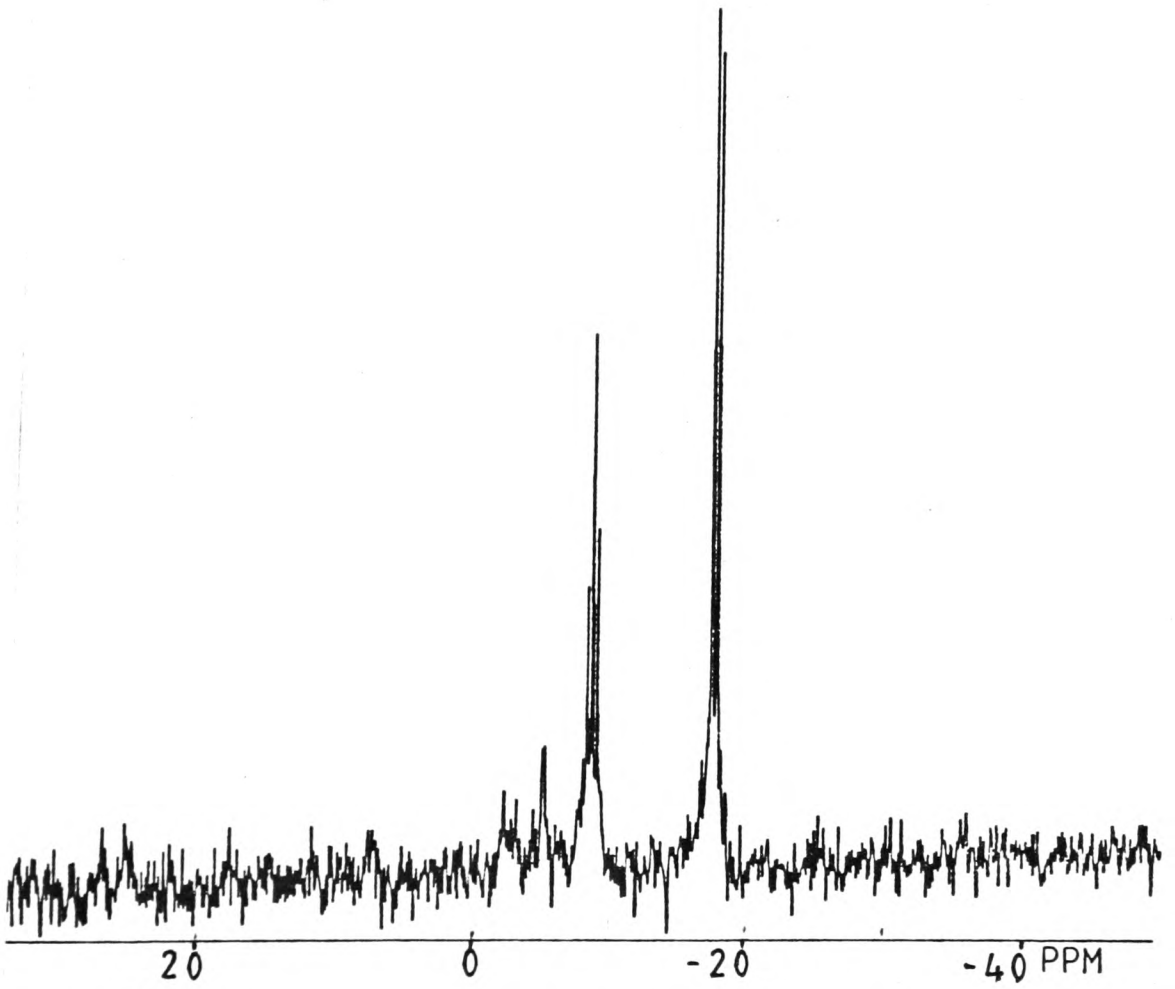


Figure 78: ^{31}P n.m.r. spectrum (121 MHz) of Complex (56).

The reaction between (56) and oct-1-ene has been monitored by ^{31}P n.m.r. spectroscopy with simultaneous measurement of the yield of octan-2-one by GLC. Figure 79 illustrates these observations together with the growth of the resonance corresponding to triphenylphosphine oxide and the decomposition of the complex under argon in the absence of olefin.

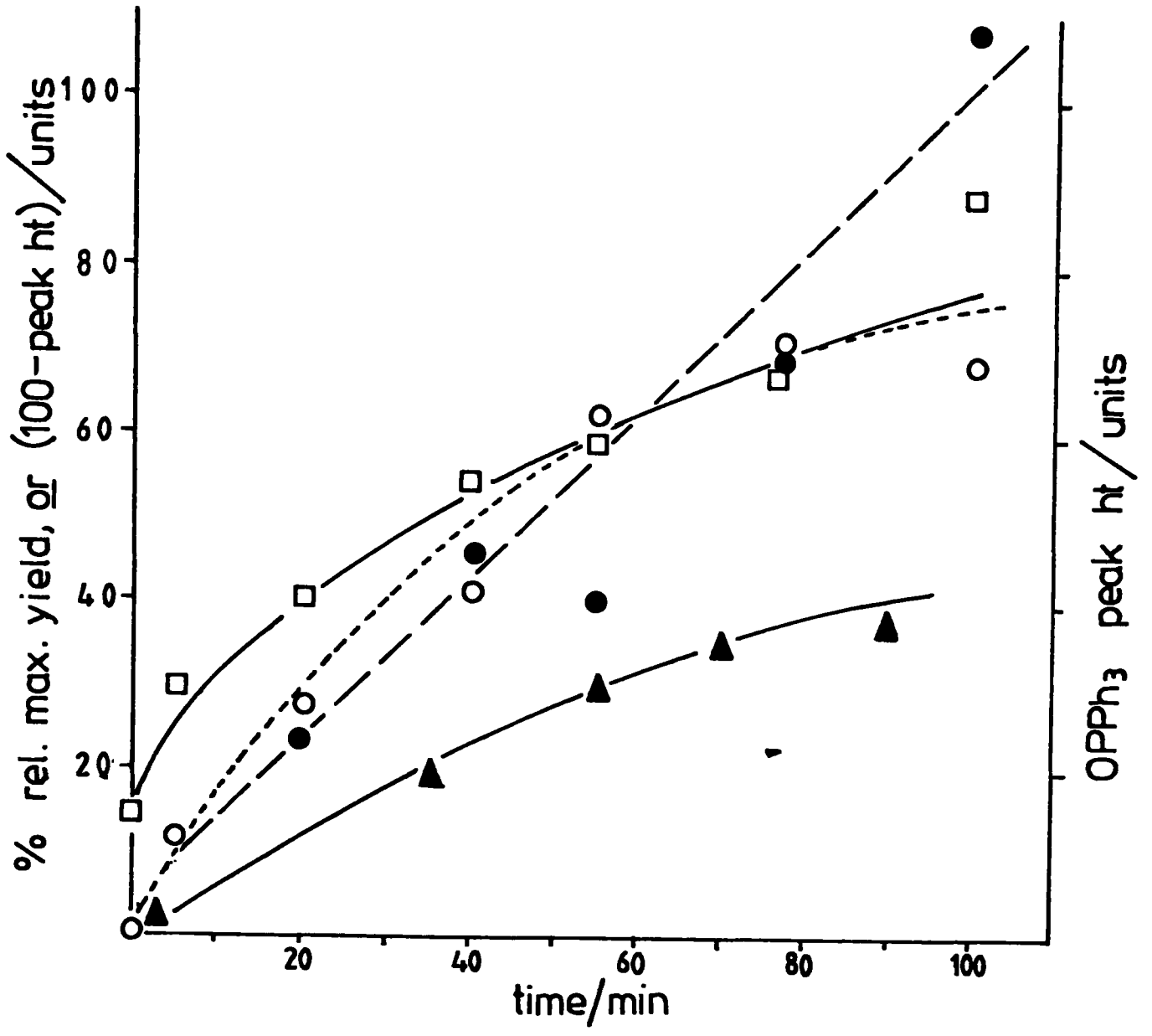


Figure 79: Simultaneous ^{31}P n.m.r. and GLC measurements for reaction of (56) in the presence and absence of oct-1-ene. Complex (56) (54 mM); argon: (^{31}P n.m.r. doublet peak height) (▲); (^{31}P n.m.r. doublet peak height) oct-1-ene (271 mM) (o); (^{31}P n.m.r. phosphine oxide singlet peak height) oct-1-ene (271 mM) (●); (GLC yield octan-2-one) oct-1-ene (271 mM) (□).

In the case of this more stable complex oxidation leads to a faster breakdown than does decomposition. The slightly higher overall yields of octan-2-one obtained with this complex are diminished in the presence of 5 mol triphenylphosphine (Table 10).

Attempts to synthesize a complex of the type $[Ir(PPh_3)_2Cl(CH(Ph)CH_2)]$ failed (vide supra) and so attention was concentrated on the styrene dimer $[Ir(C(Ph)HCH_2)_2Cl]_2$, (67). Solutions of (67) in dichloromethane were oxygenated in the presence of excess styrene and increasing molar quantities of triphenylphosphine. Figure 80 illustrates how the yield of acetophenone reaches a maximum when 4 mol triphenylphosphine per mol of dimer are added.

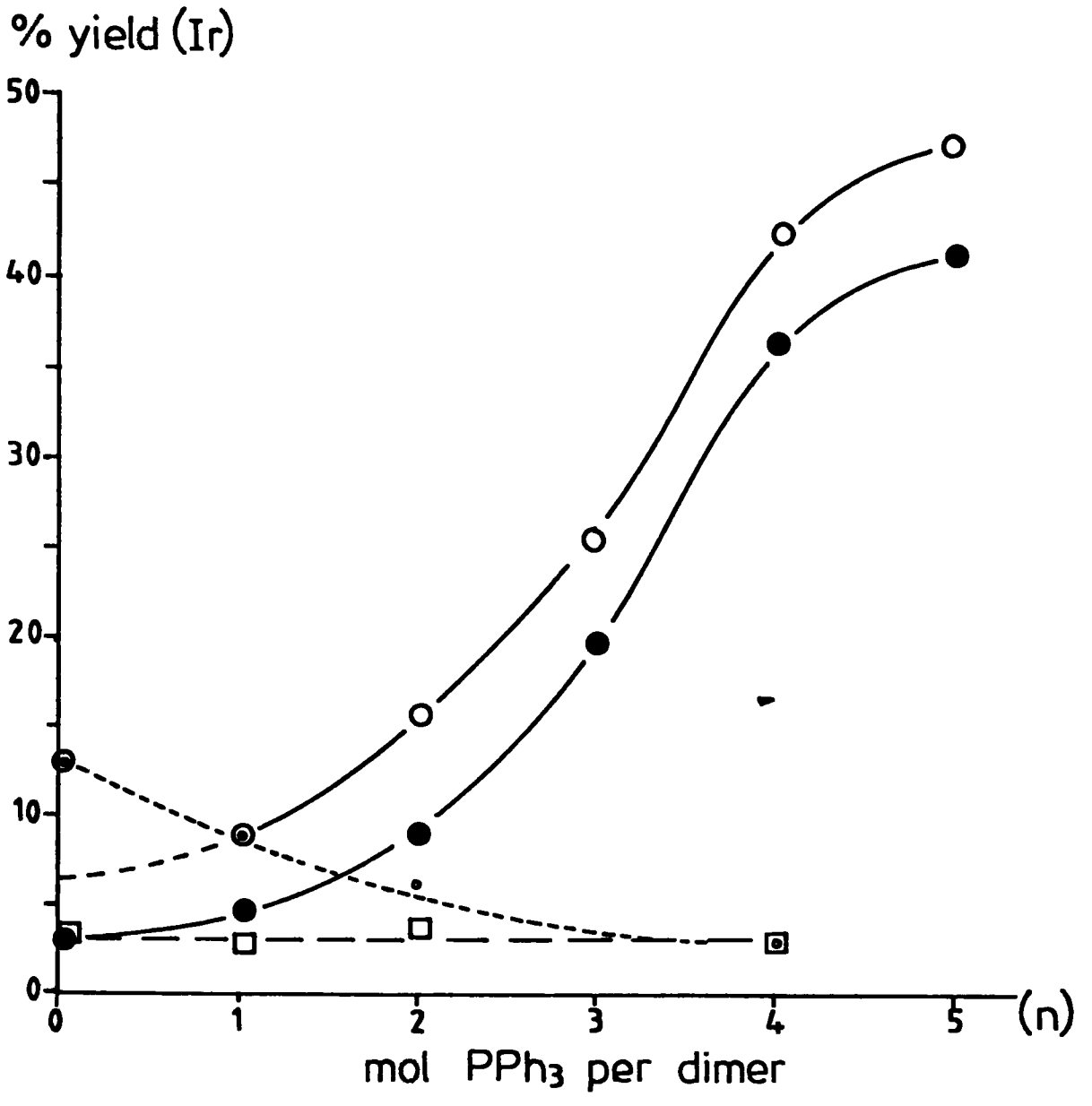


Figure 80: Addition of Triphenylphosphine to Oxygenated Solutions of $[Ir(C(Ph)HCH_2)_2Cl]_2$. Complex (67) (28 mM), styrene (280 mM), oxygen saturated: acetophenone 2h(●); acetophenone 10 h (o); benzaldehyde 2h (□); benzaldehyde 10 h (•).

Complex (67) is, overall, a less efficient oxidant and substantial quantities of benzaldehyde are formed, although this product is inhibited by increasing concentration of triphenylphosphine. Presumably triphenylphosphine serves to attack the bridging chlorides in a bimolecular nucleophilic substitution[142]. When 4 mol triphenylphosphine are employed the stoichiometry of the complex formed will be $[Ir(PPh_3)_2(C(Ph)HCH_2)Cl]$. Benzaldehyde is not usually observed as an oxidation product in the oxidation of styrene by the metal complexes employed in this study. Read has reported, however, that the oxidation of styrene catalyzed by $[Rh(PPh_3)_3Cl]$, (16), produces 1 mol of benzaldehyde per mol of catalyst together with 2 mol acetophenone[117]. It

has been demonstrated clearly by Lyons[141] that benzaldehyde may be the major product of free radical processes in the oxidation of styrene by iridium(I) complexes. The observation of induction periods and inhibition by 4-methyl-2,6-di-t-butylphenol support this view. This may not represent the only pathway for aldehyde formation, however, since Milner and co-workers[123] reported that benzaldehyde formation in the oxidation of styrene catalyzed by $[Rh(C_2H_4)_2Cl]_2$, (87), was only partially suppressed by radical inhibitors.

2.7.4 The Oxidation of Oct-1-ene by Neutral Iridium(I) Complexes

The ability of other iridium(I) complexes, described previously, to oxidise oct-1-ene was determined by GLC analysis. The final yields of octan-2-one are tabulated in Table 10. The effect of oxygen upon the oxidising ability of preformed peroxo complexes is also noted. Data for complexes (55) and (56) are presented for comparison.

The pyridine based complexes, (57) and (81) are generally poorer oxidants but the yield of octan-2-one is enhanced in all peroxo complexes when the reaction is carried out under an oxygen atmosphere. This effect may be accounted for by supposing that oxygen effectively traps the decomposition product after octan-2-one formation. The peroxo complexes (79) and (80) generated *in situ* from (62) are ineffective as oxidants. This is, perhaps, surprising considering their structural similarity to (55). They are, however, rather stable in solution, decomposing by release of ethylene only very slowly (^{1}H n.m.r.). The 'tight' binding of small molecules such as ethylene to the metal brought about by the nature of the phosphole ligands[143] may account for this unreactivity. The tricyclohexylphosphine complex, (60), is inert to oxygenation (*vide supra*) and is unreactive as an oxidant.

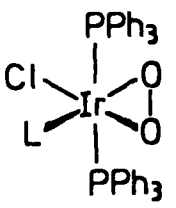
TABLE 10: Oxidation of Oct-1-ene by Iridium(I) Complexes*

Complex	Yield of Octan-2-one (%)#	
	Argon	Oxygen
(55)	42	72
(56)	48	93†
(57)	27	43
(81)	26	44
(63)	-	32
(62)	-	0
(60)	-	0

* Typically, complex (50 mM), oct-1-ene (250 mM) in dichloromethane, 40°C, 10h.

By GLC (1,2-dichlorobenzene, internal standard.

† In presence of 5 mol PPh_3 yield = 77%.

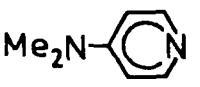


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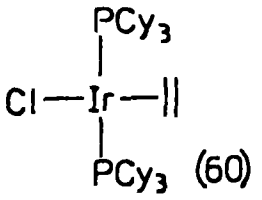
PPh_3 (56)

CH_2 CH_2 (55)

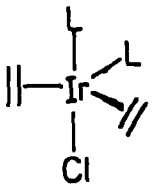
pyridine (57)

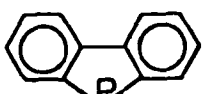


(81)



(60)





(62)

As Ph_3 (63)

Cy = C_6H_{11}

2.7.5 The Oxidation of Olefins by Cationic Iridium(I) Complexes

Some qualitative results have been obtained for the oxidation of terminal olefins by $[Ir(PPh_3)_2(C_2H_4)_3]BF_4$, (75), generated *in situ*. Addition of styrene to the colourless cation (75) in dichloromethane resulted in a deepening red colour over several minutes. Oxygenation of this solution produced a decolouration (brown to green over 1 hr). Analysis of the resulting solution showed the formation of acetophenone, benzaldehyde and 2-phenyloxirane in equal proportion. Similarly, oct-1-ene yielded octan-2-one, heptanal and 2-hexyloxirane again in equal proportion but without the initial change in colour. These results were, however, difficult to reproduce and it is not known if free radical processes are significant. Lyons and Turner[141] (*vide supra*) identified epoxide as a product in the free radical oxidation of styrene by $[Ir(PPh_3)_2(CO)Cl]$ and suggested epoxidation took place by reaction of styrene with some species (such as performic acid) derived from the oxidation of formaldehyde under the reaction conditions. Formaldehyde was formed by the oxidative cleavage of styrene in the early stages of reaction.

Complex (82), $[Ir(PPh_3)_2(CH_3(O)CH_3)_2H_2]BF_4$[135], was prepared in anticipation that the addition of an olefin would result in the formation of an iridium(I) cationic species containing both coordinated olefin and triphenylphosphine, as shown in Figure 81 (over page).

The addition of oct-1-ene to (82) in the presence of dioxygen led only to a slow decomposition to phosphine oxide-containing products (IR ν_{PO} 1195 cm^{-1}). Oxidation products derived from oct-1-ene were not detected by GLC analysis. The addition of styrene to the colourless solution of (85) in dichloromethane led to an immediate orange colouration. The resulting solution was quite stable in the presence of dioxygen and excess styrene and no products of olefin oxidation were identified by GLC

analysis*.

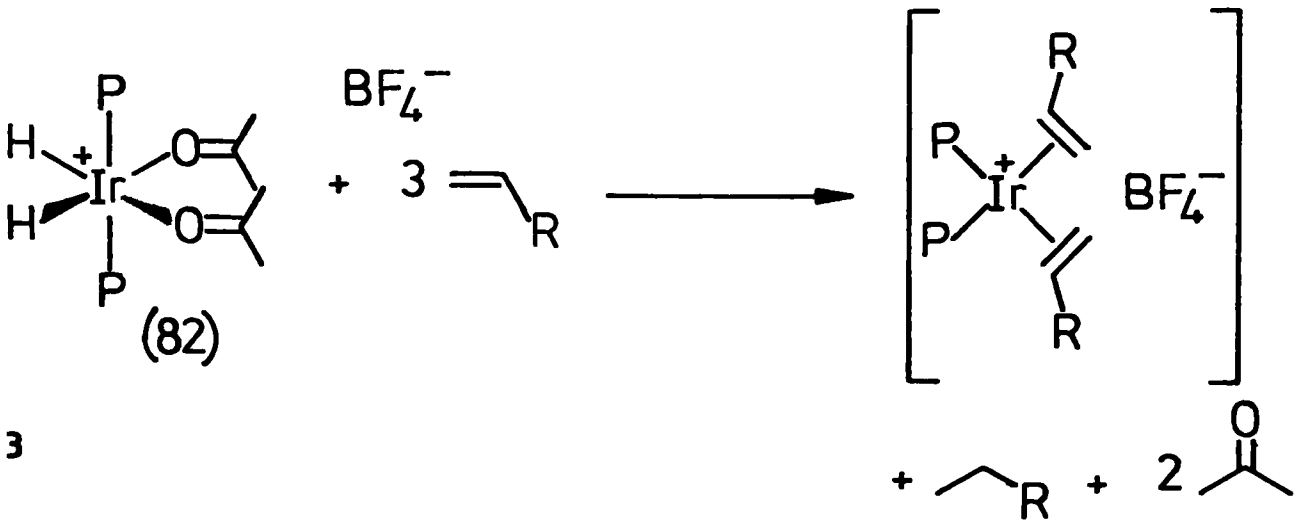


Figure 81

Conclusions

The results presented here give no direct support for a metallacyclic intermediate in the oxidation of terminal olefins by iridium(I) complexes. It has not been possible to isolate nor identify spectroscopically the iridium analogue of the metallacyclic intermediate (53) proposed by Read and others.

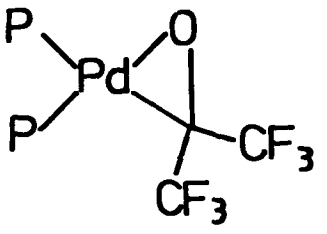
It is likely, however, that (55) reacts by a dissociative mechanism to give the transient 16-electron complex (85) (Figure 82) which decomposes in the absence of an olefinic substrate. Alternatively, in the presence of oct-1-ene, (85) forms the olefin complex (86). The remaining processes which lead to octan-2-one formation remain unclear. Pathway [A], suggested by Read[70] leads to the metallacycle (53) which breaks down to form a

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* The products of this reaction have not been identified. ^{31}P n.m.r. (36.43 MHz) indicated the formation of a single phosphorus-containing species (5.6 p.p.m. (s)). ^{1}H n.m.r. (300 MHz) suggested the presence of an arene complex of the type $[Ir(C_6H_5C_2H_5)(C(Ph)HCH_2)_2]BF_4$.

dioxetan (88) which is subsequently attacked by triphenylphosphine to give the oxidation products. A breakdown pathway [C] yielding the transient iridium oxo complex (89) and octan-2-one must also be considered.

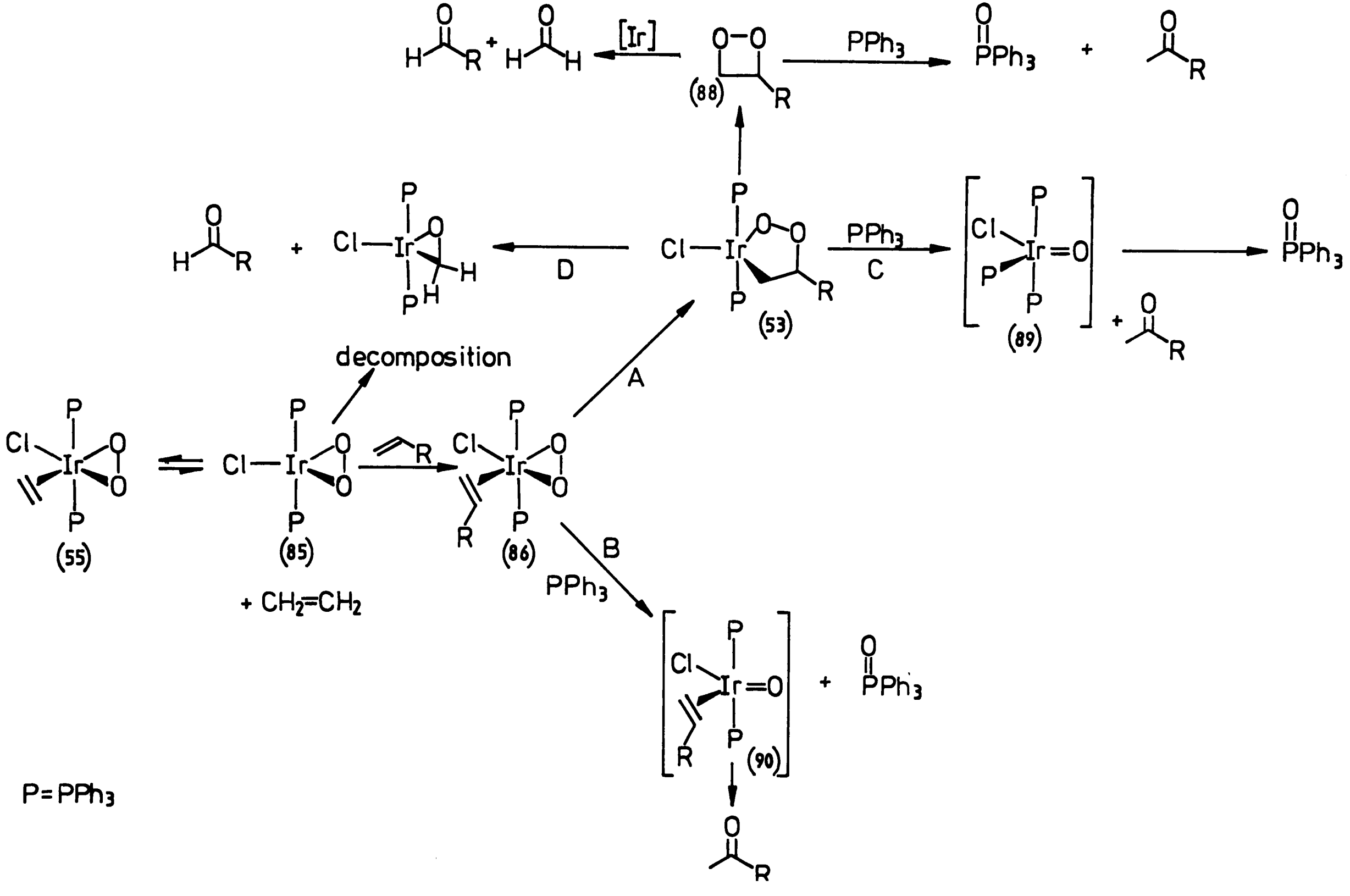
In pathway [B] oxidation of triphenylphosphine is the first step. The iridium oxo complex (90) is then the true oxidant of oct-1-ene. The presence of benzaldehyde as a co-product in the oxidation of styrene by (67) may be rationalised in considering an alternative breakdown of the dioxetan promoted by the metal centre rather than triphenylphosphine. It is known that dioxetans undergo oxidative carbon-carbon bond cleavage in the presence of metal ions[144]. The co-product in this process, formaldehyde, is not observed presumably because of its volatility. Perhaps less likely an explanation for benzaldehyde formation is the direct collapse of (53) to give the metallaoxacyclopropane, analogous to the stable palladium complex (91) prepared by Green and co-workers[145].



P = PPh_3

(91)

Figure 82


[Ir]
PPh3
(88)
D
(53)
C
(89)
decomposition
A
(55)
(85)
(86)
+ CH2=CH2
B
PPh3
(90)
P=PPh3

CHAPTER II

EXPERIMENTAL

E2.1 Instrumentation and Materials

Nuclear magnetic resonance spectra, infra-red spectra and Field-desorption mass spectra were obtained as described in Section E1.1, unless otherwise stated. Commercial solvents were prepared for use as previously described. Oct-1-ene (B.D.H. Ltd.) was distilled over sodium wire under argon. Styrene (B.D.H. Ltd.) was distilled before use and stored at -30°C for short periods. 4-(N',N'-dimethylamino)pyridine was used as obtained from Aldrich. $[Ir(PPh_3)_2(CO)Cl]$ (Ref 66) was loaned by Dr. J.M. Brown.

E2.2 Synthesis of Organometallic Complexes

Di-μ-chlorotetrakis(1,2-η)cyclooctenediiridium[134] (59)

Trichloroiridium(II).xH_2O (2g, 6.7 mmol) was suspended in isopropanol (22 ml) and water (8 ml). Cyclooctene (4 ml, 35 mmol) was added and the resulting suspension stirred at 78°C for 3 hours. A fine yellow powder separates which is collected by filtration and washed well with methanol (2 x 25 ml) and filtered under argon. The wet crude solid is dried *in vacuo* to give 1.6g (52%) fine yellow crystals.

^1H n.m.r. ($CDCl_3$, 90 MHz) 4.5 - 4.1 p.p.m. (br m, 2H), 2.0 - 1.7 p.p.m. (br m, 12H).

Di-μ-chlorotetrakis(ethene)diiridium[120], (58)

Complex (59) (200mg, 0.22 mmol) was suspended in heptane (1 ml), and degassed thoroughly, in four freeze-thaw cycles, in ethylene. The resulting white suspension (at -76°C) was filtered cold and the white solid washed twice with heptane (1 ml). This solid monomeric complex was dried *in vacuo* to yield a red powder (93 mg, 75%) which is soluble in toluene and dichloromethane but unstable in solution giving rise to metallic iridium. Complex (58) was prepared freshly before further reaction, because storage under ethylene at -30°C led to decomposition after 6 hours.

^1H n.m.r. (60 MHz, $CDCl_3$) 4.3 - 4.1 p.p.m. (br).

trans[Chlorobis(triphenylphosphine)(1,2-η)ethene iridium(I)][120], (54)

A modified procedure to that described by van der Ent[120] was employed.

Complex (58) prepared *in situ* (*vide supra*) (500 mg, 0.89 mmol) was

dissolved in argon-saturated toluene (5 ml) to give a clear deep crimson solution. Triphenylphosphine (0.92 g, 3.56 mmol) was added as a solid, under argon. The solution effervesced (ethylene) and over a period of minutes the red colour was discharged and an orange solid appeared. The crude solid was collected by filtration, washed with toluene (5 ml) and hexane (2 x 25 ml). The resulting orange crystalline solid was dried *in vacuo* to give 0.9 g (65%) of a product which was pure by ^{31}P n.m.r. and ^{1}H n.m.r. spectroscopy. M.p. 142 °C (dec).

^{31}P n.m.r. (CH_2Cl_2, argon; 36.43 MHz) 27.0 p.p.m. (s).

^{1}H n.m.r. ($CDCl_3$, argon; 300 MHz) 7.8 - 6.8 p.p.m. (m, 30H, aromatic), 5.4 p.p.m. (s, broad, free ethylene), 1.15 p.p.m. (s, broad, 4H).

IR (KBr) 1480(s), 1420(s), 1190(s), 1100(vs), 1030(m), 1000(m), 750(vs), 650(vs)

trans[Chlorobis(tricyclohexylphosphine)(1,2-η)etheneiridium(I), 60.

Complex (58) (100 mg, 0.18 mmol) was dissolved in 2 ml argon-saturated toluene. Tricyclohexylphosphine (121 mg, 0.43 mmol) was added. An immediate discharge of the deep red colour occurred to give an orange solution. This was left for 12 hr, during which time an orange crystalline solid was deposited. This was collected and washed with hexane (2 x 20 ml) to yield a product pure by ^{1}H and ^{31}P n.m.r. (40 mg, 11%).

^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) 9.4 p.p.m. (s).

^{1}H n.m.r. ($CDCl_3$, 300MHZ) 2.2 - 1.1 p.p.m. (m, 66H), 1.55 p.p.m. (t, 4H, J_{PH} 4 Hz).

IR (KBr) 2850(vs), 2820(m), 1450(m), 1090(m).

Chloro(ax,ax,equ)-tris(diphenylmethylphosphine)(1,2-η)etheneiridium(I), (65)

Complex (58) (160 mg, 0.28 mmol) was dissolved in dichloromethane (2 ml) under argon. Upon addition of diphenylmethylphosphine (250 mg,

1.2 mmol) the red colour was discharged to a bright yellow. Addition of dry argon-saturated hexane gave a bright yellow solid which was washed with hexane giving 243 mg (41%) product.

^{31}P n.m.r. (CH_2Cl_2, argon; 36.43 MHz) -14.7 p.p.m. (t, J_{PP} 14 Hz), -18.3 p.p.m. (d, J_{PP} 14 Hz).

Chlorobis(ax,equ)(5-phenyl-5H-dibenzophosphole)bis(1,2-η)etheneiridium(I), (62)

Complex (58) (100 mg, 0.18 mmol) was dissolved in 2 ml toluene under ethylene to give a pale yellow solution. 5-Phenyl-5H-dibenzophosphole [121] (400 mg, 0.65 mmol) was added to give a crude solid which was washed with toluene (5 ml) and hexane (2 x 10 ml) and dried *in vacuo* to give 420 mg (60%) pale yellow solid, m.p. 170°C (dec).

^{31}P n.m.r. (CH_2Cl_2, argon; 36.43 MHz) -14.8 p.p.m. (d, J_{PP} 12 Hz), -17.6 p.p.m. (d, J_{PP} 12 Hz).

^{1}H n.m.r. (CD_2Cl_2, 300 MHz) 7.8 - 7.0 p.p.m. (m, 26H), 3.13 p.p.m. (m, 2H), 3.02 p.p.m. (m, 2H), 2.78 p.p.m. (m, 2H), 2.52 p.p.m. (m, 2H).

IR (KBr) 3020(m), 2900(w), 1480(w), 1415(vs), 1180(m), 1150(s), 1120(m), 1090(m), 1175(m), 1160(w), 760(s), 725(s), 700(s).

Mass spectrum (field-desorption) m/e 774, 775, 776.

Microanalysis: Found C (61.47%), H (4.48%). Theoretical C (59.72%), H (4.23%); Theoretical + 0.5 mol toluene C (61.43%), H (4.47%).

Chlorobis(ax,equ)(triphenylarsine)bis(1,2-η)etheneiridium(I), (64)

Complex (58) (100 mg, 0.18 mmol) was dissolved in dry, argon-saturated toluene (1 ml). Triphenylarsine (136 mg, 0.44 mmol) was added. The deep crimson colour was immediately discharged to give a pale yellow

solid, which was collected by filtration under argon and washed with isopentane (2 x 10 ml) to give 140 mg (36%) of a pale yellow solid.
^{1}H n.m.r. (CD_2Cl_2, 300 MHz), 7.8 - 6.8 p.p.m. (m, 30H), 3.4 p.p.m. (quintet, 4H), 2.6 p.p.m. (q, 4 Hz).
IR (KBr) 3020(m), 1490(s), 1440(s), 1200(m), 1185(m), 1125(m), 1100(m), 890(w), 740(vs), 700(vs).

The complex was unstable in the absence of ethylene and on bubbling argon or oxygen through the solution a new species was observed to form which gave ^{1}H n.m.r. (CH_2Cl_2, 300 MHz) 7.8 - 6.8 p.p.m. (m, 52H), 3.85 p.p.m. (s, 4H).

Di-μ-chlorotetrakis(1,2-η)(1-phenylethene)iridium(I), (67)

Complex (59) (300 mg, 0.33 mmol) was suspended in 5 ml isopentane. Styrene (600 μl, 6 mmol) was added and the suspension stirred under argon. The yellow suspension disappeared in seconds to give a deep red solution which deposited a red solid in minutes. The solid was collected by filtration and washed with cold isopentane (in which it is slightly soluble) to remove excess styrene (2 x 5 ml). A red solid (222 mg, 77%) was collected and dried in vacuo. This was recrystallised by dissolving in minimum chloroform and then adding isopentane until cloudiness was observed. The solution was left to stand at 4°C and red crystals were collected by decanting the supernatant and washing with minimum isopentane. M.p. 130°C (dec).
^{1}H n.m.r. ($CDCl_3$, 300 MHz) 7.5 - 7.2 (m, 5H), 3.6 p.p.m. (d, 1H), 3.2 p.p.m. (dd, 1H), 2.4 p.p.m. (d, 1H).
Mass spectrum (field-desorption) m/e 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879 with intensities in agreement with isotopic patterns in Ir and Cl.
Microanalysis: Found C (43.79%), H (3.72%); theoretical C (44.0%), H (3.67%).

(2,4-pentandionato-O,O')bis(1,2-η)(phenylethene)iridium(I), (69)

Complex (67) (55 mg, 0.063 mmol) was dissolved in argon-saturated tetrahydrofuran (1 ml) to give a deep red solution. Sodium acetylacetonate (20 mg, 0.16 mmol) was added as a solid and the resulting solution stirred under argon. Within minutes the solution turned orange with a little precipitation of solid material, sodium chloride, which was removed by filtration. The volume of solvent was reduced by about half by blowing a rapid stream of argon over the solution to give a crude yellow product, which was removed by filtration. This product was redissolved in 10 ml isopentane to give a clear yellow solution. Reducing the volume of this solution by one half with cooling to 0°C gave a yellow crystalline solid, 20 mg (32%), m.p. 136-137°C.

^{1}H n.m.r. ($CDCl_3$; 300 MHz) 7.5 p.p.m. (br m, 6H), 7.3 p.p.m. (br m, 4H), 4.2 p.p.m. (br d, 2H, J_{HH} 11 Hz), 3.1 p.p.m. (br t, 2H), 2.7 p.p.m. (br d, 2H, J_{HH} 7 Hz), 1.9 p.p.m. (br s, 6H).

IR (KBr) 3020(w), 2970(w), 1560(vs), 1535(vs), 1490(m), 1380(m), 1280(m), 800(m), 780(s), 700(s).

Microanalysis: Found C (49.03%), H (4.45%); theoretical C (50.5%), H (4.6%).

Chlorobis(1,2,1',2'-η)(phenylethene)iridium(I), (71)

Complex (54) (100 mg, 0.13 mmol) was left to stand, with occasional shaking, in 2 ml phenylethene under argon in the presence of the radical inhibitor p-t-butylcatechol (10-15 p.p.m.). After four days most of the complex had dissolved to give an orange solution which was filtered to remove excess starting complex. The orange solution added dropwise to argon-saturated isopentane gave an off-white solid, 25 mg (50%) which was soluble in toluene and dichloromethane.

^{1}H n.m.r. ($CDCl_3$, 300 MHz) 7.3 - 6.9 p.p.m. (br m, 3H), 6.8 - 6.5 p.p.m. (br m, 2H), 2.0 - 1.8 p.p.m. (br m, 1H), 1.6 - 1.4 p.p.m. (br m, 2H).
IR (KBr) 3050(m), 2925(s), 1600(m), 1500(s), 1450(s), 1100(w), 1015(w), 910(w), 760(s), 700(vs).

Tris(1,2-η)(ethene)bis(ax,ax)(triphenylphosphine)iridium tetrafluoroborate, (75)

Complex (54) (100 mg, 0.13 mmol) was dissolved in ethene-saturated dichloromethane (0.5 ml). Silver tetrafluroborate (25 mg, 0.13 mmol) was added with vigorous agitation. Whilst ethene was bubbled through the suspension its orange colour was discharged to give a white precipitate and off-white solution. The precipitated silver chloride (white turning purple on standing) was removed by centrifugation. The volume of solvent was reduced by blowing a stream of ethene over the solution and white needle-like crystals appeared. Addition of toluene ensured full crystallisation. The crystals were isolated by decantation of the supernatant and washed with hexane. The white crystals obtained, 76 mg (65%) were soluble in dichloromethane to give an orange solution which turned colourless on addition of ethene. They were unstable and decomposed slowly under ethene at -30°C.

^{31}P n.m.r. (CH_2Cl_2, ethene, 36.43 MHz) -2.9 p.p.m. (s).

^{1}H n.m.r. (CD_2Cl_2, 90 MHz): 26°C, 7.5 p.p.m. (m, 36H), 6.0 p.p.m. ($CH_2=CH_2$), 4.2 p.p.m. (br, 3H), 3.8 p.p.m. (br, 12H), 3.1 p.p.m. (br, 2H); -32°C, 7.5 p.p.m. (m, 36H), 5.5 p.p.m. ($CH_2=CH_2$), 4.3 p.p.m. (br, 3H), 3.2 p.p.m. (br s, 12H), 2.8 p.p.m. (br, 2H).

Attempted Preparation of Tris(1,2-η^2)(ethene)bis(dibenzophosphole)iridium(I) tetrafluoroborate, (73)

Complex (62) (100 mg, 0.12 mmol) was dissolved in ethene-saturated dichloromethane (10 ml). Silver tetrafluoroborate (30 mg, 0.15 mmol) was added with vigorous agitation. A bright, white precipitate of silver chloride was removed by centrifugation to give a colourless solution. The volume of solvent was reduced to about 2 ml by blowing it off with a stream of ethene, to give a bright white solid which was isolated by centrifugation and washed with toluene (5 ml) and hexane (2 x 5 ml). The white solid, 68 mg (64%), was dried in vacuo.

^{31}P n.m.r. (CH_2Cl_2, ethene, 36.43 MHz), -15.5 p.p.m. (s), -7.7 p.p.m. (d, J_{PP} 10 Hz), -18.3 p.p.m. (d, J_{PP} 10 Hz).

^{1}H n.m.r. (CD_2Cl_2, ethene, 300 MHz) 6.0 - 7.0 p.p.m. (m, 52H), 5.5 p.p.m. (s, free ethene), 3.3 - 3.1 p.p.m. (m, 4H), 3.05 p.p.m. (t, 12H, J_{PH} 4 Hz), 2.8 - 2.5 p.p.m. (m, 4H), 2.4 p.p.m. (br s, 2H; disappears on addition of 5 µl D_2O).

IR (KBr) 3400(br,m), 3020(w), 1440(s), 1100(vs), 760(s), 715(s), 700(s).

The complex was too thermally unstable to given a field-desorption mass spectrum.

Chlorobis(ax,ax)(triphenylphosphine)(1,2-η)(ethene)dioxygeniridium(I),[119] (55)

A procedure modified from van der Ent[119] was used.

Complex (54) (100 mg, 0.13 mmol) was suspended in dry toluene (15 ml) in a 3-necked flask and stirred rapidly while a slow (1 bubble per second through a Pasteur pipette) stream of ethene was bubbled through the solution. A slow stream of oxygen was blown over the surface of the stirred solution. Within 15 min the orange suspension had become off-

white. The crude solid was collected by centrifugation and washed with toluene (10 ml) and hexane (3 x 10 ml) to give an off-white powder, 85 mg (79%), m.p. 135°C (dec). The solid was soluble in chlorinated solvents but insoluble in benzene, methanol or ether. Attempts to recrystallise the solid were unsuccessful because of its instability in solution.

^{31}P n.m.r. (CH_2Cl_2, ethene, 36.43 MHz) -5.3 p.p.m. (s).

^{1}H n.m.r. (CD_2Cl_2, 90 MHz) 8.0 - 7.0 p.p.m. (m, 30H), 3.35 p.p.m. (t, 4H, J_{PH} 4 Hz).

IR (KBr) 3025(w), 1480(s), 1430(s), 1110(w), 1210(w), 1190(m), 1100(s), 1030(w), 1000(w), 890(ν_{O-O}, s), 750(s), 700(s).

Field-desorption mass spectrum, m/e 779, 780, 781, 782, 783 indicating loss of dioxygen.

Chlorotris(ax,ax,equ)(triphenylphosphine)dioxygeniridium(I)[127], (56)

Complex (55) (100 mg, 0.12 mmol) was added to a stirred solution of triphenylphosphine (32 mg, 0.12 mmol) in 1 ml of toluene. The creamy suspension turned a bright yellow over several minutes. The bright yellow solid was collected by filtration and washed with toluene (1 ml) and hexane (2 x 5 ml) and dried in vacuo to give 96 mg (72%) of product, m.p. 152°C (dec.).

^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) -8.6 p.p.m. (t, J_{PP} 15 Hz), -17.7 p.p.m. (d, J_{PP} 15 Hz).

IR (KBr) 3050(m), 1480(m), 1430(s), 1190(w), 1095(s), 1030(w), 1000(w), 850(ν_{O-O})(m), 850(s), 700(s).

Chlorobis(ax,ax)(triphenylphosphine)(1-η)(pyridine)dioxygeniridium(I), (57)[127]

Complex (55) (100 mg, 0.12 mmol) was added to a stirred solution of pyridine (20 µl, 0.25 mmol) in toluene (1 ml). Over several minutes the

creamy suspension turned bright yellow. The solid was collected by filtration and washed with toluene (1 ml) and hexane (2 x 5 ml) and dried *in vacuo* to give 72 mg (65%) of a bright yellow solid, m.p. 161°C.
^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) -6.3 p.p.m. (s).
IR (KBr) 3050(m), 1480(s), 1430(s), 1190(m), 1160(w), 1100(s), 1030(w), 1000(w), 840(ν_{O-O})(m), 750(m), 700(vs).

Chlorobis(ax,ax)(triphenylphosphine)(1-η)-4-(N',N'-dimethylamino)pyridine-dioxygeniridium(I), (81)

Complex (55) (50 mg, 0.062 mmol) was added to a solution of 4-(N',N'-dimethylamino)pyridine (8 mg, 0.12 mmol) in 2 ml toluene under argon. Over 20 min the off-white suspension turned bright yellow. The crude solid was collected by filtration and dried *in vacuo*. Recrystallisation from dichloromethane and isopentane (concentric tubes) gave yellow needles, 36 mg (66%), m.p. 110°C (dec).
^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) -8.1 p.p.m. (s).
Field-desorption mass spectrum could not be obtained because of the instability of the complex.
Microanalysis: Found C (58.26%) H (5.3%) P (2.87%); theoretical C (57.0%) H (4.4%) P (3.1%); theoretical + 0.5 molar equivalent toluene C (58.6%) H (4.6%) P (3.0%).
IR (KBr) 3048(w), 1605(s), 1510(m), 1480(m), 1430(s), 1380(m), 1210(m), 1180(w), 1090(s), 1020(m), 850(m), 805(m), 740(s), 700(vs).

Oxygenation of Complex (62)

(i) Complex (62) (15 mg, 18 μmol) was dissolved in 0.25 ml 1,2-dichloroethane to give a pale yellow solution. Stirring under a blanket of oxygen for 3 hr discharged the yellow colour to give a slight pale

green colouration. Hexane (2 ml) was added to give an off-white solid (10 mg, 61%).

IR (KBr) 3025(w), 1480(w), 1440(vs), 1290(w), 1285(w), 1190(w), 1160(w), 1145(w), 1100(m), 1050(w), 1000(w), 870(m), 760(s), 720(s), 700(s).

^{1}H n.m.r. (C_6D_6, 300 MHz) 8.3 - 6.8 p.p.m. (m, aromatic), 3.95 p.p.m. (br d, 8H), 3.5 p.p.m. (br m, 8H), 2.9 p.p.m. (t, 4H, J_{PH} 5 Hz).

^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz), 33.0 p.p.m. (s), -13.6 p.p.m. (s), -20.3 p.p.m. (d, J_{PP} 10 Hz), -21.6 p.p.m. (d, J_{PP} 10 Hz).

Field desorption mass spectrum m/e 774/775/776 indicating loss of dioxygen.

(ii) The oxygenation of complex (62) was observed directly by ^{1}H n.m.r. spectroscopy. Complex (62) (15 mg, 18 μmol) was dissolved in 0.25 ml chloroform-d under argon. A slow stream of oxygen was bubbled into the pale yellow solution. The ^{1}H n.m.r. spectra (300 MHz) were obtained after 30 minutes and 6 hours. The spectra obtained are displayed in Chapter II. After 6 hrs an IR (KBr) spectrum was obtained from this sample by precipitation in excess hexane and drying the off-white solid in vacuo.

IR (KBr) 3050(m), 1600(w), 1480(w), 1440(vs), 1270(m), 1100(vs), 880(m), 805(m), 760(s), 730(s), 700(s).

Dihydrobis(propan-2-one)bis(triphenylphosphine)iridium tetrafluoroborate, (82)[135]

$[Ir(cod)(PPh_3)_2]BF_4$ (100.4 mg, 0.11 mmol) was dissolved in a minimum of dry acetone (ca. 1.5 ml), under argon. The solution was saturated with hydrogen in three freeze-thaw cycles and stirred vigorously. Within 10 mins the deep crimson solution had become colourless. The reaction mixture was then transferred to a Craig tube and

hexane added to precipitate the product, which was isolated as an off-white solid by centrifugation. The crude product was washed with hexane and dried *in vacuo* giving 7.88 mg (77%) of white powder, m.p. 145°C (decomposing).
IR (KBr) 2230(m), 2260(m), 1650(s), 1660(s).
^{1}H n.m.r. (300 MHz, $CDCl_3$) 7.5 - 7.3 p.p.m. (m, 30H), 1.43 p.p.m. (br s, 6H), -27.7 p.p.m. (t, 2H, J_{PH} 15 Hz).
^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) 28.0 p.p.m. (s).

[(1,2,5,6-η)-1,5-cyclooctadiene]bistriphenylphosphineiridium tetrafluroborate, (83)[136,137]

$[Ir(cod)Cl]_2$ (67 mg, 0.1 mmol), triphenylphosphine (131 mg, 0.5 mmol) and silver tetrafluroborate (58 mg, 0.3 mmol) were placed in a Schlenk tube. Ethanol (1 ml) and dichloromethane (1 ml) were added and the sølution stirred. There was an immediate red colouration and formation of a purple precipitate (silver chloride). The red solution was decanted by pipette after centrifugation and reduced in volume to *ca.* 1 ml, under vacuum. Diethyl ether was added until precipitation ceased. The red solid obtained was filtered off, washed with diethyl ether and dried *in vacuo* to give 141 mg (78%) of product, m.p. 201-202°C.
^{1}H n.m.r. ($CDCl_3$, 300 MHz) 7.7 - 7.2 p.p.m. (m, 30H), 4.20 p.p.m. (br s, 4H), 2.36 p.p.m. (br d, 4H), 1.95 p.p.m. (m, 4H).

Di-μ-chlorobis(1,2,5,6-η)-1,5-cyclooctadiene iridium, (84)[138]

Iridium trichloride (2.0 g, 4.2 mmol) was refluxed with 1,5-cyclooctadiene (2 ml, 21 mmol) in ethanol 20 ml) and water (10 ml) under argon for 24 hr. The solution was then cooled, the precipitate collected by filtration and washed with cold ethanol. After drying the solid *in vacuo* 0.92 g (32%) of bright red crystals were obtained, m.p. 175°C (dec).

^{1}H n.m.r. ($CDCl_3$, 60 MHz) 4.3 - 4.1 p.p.m. (br m, 4H), 2.5 - 2.0 p.p.m. (br m, 4H), 1.7 - 1.2 p.p.m. (br m, 4H).

E2.3 Experimental Details

Decarbonylation of α,β-unsaturated aldehydes

Complex (54) (50 mg, 0.06 mmol) in argon-saturated dichloromethane (1 ml) was added to trans but-2-enal (30 µl, 0.3 mmol). The colour of the solution changed from orange to canary yellow in 30 min. The ^{31}P n.m.r. spectrum (36.43 MHz) revealed a single species at 25.3 p.p.m. After 2 hr yellow needles crystallised out of the medium.

IR (KBr) 1960(vs), 1490(m), 1440(s), 1190(w), 1100(s), 1000(w), 750(s), 710(m), 700(s).

The ^{31}P n.m.r. spectrum and IR spectrum were identical to a sample of complex (66) (loaned by Dr. J.M. Brown). Complex (54) (90 mg, 0.16 mmol) in argon-saturated dichloromethane was added to trans 3-phenylpropenal (15 µl, 0.16 mmol). After 5 hours the yellow solution was analysed by GLC (15% OV17 on diatonite C-AW 100-120 mesh, 85°C, styrene R.T. = 4.1 min) using 1,2-dichlorobenzene as an internal standard. Styrene was produced in 93% yield. Yellow crystals precipitated out of the solution and gave an IR spectrum (KBr) identical to complex (66).

Decomposition of $[Ir(PPh_3)_2(Cl)(O_2)(C_2H_4)]$, (55)

Complex (55) (50 mg, 60 µmol) was placed in an 8 mm n.m.r. tube fitted to a vacuum line. Dichloromethane (2.5 ml), previously saturated in the desired gas by the freeze-thaw method, was transferred to the n.m.r. tube by steel tube. The tube was sealed by flame under the atmosphere of choice. In preliminary runs the tube was sealed using a rubber septum cap. The rate of decomposition of the complex under an argon, oxygen or ethylene atmosphere was monitored by ^{31}P n.m.r. spectroscopy. The absolute intensity of the singlet resonance at -5.3 p.p.m. was measured against time

and the data obtained displayed in Figure 73. A pale green solid could be isolated from the decomposition by precipitation with isopentane. IR (KBr) 3025(m), 2025(m), 1480(m), 1435(s), 1195(m)(ν_{PO}), 1100(s), 1000(w), 750(m), 700(vs).

The rate of addition of triphenylphosphine to complex (55) was monitored by ^{31}P n.m.r. Complex (55) (50 mg, 60 μmol) was dissolved in 2.5 ml argon-saturated dichloromethane and the ^{31}P n.m.r. spectrum obtained immediately (typically within 10 min). Triphenylphosphine (16 mg, 60 μmol) was added to the solution and the spectrum obtained immediately.

Oxidation of Olefins by $[Ir(PPh_3)_2Cl(O_2)(C_2H_4)]$, (55)

In a typical procedure for the oxidation of oct-1-ene, complex (55) (10 mg, 12 μmol) in 0.25 ml dichloromethane (4.8 mM) was added to oct-1-ene (10 μl, 60 μmol) in a drawn 5 mm tube. The tube was flame-sealed under oxygen or argon, when aliquots were not required. When samples were required to be analysed over a time course the reaction was carried out as above in a 1.5 cm tube fitted with a rubber septum cap. For ^{31}P n.m.r. observation the reactants were mixed in an 8 mm n.m.r. tube which was subsequently flame-sealed under the chosen atmosphere.

GLC analysis: (15% OV17 on diatonite C-AW 100-120 mesh, 121°C). Samples of oxidation reactions were removed by microsyringe (100 μl) and injected into 2 ml cold isopentane. The mixture was stored at -30°C and the supernatant pipetted from the precipitate. This solution was used for GLC analysis. In runs employing an internal calibrant, 5 μl 10% 1,2-dichlorobenzene in dichloromethane were added to the reaction mixture before sealing the tube. The internal standard was calibrated using accurately measured solutions of octan-2-one. Retention times (121°C), dichlorobenzene 6.1 min, octan-2-one 4.2 min. For analysis of styrene oxidation products

a column oven temperature of 161°C was employed. Retention times (161°C) acetophenone 6.1 min, 1,2-dichlorobenzene 3.9 min.

^{31}P n.m.r. analysis was performed in the manner previously described. Complex (55) (10 mg, μmol) in dichloromethane under argon was added to penta-1,3-diene (10 μl, 62 μmol) in an n.m.r. tube. The tube was flame-sealed and the reaction observed by ^{1}H n.m.r. (90MHz). The resonance corresponding to coordinated ethylene in (55) was observed to diminish in intensity with concomitant growth of a singlet at 2.25 p.p.m. and a doublet at 1.9 p.p.m. (J_{HH} 7.5 Hz), assignable to pent-3-en-2-one (confirmed by an authentic sample, R.N. Emanuel Research Chemicals). The above oxidations were unaffected by the presence of 4-methyl-2,6-di-t-butylphenol in a concentration 10% that of Ir complex.

Oxidation of Olefins by $[Ir(PPh_3)_3(O_2)Cl]$, (56)

Typically, complex (56) (13.2 mg, 12 μmol) in dichloromethane (0.25 ml) under either an argon or ethylene atmosphere was added to the olefin e.g. oct-1-ene (10 μl, 60 μmol) in a drawn 5 mm tube and heat-sealed, when aliquots were not required. When the reaction was monitored against a time course the reactants were mixed under the desired atmosphere in a 1.5 cm tube fitted with a rubber septum cap. Samples which were monitored by ^{31}P n.m.r. were made up as previously described. GLC analysis: aliquots were removed by microsyringe (100 μl) and added to cold isopentane. The estimation of octan-2-one yield was determined as previously described. For runs in which the yield of oxidation products was estimated by GLC with simultaneous observation of the ^{31}P n.m.r. spectrum, samples were removed from the n.m.r. probe, an aliquot was taken through the septum cap and the sample replaced in the probe immediately. Each aliquot was added to 2.5 ml cold isopentane. The rate of breakdown of the complex was monitored by measuring the absolute intensity of the doublet resonance at -17.4

p.p.m. against time. The rate at which triphenylphosphine oxide was formed was estimated by measuring its resonance at 27.0 p.p.m.

Oxidation of Styrene by $[Ir(CH(Ph)CH_2)_2Cl]_2$, (67)

Dichloromethane (0.5 ml) was added to a mixture of complex (67) (25 mg, 29 μmol), triphenylphosphine (8 mg, 30 μmol; 16 mg, 60 μmol; 24 mg, 90 μmol; 32 mg, 120 μmol; 40 mg, 150 μmol), 1,2-dichlorobenzene (2 μl) and styrene (37 μl, 290 μmol) in five experiments. Similarly to one sample triphenylphosphine was omitted. The reaction tubes (5 mm) were flame-sealed under an oxygen atmosphere. Samples containing phosphine changed colour from bright red to brown within minutes. The solution containing no triphenylphosphine maintained its red colour over the time period of the experiment. The reaction tubes were allowed to stand at 21°C for 2 hrs when the seal was broken and an aliquot removed for GLC analysis (vide supra). The tubes were resealed under oxygen and a second aliquot taken after 10 hr. The oxidation products were estimated against the internal standard. Benzaldehyde was identified by comparison with an authentic sample (GLC; retention time 3.6 min (161°C). TLC; silica, dichloromethane, positive test with Brady's reagent.

Oxidation of Olefin by $[Ir(PPh_3)_2L(O_2)Cl]$ (L = pyridine, (57), 4-(N',N'-dimethylamino)pyridine, (81))

The oxidation of oct-1-ene by complexes (57) and (81) was monitored as described for complex (56) above (5 mm sealed tube, under oxygen or argon atmosphere). The final yield of octan-2-one was estimated by GLC analysis against 1,2-dichlorobenzene internal standard (both 27% (argon); 43% (oxygen)).

Oxidation of Oct-1-ene by $[Ir(AsPh_3)_2(C_2H_4)_2Cl]$, (63)

Complex (63) (10 mg, 11 μmol) and oct-1-ene (10 μl, 60 μmol) were dissolved in dichloromethane (0.25 ml) saturated with oxygen. The tube was sealed and maintained at 40°C for 10 hr. The yield of octan-2-one was estimated by GLC analysis (vide supra). No other volatile products were detected by GLC. Yield of octan-2-one 32% (based on Ir).

Attempted Oxidation of Oct-1-ene by $[Ir(5\text{-phenyl-5H-dibenzophosphole})_2(O_2)(C_2H_4)Cl]$, isomers (79), (80)

The isomer mixture, (79), (80) (10 mg, 12 μmol) and oct-1-ene (10 μl, 60 μmol) were stirred under oxygen for 18 hr at 40°C. Less than 2% (based on Ir) of octan-2-one was detected by GLC analysis (vide supra) by this time.

Attempted Oxidation of Olefins by Ir(I) cationic complexes

The complex $[Ir(PPh_3)_2(C_2H_4)_3]BF_4$, (75), was prepared in situ (10 mg, 12 μmol) as described (vide supra) to give a colourless or pale orange solution, under an ethylene atmosphere. Addition of styrene (15 μl, 60 μmol) followed by very gentle bubbling of argon through the solution produced a deepening in colour to red over several minutes. The admission of a blanket of dioxygen over this solution resulted in a loss of the bright red colour to give a brown solution. Analysis of the solution by GLC (vide supra) showed acetophenone, 2-phenyloxirane and benzaldehyde in equal proportion, but unknown absolute yield (identified against known substances, Retention time, 2-phenyloxirane, 5.4 min (standard conditions); TLC, silica, dichloromethane, positive blue spot with anisaldehyde spray).

When oct-1-ene was used in place of styrene no red colouration was observed but the release of ethylene was detected. GLC analysis showed octan-2-one, 2-hexyloxirane and heptanol in equal proportion by unknown yield.

$[Ir(PPh_3)_2(CH_3(O)CH_3)_2H_2]BF_4$, (82) (11 mg, 12 μmol) and oct-1-ene (10 μl, 60 μmol) were dissolved in dichloromethane (0.25 ml) under an oxygen atmosphere in a sealed tube, kept at 40°C. After 3 hrs no oxidation products were observed by GLC analysis (vide supra).

A similar result was obtained when styrene was used in place of oct-1-ene. In this case, however, the colourless solution became bright orange on addition of styrene.

^{31}P n.m.r. (CH_2Cl_2, 36.43 MHz) 5.6 p.p.m. (s), stable in solution under oxygen.

^{1}H n.m.r. ($CDCl_3$, 300 MHz) 8.5 - 7.5 p.p.m. (m, 30H), 7.0 p.p.m. (t, 2H), 5.4 p.p.m. (d, 2H), 5.0 p.p.m. (d, 2H), 2.6 p.p.m. (q, 2H), 1.2 p.p.m. (t, 3H).

REFERENCES

1a) R.A. Sheldon, J.K. Kochi, Adv. Catal., 1976, 25, 272;

1b) J.E. Lyons 'Transition Metal Complexes as Catalysts for the Addition of Oxygen to Reactive Organic Substrates' in Aspects of Homogeneous Catalysis Vol. 3, R. Ugo, Ed. Reidel 1977;

1c) R.A. Sheldon 'Metal Catalysed Epoxidations of Olefin with Hydroperoxides' in Aspects of Homogeneous Catalysis Vol. 4, R. Ugo, Ed. Reidel 1981.

2a) L. Vaska, Acc. Chem. Res., 1976, 9, 175;

2b) B.R. James 'Dioxygen and Metalloporphyrins' in 'The Porphyrins', D. Dolphin, Ed; Vol 5, P. 205. Academic Press. New York, 1978.

3) S. Sakaki, K. Hori, A. Olyoshi, Inorg. Chem., 1978, 17, 3183; R. Boca, J. Mol. Struct., 1980, 65, 173.

4) G. Henrici-Olvie, S. Olive, Angew. Chem. Internat. Ed., 1974, 13, 29.

5) J. Valentine, Chem. Rev., 1973, 73, 235.

6) L. Vaska, Science, 1963, 140, 809.

7) C.J. Nyman, L.E. Wymore, G. Wilkinson, J. Chem. Soc., A, 1968, 561.

8) P. Cheng, C. Cook, S. Nyberg, K. Wan, Can. J. Chem., 1971, 49, 3772.

9) T. Yoshida, K. Tatsumi, S. Otsuka, Pure Appl. Chem., 1980, 52, 713.

10) S. Bhaduri, L. Castella, R. Ugo, R. Raithby, C. Zuccaro, M.B. Hursthouse, J. Chem. Soc. Dalton Trans., 1979, 1624.

11) A. Nakamura, Y. Tatsuno, S. Otsuka, Inorg. Chem.,

1972, 11, 2058.

12) J.A. McGinnety, N.C. Payne, J.A. Ibers, J. Am. Chem. Soc., 1969, 91, 6301.

13) L. Vaska, L.S. Chen, C.V. Senolt, Science, 1971, 174, 587.

14) J.P. Collman, Acc. Chem. Res., 1977, 10, 265.

15) R.S. Gall, J.F. Rogers, W.P. Schaefer, G.G. Christoph, J. Am. Chem. Soc., 1976, 98, 5135; and A. Avdeef, W.P. Schaefer, J. Am. Chem. Soc., 1976, 98, 5153.

16) For example B.W. Griffin, J.A. Peterson, R.W. Estabrook, Cytochrome P-450: Biophysical Properties and Catalytic Function, in 'The Porphyrins', D. Dolphin, Ed., Vol. VII, Chapter 7. Academic Press. New York 1979.

17) 'Selective Catalytic Oxidation of Hydrocarbons: A Critical Analysis'. Catalytica Associates Inc., Santa Clara, CA., Multicentre Study No. 1077, 1979.

18) H.A. Wittcoff, B.G. Reuben, 'Industrial Organic Chemicals in Perspective'. Parts I and II. Wiley Interscience. New York. 1980.

19) J.K. Kodic, 'Organometallic Mechanisms and Catalysis'. P. 50. Academic Press, London 1978.

20) F. Haber, J. Weiss., Proc. R. Soc. Ser. A., 1934, 147, 332.

21) G. Sosnovsky, D.J. Rawlinson in 'Organic Peroxides' D. Swern (Ed.) Vol. 2 P. 269. Wiley, New York 1971.

22) J.T. Groves, M. Van der Puy, J. Am. Chem. Soc., 1976, 98, 5290.

23) D.R. Paulson, R. Ullman, R.B. Sloane, G.L. Closs, J. Chem. Soc. Chem. Commun., and M. Baccouche, J. Ernst, J.H. Fuhrop,

R. Schlosser, H. Arzoumanian, J. Chem. Soc. Chem. Commun., 1977, 821.

24) J.P. Collman, M. Kubota, J.W.J. Hosking, J. Am. Chem. Soc., 1967, 89, 4809.

25) A. Fusi, R. Ugo, A. Pasini, S. Cerini, J. Organomet. Chem., 1971, 26, 417.

26) B.R. James, E. Ochiai, Can. J. Chem., 1971, 49, 975.

28) R.A. Budnik, J.K. Codic, J. Org. Chem, 1976, 41, 1384.

29) A.M. Brownstein (Ed.) in 'U.S. Petrochemicals: Technologies, Markets and Economics'. The Petroleum Publishing Co., Tulsa, U.S.A., 1972.

30) For example Polyether antibiotic synthesis see T. Fukayama, B. Vranesic, D.P. Nagri, Y. Kishi, Tetrahedron Lett., 1978, 31, 2741.

31) N. Milas, S. Sussman, J. Am. Chem. Soc., 1936, 58, 1302 and numerous patents eg. U.S. Pat. 2437648 (1948).

32) H.C. Stevens, A.J. Kaman, J. Am. Chem. Soc., 1965, 87, 734.

33) A.M. Matacci, E. Perrotti, A. Santobrogio, J. Chem. Soc. Chem. Commun., 1970, 1198.

34) J.P. Schirmann, S.Y. Delavarenne, Germ. Pat. 2752626 (1978).

35) For example E.G.E. Hawkins, J. Chem. Soc., 1950, 2169.

36) K.B. Sharpless, T.R. Verhoeven, Aldrichimica Acta., 1979, 12, 63. Deals with t-butylhydroperoxide in particular. Practical considerations and mechanisms.

37) H. Mimoun, I. Seree de Roch, L. Sajus, Tetrahedron, 1970, 26, 37.

38a) K.B. Sharpless, J.M. Townsend, D.R. Williams, J. Am. Chem. Soc., 1972, 94, 295.

38b) J. Kalonstian, L. Lena, J. Metzger, Tetrahedron Lett., 1975, 26, 37.

39) A.O. Chong, K.B. Sharpless, J. Org. Chem., 1977, 42, 1587.

40) R.A. Sheldon, J.A. Van Doorn, J. Catal., 1973, 31, 427.

41) The M = O bond is ubiquitous and recently theoretical studies indicate it is essential for high reactivity see A.K. Rappe, W.A. Goddard III, Nature, 1980, 285, 311.

42) K.B. Sharpless, R.C. Michaelson, J. Am. Chem. Soc., 1973, 95, 6136.

43) S. Yamada, T. Mashiko, S. Terashimo, J. Am. Chem Soc., 1977, 99, 1988.

44) K. Oshima, K.B. Sharpless, J. Am. Chem. Soc., 1977, 99, 1990.

45) K. Oshima, K.B. Sharpless, unpublished results, see Ref. 36.

46) T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc., 1980, 102, 5976.

47a) B.E. Rossiter, T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc., 1981, 103, 464.

47b) K. Mori, T. Ebata, Tetrahedron Lett., 1981, 22, 4281.

48) S.L. Regan, G.M. Whitesides, J. Organomet. Chem., 1973, 59, 293.

49) H. Arakira, Y. Moro-oka, A. Ozaki, Bull. Chem. Soc. Jap., 1974, 47, 2958.

50) For alternative mechanisms see Ref. 38a and A.A. Achrem, T.A. Timoschtshuk, D.I. Metelitza, Tetrahedron, 1974, 30, 3165.

51) H.B. Kagan, H. Mimoun, C. Mark, V. Schurig, Angew. Chem. Int. Ed. Engl., 1979, 18, 485.

52) M.J.Y. Chen, J.K. Kochi, J. Chem. Soc. Chem. Commun., 1977, 204.

53. I. Tabushi, N. Koga in 'Biomimetic Chemistry'; D. Dolphin, Ed; A.C.S., Adv. Chem. Ser., 1981, 191, 291.

54) J.T. Groves, W.J. Kraper, T.E. Nemo, R.S. Myers, J. Mol. Catal., 1980, 7, 169.

55) P.A. Kilty, W.M.H. Sarhtler, Catal. Rev., 1974, 10, 1., and 'Proceedings of the First Berkeley Catalysis and Surface Science Conference' in Catal. Rev., 1981, 23, 127, 151, 163.

56) E.L. Force, A.T. Bell, J. Catal., 1975, 38, 440., and M. Stoukides, C.G. Vayeras, J. Catal., 1981, 70, 137.

57) J. Smidt, W. Hafner, R. Jira, T. Sedlmeir, R. Sieber, R. Ruttinger, H. Kojer, Angew. Chem., 1959, 71, 176.

58) For a review see P.M. Henry, Adv. Organomet. Chem., 1975, 13, 363.

59) Support for trans attack can be found in J.E. Backvall, B. Akermark, S.O. Ljunggren, J. Am. Chem. Soc., 1979, 101, 2411; Y. Sacto, S. Shinoda, J. Mol. Catal., 1980, 9, 461; J.K. Stille, R. Divakarumi, J. Am. Chem. Soc., 1978, 100, 1303; J. Majima, H. Kurosawa, J. Chem. Soc. Chem. Commun., 1977, 610.

60) P.M. Maitlis 'Organic Chemistry of Palladium' Academic Press. New York, 1971. Vol. III P. 77 and references therein.

61) For example see D.R. Fahey, E.A. Zeach, J. Org. Chem., 1974, 39, 22.

62) P.R. Stapp, Euro. Pat. 143 (to Phillips Petroleum Co.) 1978.

63) M. Roussel, H. Mimoun, J. Org. Chem., 1980, 45, 5387.

64) F. Ingersheim, H. Mimoun, Nouv. J. Chim., 1980, 4, 711.

65) H. Mimoun, R. Charp entier, A. Mitschler, S. Fischer, R. Weiss, J. Am. Chem. Soc., 1980, 102, 1047.

66) H. Mimoun, R. Charpentier, French Demande, 7900828 (1979).

67) H. Mimoun, M.M. Perex Machirant, I. Seree de Roch, J. Am. Chem. Soc., 1978, 100, 5437.

68) F. Ingersheim, H. Mimoun, Nouv. J. Chim., 1980, 4, 161.

69) C.W. Dudley, G. Read, P.J.C. Walker, J. Chem. Soc. Dalton Trans., 1974, 1926.

70) G. Read, P.J.C. Walker, J. Chem. Soc. Dalton Trans., 1977, 883.

71) R. Tang. F. Mares, N. Neary, D.E. Smith, J. Chem. Soc. Chem. Commun., 1979, 274.

72) B.S. Tourog, S.E. Diamond, F. Mares, J. Am. Chem. Soc., 1979, 101, 270.

73) F. Mares., Presented at the 177th Meeting of the American Chemical Society, Honolula, HI, April 1979.

74) K.P. Kelly, M.A. Andrews. Presented at the 181st Meeting of the American Chemical Society, Atlanta, GA, March 1981.

75) Y. Tatsuno and S. Otsuka, J. Am. Chem. Soc., 1981, 103, 5832.

76) P.J. Hayword, D.M. Blake, G. Wilkinson, C.J. Nyman, J. Am. Chem. Soc., 1970, 92, 5873.

77) R. Ugo, F. Conti, S. Lenini, R. Mason, G.B. Robertson, J. Chem. Soc. Chem. Commun., 1968, 1498.

78) R.A. Sheldon, J.A. Van Doorn, J. Organomet. Chem., 1975, 94, 115.

79) Y. Tatsuno, S. Otsuka, J. Am. Chem. Soc., 1981, 103, 5832.

80) R. Ugo, G.M. Sanderighi, A. Fusi, D. Carreri, J. Am. Chem. Soc., 1980, 102, 3745.

81) S.L. Regan, G. Whitesides, J. Organomet. Chem., 1973, 59, 293.

82) F.H. Allen, A. Pidcock, J. Chem. Soc. A, 1968, 2700.

83) G.C. Levy, D.M. White, F.A.L. Avet, J. Magn. Réson., 1972, 6, 453.

84) J.-Y. Lallemand, J. Soulié, J.-C. Choffard, J. Chem. Soc. Chem. Commun., 1980, 436.

85) M. Green, J.A.K. Howard, P. Mitrachachon, M. Pferrer, J.L. Spenser, F.G.A. Stone, P. Woodward, J. Chem. Soc. Dalton Trans., 1979, 306.

86) B.W. Erikson, Org. Synth., 1974, 54, 19.

87) H.C. Clark, A.B. Goel, C.S. Wong, J. Am. Chem. Soc., 1978, 100, 6241.

88) D. Swern, Ed., 'Organic Peroxides' Vols I, II, Wiley, London 1971.

89) D.M. Blake, D.M. Roundhill, Inorg. Synth., 1978, XVIII, 121.

90) M.R. Johnson, B. Rickborn, J. Org. Chem., 1970, 35, 1041.

91) F. Calderazzo, Angew. Chem. Int. Ed. Engl., 1977, 16, 299.

92) P. Chini, G. Longoni, J. Chem. Soc. A, 1970, 1542.

93) L. Malatesta, Prog. Inorg. Chem., 1959, 1.

94) Y. Yamamoto, H. Yamazaki, Coord. Chem. Rev., 1972, 8, 225.

95) P.M. Treichel, R.W. Heiss, J. Am. Chem. Soc., 1970, 92, 4731.

96) G. Booth, J. Chatt, J. Chem. Soc. A, 1966, 634.

97) M. Angaletta, Gazz. Chim. Ital., 1959, 89, 2359; ibid., idem, 1960, 90, 1021.

98) P.S. Pregosin, R.W. Kunz, 'NMR 16: Basic Principles and Progress', Springer-Verlag Berlin 1979, p.54.

99) J.M. Brown, P.A. Chaloner, J. Am. Chem. Soc., 1978, 103, 4309.

100) G.B. Payne, J. Org. Chem., 1961, 26, 250.

101) A. Dobson, S.D. Robinson, M.F. Uttley, Inorg. Synth., 1977, XVII, 124.

102) M. Suzuki, A. Watanabe, R. Noyori, J. Am. Chem. Soc., 1980, 102, 2095.

103) M. Bartok, F. Notheisz, J. Chem. Soc. Chem. Commun., 1979, 139.

104) H.O. House, 'Modern Synthetic Reactions', 2nd ed., Benjamin, London 1972, p.306.

105) A. Sen, J. Halpern, J. Am. Chem. Soc., 1977, 99, 8337.

106) D.B. Denny, W.F. Goodyear, B. Goldstein, J. Am. Chem. Soc., 1960, 82, 1393.

107) A. Sen, J. Halpern, Inorg. Chem., 1980, 19, 1073.

108) C.A. Tolman, W.C. Siedel, D.H. Gerlach, J. Am. Chem. Soc., 1972, 94, 2669.

109) G. Montando, V. Librando, S. Caccamesa, P. Maravigna, J. Am. Chem. Soc., 1973, 95, 6365.

110) A.J. Gordon, P.A. Ford, "The Chemist's Companion; A Handbook of Practical Data, References and Techniques", Wiley, New York, 1972.

111) L. Malatesta, C. Cariello, J. Chem. Soc., 1958, 2323.

112) R. Ugo, F. Cariati, G. La Monica, Inorg. Synth., 1968, XI, 105.

113) C.D. Cook, G.S. Janhal, J. Am. Chem. Soc., 1968, 90, 1464.

114) S. Cenini, R. Ugo, G. La Monica, J. Chem. Soc. A, 1971, 409.

115) G.W. Gorkel, R.P. Widera, W.P. Weber, Org. Synth., 1976, 55, 96.

116) G. Mannich, Chem. Ber., 1920, 1874.

117) L. Carlton, G. Read, J. Mol. Catal., 1981, 10, 133.

118) M.J. Bennett, P.B. Donaldson, J. Am. Chem. Soc., 1971, 93, 3307.

119) H. van Gaal, H.G.A.M. Cuppers, A. van der Ent, J. Chem. Soc. Chem. Commun., 1970, 1694.

120) A. van der Ent, T.C. van Soest, J. Chem. Soc. Chem. Commun., 1970, 225.

121) H. Hoffman, Chem. Ber., 1962, 95, 2563.

122) J. Tsuji in 'Organic Synthesis via Metal Carbonyls', I. Wendor and P. Pino, eds., Wiley 1977, Vol II, p.595.

123) J. Farrar, D. Holland, D.J. Milner, J. Chem. Soc. Dalton Trans., 1975, 815.

124) J. Ashley-Smith, J. Donek, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans., 1972, 1776.

125) M. Green, T.A. Kuc, J. Chem. Soc. Dalton Trans., 1972, 832.

126) R.E. Davis, R. Pettit, J. Am. Chem. Soc., 1970, 92, 716.

127) A. van der Ent, A.L. Onderdelinden, Inorg. Chim. Acta, 1973, 7, 203.

128) L. Vaska, L.S. Chen, J. Chem. Soc., Chem. Commun., 1971, 1080.

129) A.J. Deeming in 'M.T.P. International reviews of Science. Reaction Mechanisms in Inorganic Chemistry', Inorganic Series One, Vol 9, Butterworths, London 1972, pp. 144 and 148.

130) W.J. Louw, T.I.A. Gerber, D.J. de Waal, J. Chem. Soc., Chem. Commun., 1980, 760.

131) B.R. James, M. Preece, S.D. Robinson, A paper presented at a meeting of the American Chemical Society, "Catalytic Aspects of Metal Phosphine Complexes', Guelph, Ontario, June 5-7, 1980.

132) For a review of the fluxional behaviour of π-complexes see J.W. Faller, Adv. Organomet. Chem., 1977, 16, 211.

133) K. Moseley, J.W. Kang, P.M. Maitlis, J. Chem. Soc. A, 1970, 2875.

134) J.L. Herdé, C.V. Senoff, Inorg. Nuc. Chem. Lett., 1971, 7, 1029.

135) R.H. Crabtree, J.M. Mihelcic, J.M. Quirck, J. Am. Chem. Soc., 1979, 101, 7738.

136) L.M. Haines, E. Singleton, J. Chem. Soc. Dalton Trans., 1972, 1891.

137) T.D. McLean, Part II Thesis, Oxford 1981.

138) G.W. Parshall, Inorg. Synth., , XV, 18.

139) V.P. Kurkov, J.Z. Pasky, J.B. Lavigne, J. Am. Chem. Soc., 1968, 90, 4743.

140) J.E. Baldwin, J.C. Swallow, Angew. Chem. Int. Ed., 1969, 8, 601.

141) J.E. Lyons, J.O. Turner, Tetrahedron Lett., 1972, 2903.

142) F. Basolo, R.G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd ed., Wiley, 1967, p.407.

143) A.G. Kent, D.Phil. thesis, Oxford 1981.

144) P.D. Bartlett, Chem. Soc. Rev., 1976, 5, 149.

145) M. Green, R.B.L. Osborn, A.J. Rest, F.G.A. Stone, J. Chem. Soc. Chem. Commun., 1966, 502.

Biographical Note

Robert Alun John was born in Cornelly, Wales, in 1956. He underwent secondary education at Ysgol Cynffig, Kenfig Hill. After spending one year at I.C.I. Pharmaceuticals Division, Alderley Edge, he moved to the University of Bristol where, in 1978, he obtained the degree of Bachelor of Science in the Honours School of Chemistry. The same year he accepted an SRC CASE award jointly with Roche Products and Wolfson College, Oxford, and from January 1982 takes up a Research Associateship with Professor E. Negishi at Purdue University, Indiana.

APPENDIX

SCHEME C program

```
240 CLEAR
310 DISP "INITIAL VALUES OF A A
    T B"
    INPUT A0,B0

    PRINT "A0=";A0;"B0=";B0
    DISP "RATE CONSTANTS IN UNIT
    S OF SEC-1"
350 INPUT K1,K2
360 PRINT "K1=";K1;"K2=";K2
370 DISP "TOTAL TIME IN SECS"
380 INPUT T
390 PRINT "TOTAL TIME=";T
400 DISP "NO OF INCREMENTS"
410 INPUT N
420 PRINT "NO.OF INCREMENTS=",N
440 GCLEAR
450 PENUP
460 SCALE -T/20,T+T/20,0,100
470 XAXIS 0,T/10,0,T
480 YAXIS 0,10,0,100
490 PENUP
500 MOVE 0,0
510 A=A0
511 B=B0
512 C=.0001
513 D=.0001
514 E=.0001
515 F=.0001
520 FOR X=2.5 TO N STEP 2.5
530 A=A-K1*A*B+K2*C*D-K2*A*B
532 B=B-K1*A*B+K1*C*D+K2*C*D-K2*
    A*B
534 C=C-K1*C*D+K2*A*B-K2*C*D
536 D=D-K1*C*D+K1*A*B+K2*A*B-K2*
    C*D
538 E=E+K1*C*D
540 F=F+K1*A*B
544 A1=A
546 B1=B
548 C1=C
550 D1=D
551 B1=B
552 E1=E
554 F1=F
558 A1=A1-K1*A1*B1+K2*C1*D1-K2*A
    1*B1
560 B1=B1-K1*A1*B1+K1*C1*D1+K2*C
    1*D1-K2*A1*B1
562 C1=C1-K1*C1*D1+K2*A1*B1-K2*C
    1*D1
564 D1=D1-K1*C1*D1+K1*A1*B1+K2*A
    1*B1-K2*C1*D1
566 E1=E1+K1*C1*D1
568 F1=F1+K1*A1*B1
572 A2=A1
574 B2=B1
576 C2=C1
578 D2=D1
580 E2=E1
581 B2=B1
586 A2=A2-K1*A2*B2+K2*C2*D2-K2*A
    2*B2
588 B2=B2-K1*A2*B2+K1*C2*D2+K2*C
    2*D2-K2*A2*B2
```

```
590 C2=C2-K1*C2*D2+K2*A2*B2-K2*C
    2*D2
592 D2=D2-K1*C2*D2+K1*A2*B2+K2*A
    2*B2-K2*C2*D2
594 E2=E2+K1*C2*D2
596 F2=F2+K1*A2*B2
600 A3=A2
602 B3=B2
604 C3=C2
606 D3=D2
608 E3=E2
610 F3=F2
614 A3=A3-K1*A3*B3+K2*C3*D3-K2*A
    3*B3
616 B3=B2-K1*A3*B3+K1*C3*D3+K2*C
    3*D3-K2*A3*B3
618 C3=C3-K1*C3*D3+K2*A3*B3-K2*C
    3*D3
620 D3=D3-K1*C3*D3+K1*A3*B3+K2*A
    3*B3-K2*C3*D3
622 E3=E3+K1*C3*D3
624 F3=F3+K1*A3*B3
627 A=(A+2*A1+2*A2+A3)/6
628 B=(B+2*B1+2*B2+B3)/6
630 C=(C+2*C1+2*C2+C3)/6
632 D=(D+2*D1+2*D2+D3)/6
634 E=(E+2*E1+2*E2+E3)/6
636 F=(F+2*F1+2*F2+F3)/6
660 DRAW X/N*T,100*A/(A+C)
670 NEXT X
790 YAXIS 0,10,0,100
800 PENUP
810 MOVE 0,0
820 A=A0
830 B=B0
840 C=.0001
850 D=.0001
860 E=.0001
870 F=.0001
890 FOR X=2.5 TO N STEP 2.5
900 A=A-K1*A*B+K2*C*D-K2*A*B
910 B=B-K1*A*B+K1*C*D+K2*C*D-K2*
    A*B
920 C=C-K1*C*D+K2*A*B-K2*C*D
930 D=D-K1*C*D+K1*A*B+K2*A*B-K2*
    C*D
940 E=E+K1*C*D
950 F=F+K1*A*B
970 A1=A
980 B1=B
990 C1=C
1000 D1=D
1010 E1=E
1020 F1=F
1040 A1=A1-K1*A1*B1+K2*C1*D1-K2*
     A1*B1
1050 B1=B1-K1*A1*B1+K1*C1*D1+K2*
     C1*D1-K2*A1*B1
1060 C1=C1-K1*C1*D1+K2*A1*B1-K2*
     C1*D1
```

```
1070 D1=D1-K1*C1*D1+K1*A1*B1+K2*
     A1*B1-K2*C1*D1
1080 E1=E1+K1*C1*D1
1090 F1=F1+K1*A1*B1
1110 A2=A1
1120 B2=B1
1130 D2=D1
1140 E2=E1
1150 C2=C1
1160 F2=F1
1180 A2=A2-K1*A2*B2+K2*C2*D2-K2*
     A2*B2
1190 B2=B2-K1*A2*B2+K1*C2*D2+K2*
     C2*D2-K2*A2*B2
1200 C2=C2-K1*C2*D2+K2*A2*B2-K2*
     C2*D2
1210 D2=D2-K1*C2*D2+K1*A2*B2+K2*
     A2*B2-K2*C2*D2
1220 E2=E2+K1*C2*D2
1230 F2=F2+K1*A2*B2
1250 A3=A2
1260 B3=B2
1270 C3=C2
1280 D3=D2
1290 E3=E2
1300 F3=F2
1310 B3=B2
1330 A3=A3-K1*A3*B3+K2*C3*D3-K2*
     A3*B3
1340 B3=B3-K1*A3*B3+K1*C3*D3+K2*
     C3*D3-K2*A3*B3
1350 C3=C3-K1*C3*D3+K2*A3*B3-K2*
     C3*D3
1360 D3=D3-K1*C3*D3+K1*A3*B3+K2*
     A3*B3-K2*C3*D3
1370 E3=E3+K1*C3*D3
1380 F3=F3+K1*A3*B3
1400 A=(A+2*A1+2*A2+A3)/6
1410 B=(B+2*B1+2*B2+B3)/6
1420 C=(C+2*C1+2*C2+C3)/6
1430 D=(D+2*D1+2*D2+D3)/6
1440 E=(E+2*E1+2*E2+E3)/6
1450 F=(F+2*F1+2*F2+F3)/6
1460 DRAW X/N*T,100*F/(E+F)
1470 NEXT X
2000 YAXIS 0,10,0,100
2010 PENUP
2020 MOVE 0,0
2030 A=A0
2040 B=B0
2050 C=.0001
2060 D=.0001
2070 E=.0001
2080 F=.0001
2100 FOR X=2.5 TO N STEP 2.5
2110 A=A-K1*A*B+K2*C*D-K2*A*B
2120 B=B-K1*A*B+K1*C*D+K2*C*D-K2
     *A*B
2130 C=C-K1*C*D+K2*A*B-K2*C*D
2140 D=D-K1*C*D+K1*A*B+K2*A*B-K2
     *C*D
```

```
2150 E=E+K1*C*D
2160 F=F+K1*A*B
2180 A1=A
2190 B1=B
2200 C1=C
2210 D1=D
2220 E1=E
2230 F1=F
2250 A1=A1-K1*A1*B1+K2*C1*D1-K2*
     A1*B1
2260 B1=B1-K1*A1*B1+K1*C1*D1+K2*
     C1*D1-K2*A1*B1
2270 C1=C1-K1*C1*D1+K2*A1*B1-K2*
     C1*D1
2280 D1=D1-K1*C1*D1+K1*A1*B1+K2*
     A1*B1-K2*C1*D1
2290 E1=E1+K1*C1*D1
2300 F1=F1+K1*A1*B1
2330 A2=A1
2340 B2=B1
2350 D2=D1
2360 E2=E1
2370 C2=C1
2380 F2=F1
2400 A2=A2-K1*A2*B2+K2*C2*D2-K2*
     A2*B2
2410 B2=B2-K1*A2*B2+K1*C2*D2+K2*
     C2*D2-K2*A2*B2
2420 C2=C2-K1*C2*D2+K2*A2*B2-K2*
     C2*D2
2430 D2=D2-K1*C2*D2+K1*A2*B2+K2*
     A2*B2-K2*C2*D2
2440 E2=E2+K1*C2*D2
2450 F2=F2+K1*A2*B2
2470 A3=A2
2480 B3=B2
2490 C3=C2
2500 D3=D2
2510 E3=E2
2520 F3=F2
2530 B3=B2
2550 A3=A3-K1*A3*B3+K2*C3*D3-K2*
     A3*B3
2560 B3=B3-K1*A3*B3+K1*C3*D3+K2*
     C3*D3-K2*A3*B3
2570 C3=C3-K1*C3*D3+K2*A3*B3-K2*
     C3*D3
2580 D3=D3-K1*C3*D3+K1*A3*B3+K2*
     A3*B3-K2*C3*D3
2590 E3=E3+K1*C3*D3
2600 F3=F3+K1*A3*B3
2620 A=(A+2*A1+2*A2+A3)/6
2630 B=(B+2*B1+2*B2+B3)/6
2640 C=(C+2*C1+2*C2+C3)/6
2650 D=(D+2*D1+2*D2+D3)/6
2660 E=(E+2*E1+2*E2+E3)/6
2670 F=(F+2*F1+2*F2+F3)/6
2680 DRAW X/N*T,100*(E+F)/(A+C+E
     +F)
2690 NEXT X



3700 COPY
3020 END
```

SCHEME B program

```
240 CLEAR
310 DISP "INITIAL VALUES OF A A
    D B"
320 INPUT A0,B0

330 PRINT "A0=";A0;"B0=";B0
340 DISP "RATE CONSTANTS IN UNIT
    S OF SEC-1"
350 INPUT K1,K2,K3
360 PRINT "K1=";K1;"K2=";K2;"K3=
    ";K3
370 DISP "TOTAL TIME IN SECS"
380 INPUT T
390 PRINT "TOTAL TIME=";T
400 DISP "NO OF INCREMENTS"
410 INPUT N
420 PRINT "NO OF INCREMENTS=";N
430 D1=T/N
440 GCLEAR
450 PENUP
460 SCALE -T/20,T+T/20,0,100
470 XAXIS 0,T/10,0,T
480 YAXIS 0,10,0,100
490 PENUP
500 MOVE 0,0
510 A=A0
511 B=B0
512 C=.0001
513 D=.0001
514 E=.0001
515 F=.0001
516 G=.0001
520 FOR X=2.5 TO N STEP 2.5
530 A=A+K1*A+K3*D*G
532 B=B+K1*C-K2*B*G+K1*C
534 C=C+K2*B*G-K1*C
536 D=D+K2*B*G+K1*A
538 E=E+K2*G*B
540 F=F+K2*G*D
542 G=G+K1*A+K1*C+K2*B*G+K3*G*D-K3*G*B-
    K2*G*D-K2*G*B
544 A1=A
546 B1=B
548 C1=C
550 D1=D
551 B1=B
552 E1=E
554 F1=F
556 G1=G
558 A1=A1-K1*A1+K3*D1*G1
560 B1=B1-K3*B1*G1-K2*B1*G1+K1*C
    1
562 C1=C1-K1*C1+K3*B1*G1
564 D1=D1-K3*D1*G1-K2*B1*G1+K1*A
    1
566 E1=E1+K2*G1*D1
568 F1=F1+K2*G1*B1
570 G1=G1+K1*A1+K1*C1-K3*G1*D1-K
    3*G1*B1-K2*G1*D1-K2*G1*B1
572 A2=A1
574 B2=B1
576 C2=C1
578 D2=D1
580 E2=E1
581 B2=B1
```

```
580  F2=F1
584  G2=G1
586  A2=A2-K1*A2+K3*D2*G2
588  B2=B2-K3*B2*G2-K2*B2*G2+K1*C
     2
590  C2=C2-K1*C2+K3*B2*G2
592  D2=D2-K3*D2*G2-K2*B2*G2+K1*A
     2
594  E2=E2+K2*G2*D2
596  F2=F2+K2*G2*B2
598  G2=G2+K1*A2+K1*C2-K3*G2*D2-K
     3*G2*B2-K2*G2*D2-K2*G2*B2
600  A3=A2
602  B3=B2
604  C3=C2
606  D3=D2
608  E3=E2
610  F3=F2
612  G3=G2
614  A3=A3-K1*A3+K3*D3*G3
616  B3=B3-K3*B3*G3-K2*B3*G3+K1*C
     3
618  C3=C3-K1*C3+K3*B3*G3
620  D3=D3-K3*D3*G3-K2*B3*G3+K1*A
     3
622  E3=E3+K2*G3*D3
624  F3=F3+K2*G3*B3
626  G3=G3+K1*A3+K1*C3-K3*G3*D3-K
     2*G3*B3-K2*G3*D3-K2*G3*B3
628  A=(A+2*A1+2*A2+A3)/6
630  B=(B+2*B1+2*B2+B3)/6
632  C=(C+2*C1+2*C2+C3)/6
634  D=(D+2*D1+2*D2+D3)/6
636  E=(E+2*E1+2*E2+E3)/6
636  G=(G+2*G1+2*G2+G3)/6
660  DRAW X/N*T,100*A/(A+C)
670  NEXT X
790  YAXIS 0,10,0,100
800  PENUP
810  MOVE 0,0
820  A=A0
830  B=B0
840  C=.0001
850  D= 0001
860  E=.0001
870  F=.0001
880  G=.0001
890  FOR X=2.5 TO N STEP 2.5
900  A=A-K1*A+K3*D*G
910  B=B-K3*B*G-K2*B*G+K1*C
920  C=C-K1*C+K3*B*G
930  D=D-K3*D*G-K2*B*G+K1*A
940  E=E+K2*G*D
950  F=F+K2*G*B
960  G=G+K1*A+K1*C-K3*G*D-K3*G*B-
     K2*G*D-K2*G*B
970  A1=A
980  B1=B
990  C1=C
1000 D1=D
```

```
1010 E1=E
1020 F1=F
1030 G1=G
1040 A1=A1-K1*A1+K3*D1*G1
1050 B1=B1-K3*B1*G1-K2*B1*G1+K1*
     C1
1060 C1=C1-K1*C1+K3*B1*G1
1070 D1=D1-K3*D1*G1-K2*B1*G1+K1*
     A1
1080 E1=E1+K2*G1*D1
1090 F1=F1+K2*G1*B1
1100 G1=G1+K1*A1+K1*C1-K3*G1*D1-
     K3*G1*B1-K2*G1*D1-K2*G1*B1
1110 A2=A1
1120 B2=B1
1130 D2=D1
1140 E2=E1
1150 C2=C1
1160 F2=F1
1170 G2=G1
1180 A2=A2-K1*A2+K3*D2*G2
1190 B2=B2-K3*B2*G2-K2*B2*G2+K1*
     C2
1200 C2=C2-K1*C2+K3*B2*G2
1210 D2=D2-K3*D2*G2-K2*B2*G2+K1*
     A2
1220 E2=E2+K2*G2*D2
1230 F2=F2+K2*G2*B2
1240 G2=G2+K1*A2+K1*C2-K3*G2*D2-
     K3*G2*B2-K2*G2*D2-K2*G2*B2
1250 A3=A2
1260 B3=B2
1270 C3=C2
1280 D3=D2
1290 E3=E2
1300 F3=F2
1310 B3=B2
1320 G3=G2
1330 A3=A3-K1*A3+K3*D3*G3
1340 B3=B3-K3*B3*G3-K2*B3*G3+K1*
     C3
1350 C3=C3-K1*C3+K3*B3*G3
1360 D3=D3-K3*D3*G3-K2*B3*G3+K1*
     A3
1370 E3=E3+K2*G3*D3
1380 F3=F3+K2*G3*B3
1390 G3=G3+K1*A3+K1*C3-K3*G3*D3-
     K3*G3*B3-K2*G3*D3-K2*G3*B3
1400 A=(A+2*A1+2*A2+A3)/6
1410 B=(B+2*B1+2*B2+B3)/6
1420 C=(C+2*C1+2*C2+C3)/6
1430 D=(D+2*D1+2*D2+D3)/6
1440 E=(E+2*E1+2*E2+E3)/6
1450 G=(G+2*G1+2*G2+G3)/6
1460 DRAW [illegible]*T,100*E/(E+F)
1470 NEXT X
2000 YAXIS 0,10,0,100
2010 PENUP
2020 MOVE 0,0
2030 A=A0
```

```
2040 B=80
2050 C=.0001
2060 D=.0001
2070 E=.0001
2080 F=.0001
2090 G=.0001
2100 FOR X=2.5 TO N STEP 2.5
2110 A=A-K1*A+K3*D*G
2120 B=B-K3*B*G-K2*B*G+K1*C
2130 C=C-K1*C+K3*B*G
2140 D=D-K3*D*G-K2*B*G+K1*A
2150 E=E+K2*G*D
2160 F=F+K2*G*B
2170 G=G+K1*A+K1*C-K3*G*D-K3*G*B
     -K2*G*D-K2*G*B
2180 A1=A
2190 B1=B
2200 C1=C
2210 D1=D
2220 E1=E
2230 F1=F
2240 G1=G
2250 A1=A1-K1*A1+K3*D1*G1
2260 B1=B1-K3*B1*G1-K2*B1*G1+K1*
     C1
2270 C1=C1-K1*C1+K3*B1*G1
2280 D1=D1-K3*D1*G1-K2*B1*G1+K1*
     A1
2290 E1=E1+K2*G1*D1
2300 F1=F1+K2*G1*B1
2320 G1=G1+K1*A1+K1*C1-K3*G1*D1-
     K3*G1*B1-K2*G1*D1-K2*G1*F1
2330 A2=A1
2340 B2=B1
2350 D2=D1
2360 E2=E1
2370 C2=C1
2380 F2=F1
2390 G2=G1
2400 A2=A2-K1*A2+K3*D2*G2
2410 B2=B2-K3*B2*G2-K2*B2*G2+K1*
     C2
2420 C2=C2-K1*C2+K3*B2*G2
2430 D2=D2-K3*D2*G2-K2*B2*G2+K1*
     A2
2440 E2=E2+K2*G2*D2
2450 F2=F2+K2*G2*B2
2460 G2=G2+K1*A2+K1*C2-K3*G2*D2-
     K3*G2*B2-K2*G2*D2-K2*G2*B2
2470 A3=A2
2480 B3=B2
2490 C3=C2
2500 D3=D2
2510 E3=E2
2520 F3=F2
2530 B3=B2
2540 G3=G2
2550 A3=A3-K1*A3+K3*D3*G3
2560 B3=B3-K3*B3*G3-K2*B3*G3+K1*
     C3
```

```
2570 C3=C3-K1*C3+K3*B3*G3
2580 D3=D3-K3*D3*G3-K2*B3*G3+K1*
     A3
2590 E3=E3+K2*G3*D3
2600 F3=F3+K2*G3*B3
2610 G3=G3+K1*A3+K1*C3-K3*G3*D3-
     K3*G3*B3-K2*G3*D3-K2*G3*B3
2620 A=(A+2*A1+2*A2+A3)/6
2630 B=(B+2*B1+2*B2+B3)/6
2640 C=(C+2*C1+2*C2+C3)/6
2650 D=(D+2*D1+2*D2+D3)/6
2660 E=(E+2*E1+2*E2+E3)/6
2670 G=(G+2*G1+2*G2+G3)/6
2680 DRAW X/N*T,100*(E+F)/(A+C+E
     +F)
2690 NEXT X
2700 COPY
4020 END
```