ASLIB ABSTRACT

Ligand Design and Mechanism in Hydroformylation

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D.Phil
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In this work the synthesis of new potentially *trans*-chelating biphosphine ligands is described and their value in rhodium catalysed hydroformylation evaluated. The reactions of biphosphine diolefin rhodium complexes with hydrogen in methanol, monitored by ^{1}H- and ^{31}P-NMR spectroscopy were used to determine *trans*-chelating ability. Complexes of 1,5-*bis*(diphenylphosphino)-3-oxapentane and 1,3-*bis*-(4-diphenylphosphinobenzyl)benzene formed rhodium dihydrides solely whereas the more flexible 1,7-*bis*(diphenylphosphino)-4-oxaheptane gave isomeric rhodium dihydrides and a solvate complex. The reaction of diolefin complexes with hydrogen and carbon monoxide in dichloromethane was also investigated. The 3-oxapentane ligand, readily synthesized from 3-oxapentane-1,5-diol, as its rhodium complex gave a *n*-/*iso* aldehyde ratio of 9:1 for 1-octene hydroformylation (100°, 80 psi, 1:1 hydrogen/carbon monoxide).

Secondly, reactive intermediates relevant to hydroformylation were identified using ^{13}C- and ^{2}H-labelling and ^{1}H, ^{13}C and ^{31}P-NMR spectroscopy. Hydridodicarbonyl*bis*(triphenylphosphine)rhodium(I), the probable catalytic cycle initiator, was conclusively shown to be the initial product of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) under hydroformylation conditions. The kinetics of interconversion of these latter two complexes were examined by saturation transfer ^{31}P-NMR. On reaction of the dicarbonyl complex with styrene no alkyl-rhodium complexes were observed, but an *iso*-acyl intermediate which isomerizes rapidly at ambient temperature was identified and a structure proposed. A similar *n*-acyl complex, from 1-octene, shows dynamic NMR behaviour explained in terms of triphenylphosphine isomerization at lower temperature and acyl-alkyl interconversion at high temperature.

Ligand Design and Mechanism in Hydroformylation

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

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Michaelmas Term 1981

To Catherine

The heights by great men reached and kept

Were not attained by sudden flight,

But they, while their companions slept,

Were toiling upward in the night.

Longfellow, 'The Ladder of Saint Augustine' (1858).

ACKNOWLEDGEMENTS

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C O N T E N T S

CHAPTER I - INTRODUCTION

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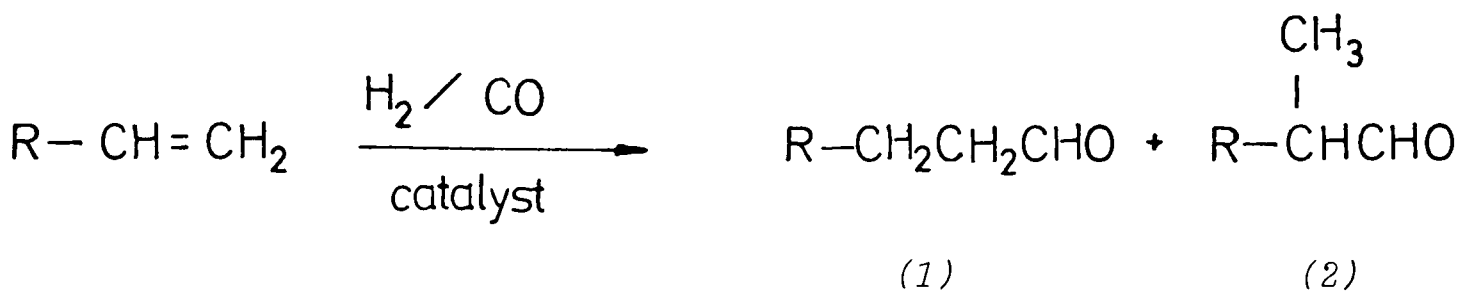
1. *General Introduction*

The term OXO reaction (or more correctly hydroformylation) is applied to the reaction of an olefin with carbon monoxide and hydrogen to produce aldehydic products and was discovered by Otto Roelen[1,2,3] working in Germany in 1938. The process requires a catalyst, Roelen's being heterogeneous and consisting mainly of cobalt on silica. Subsequent studies by Adkins *et.al.*[4] and Wender and co-workers[5] suggested the homogeneous nature of their cobalt catalysts and identified octacarbonyl-dicobalt as a potential precursor. This led to the development of various transition-metal hydroformylation catalysts whose industrial applications have been pursued to an extent such that *ca.* 4.5 million tonnes of aldehydes and their derivatives are produced annually.[6]

In principle two isomeric aldehydes (*1*) and (*2*) can be produced by hydroformylation of a terminal olefin and factors which determine commercial viability include the *n*-aldehyde to *iso*-aldehyde ratio in addition to operating conditions. The major use of the OXO process

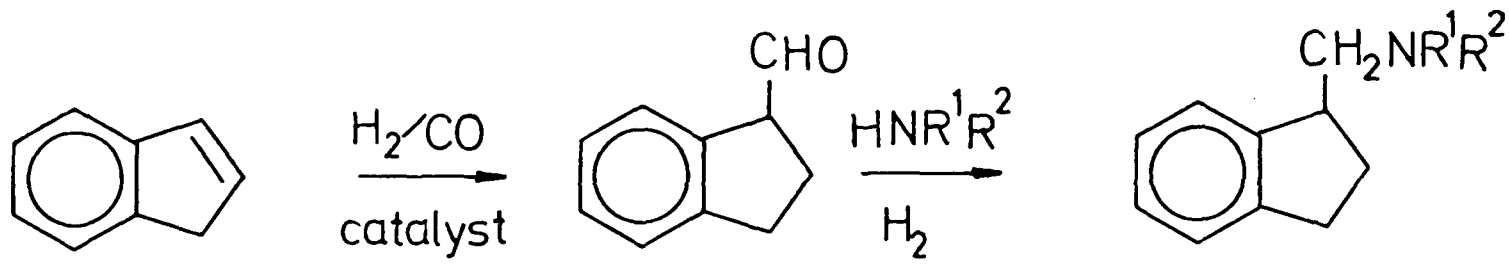


(1) *(2)*

is the conversion of propylene into *n*- and *i*-C_4 aldehydes, *n*-butanal being by far the most important product. Reduction (either under the operating conditions or *via* a separate stage) yields *n*-butanol, a useful

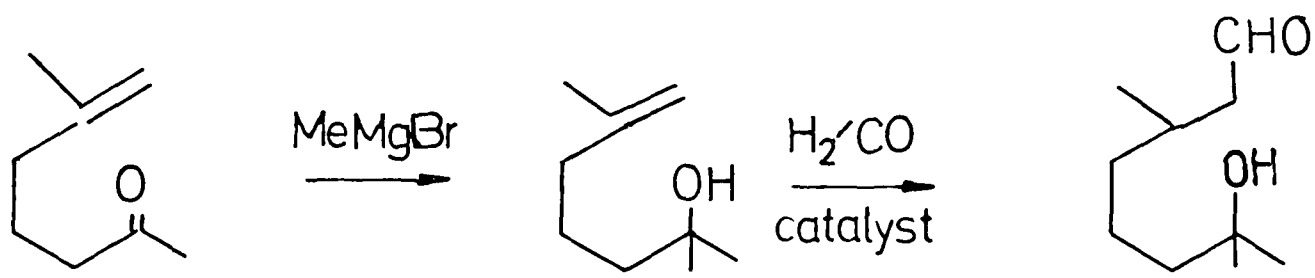
solvent, whereas an aldol-type condensation followed by reduction gives 2-ethylhexanol. This may be esterified with phthalic anhydride to give dioctylphthalate which is employed as a plasticizer. Hydroformylation of longer chain length olefins produces fatty acid precursors; the *n*-isomers of these are used in the preparation of biodegradable detergents and esters of adipic acid.

Applications of hydroformylation extend to organic synthesis; for example β-phenylethylamines *(3)*, which have interesting hypotensive properties, are accessible by hydroformylation of indene.[7]



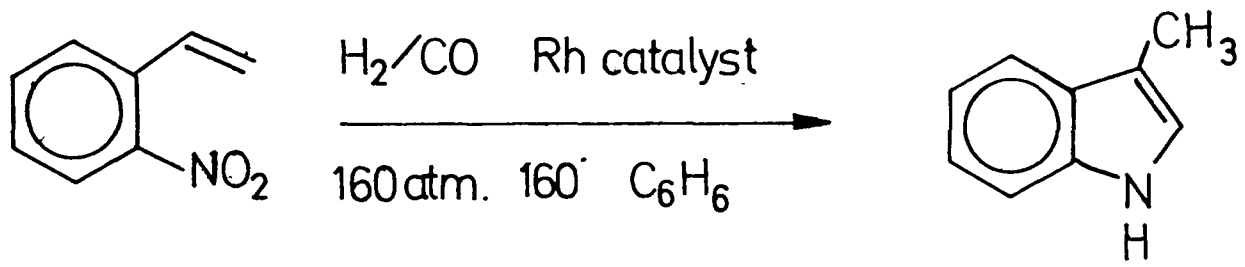
(3)

Furthermore hydroxycitronellal *(4)*, an important perfumery ingredient, can be prepared from 6-methyl-6-hepten-2-one *(5)* in two steps.[8] The



(5) *(4)*

synthesis of intermediates useful for vitamin and terpene chemistry has been reviewed by Himmele.[9] 3-Substituted indoles are biochemical intermediates which can be important in pharmacology and 3-methylindole *(6)* is obtained by hydroformylation of 2-nitrostyrene *(7)* in one step under the reaction conditions below:[10]



(7) *(6)*

The evident utility of hydroformylation has stimulated much investigation over the last twenty-five years and led to major improvements in the catalyst. Work by Schiller[11] in 1956 demonstrated that rhodium carbonyl catalysts were more active and required milder reaction conditions than their cobalt counterparts. A drawback of simple cobalt catalysts is their volatility and instability, whereas *tri*-*n*-butyphosphine-modified cobalt catalysts, developed by Slaugh and Mullineaux[12] at Shell in 1963 overcame these problems. The corresponding rhodium and ruthenium carbonyl phosphine complexes are also active and in all cases a significant improvement in the *n*- to *iso*-aldehyde ratio was achieved.[13] The most significant development to date is due to Wilkinson and co-workers who showed in a classic series of papers[14-18] that hydridocarbonyl*tris*(triphenyl-

phosphine)rhodium (I) was an active catalyst under very mild conditions, namely one atmosphere of hydrogen and carbon monoxide at 25° in benzene solution. Typical *n*-/*iso*-aldehyde ratios obtained were 3:1 whereas the unmodified process operating at much higher temperature and pressures produced comparable amounts of the two isomers.

One remarkable feature of hydroformylation is the variation in reactivity of catalysts derived from different metals, partially summarized below.

Metal	Rh	Co	Ru	Mn	Fe	Cr W Mo Ni
K_{rel}	10^3	1	10^{-2}	10^{-4}	10^{-6}	*ca.* 0

This contrasts with hydrogenation where iridium[19] and ruthenium[20] catalysts are at least comparable in reactivity with rhodium complexes. The only metal whose complexes might rival rhodium in reactivity and selectivity in hydroformylation is platinum, since *cis-bis*(triphenylphosphine) platinum dichloride in the presence of stannous chloride can effect hydroformylation of 1-hexene with similar selectivity and slightly reduced activity when compared to Wilkinson's catalyst.[21]

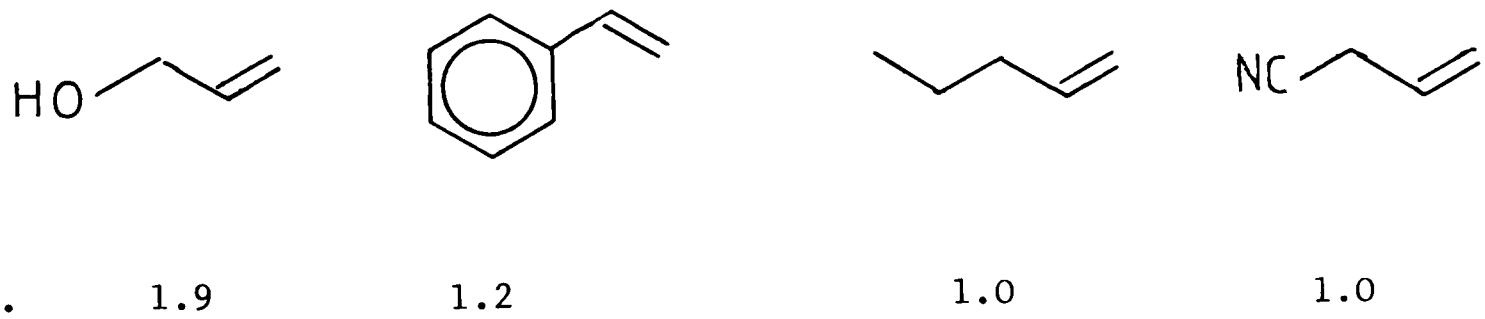
Despite intensive effort in the last ten years there has been little improvement on the catalyst introduced by Wilkinson. The detailed mechanism will be discussed in context later (page 22) but it is worthwhile to note the detailed characteristics of the reaction. When utilized industrially as in the synthesis of 2-ethylhexanol *via* hydroformylation of propene, the reaction is conducted under 15-25 atmospheres of a $>$ 1:1 mixture of hydrogen and carbon monoxide with a large excess of triphenyl-

phosphine. This is because the isomer ratio of *n*-butanol to 2-methylpropanal is critically dependent on reaction conditions in a manner which is not yet well understood. Attempts to vary the phosphine ligand have little positive effect; of a wide variety studied phenyl-dibenzophosphole has been identified[22] as being comparable in rate, whereas alkyl substitution at phosphorus leads to inferior catalysts. Other modifications have been investigated: Supported rhodium-phosphine catalysts, which combine the activity, selectivity and resistance to poisons of homogeneous catalysts with the ease of separation and recycling of heterogeneous ones, have been prepared and their performance evaluated.[23-25] Rhodium complexes of water-soluble phosphines have been examined as two-phase hydroformylation catalysts.[26,27] Replacement of phosphines by tertiary amines produces alcohols as major reaction products in certain circumstances.[28]

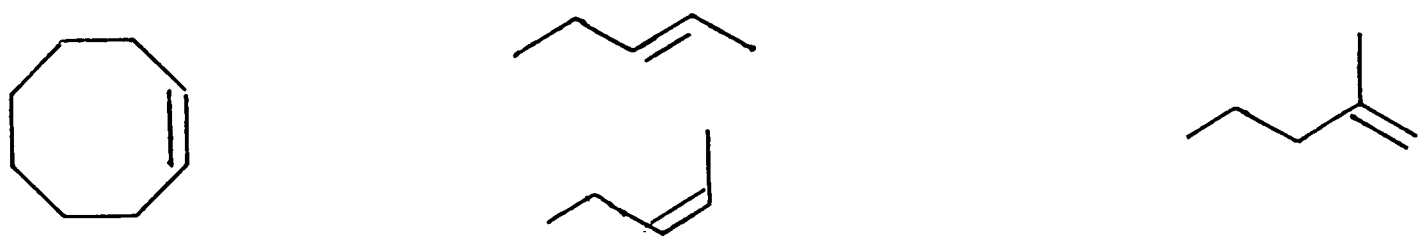
Rhodium catalysts show considerable selectivity toward different olefins[18] (Figure I.1.1). Terminal alkenes react readily and generally give a predominance of *n*-aldehyde. The exception is styrene where 2-phenylpropanal, the product of addition to the benzylic site is always dominant.

Internal olefins are almost thirty times less reactive and tri- or tetrasubstituted olefins less reactive still. The selectivity is much greater than in hydrogenation by rhodium (I) — phosphine complexes[29] suggesting contrasting coordination states in the two catalytic cycles.

The catalytic process is limited by substituents on the substrate. For example di-1,4-hydroformylation of butadiene produces 1,6-hexanedial potentially of use in the manufacture of adipic acid and 1,6-hexanediol; however Fell *et.al.*[30] have shown that *mono*hydroformylation is predominant,



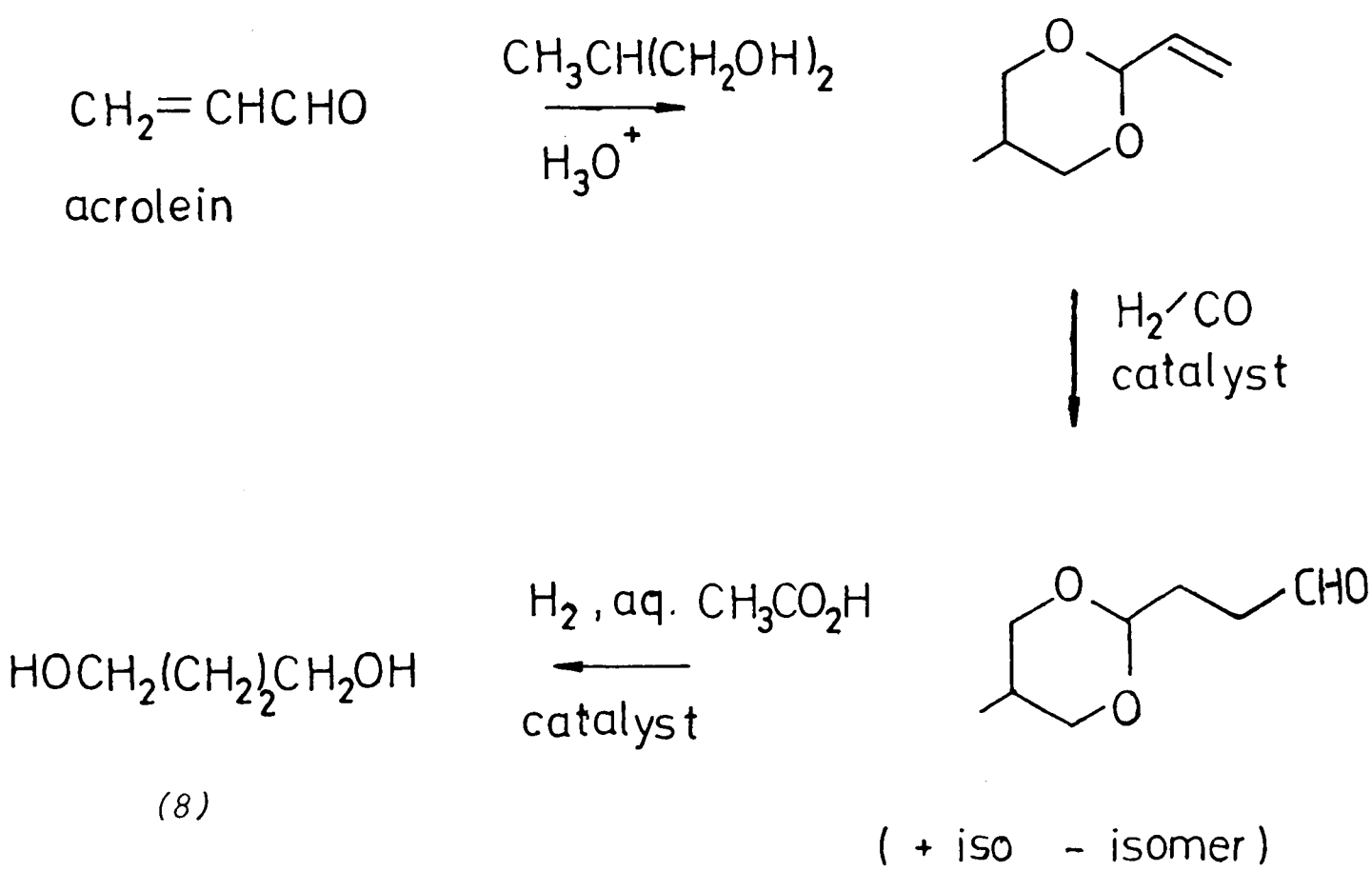
$K_{rel.}$ 1.9 1.2 1.0 1.0



$K_{rel.}$ 0.07 0.04 0.02

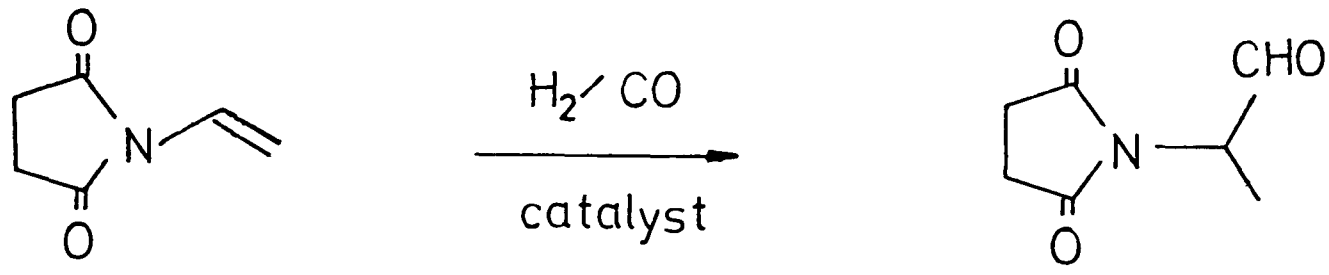
Figure I.1.1 Relative rates of hydroformylation for a range of olefinic substrates with $HRh(CO)(PPh_3)_3$ catalyst

possibly due to the intervention of π-allyl-rhodium complex intermediates. Similarly acrolein, a precursor of 1,4-butanediol *(8)* (a co-monomer employed in the production of the thermoplastic polybutylene terephthalate) must first be converted into its acetal before successful hydroformylation can be accomplished.[31]



Scheme I.1.1

Hydroformylation is compatible with some unsaturated esters, unsaturated ethers and unsaturated nitrogen compounds, for example *N*-vinylsuccinimide *(9)* produces α-(*N*-succinimido)propionaldehyde *(10)* in high yield.[32]

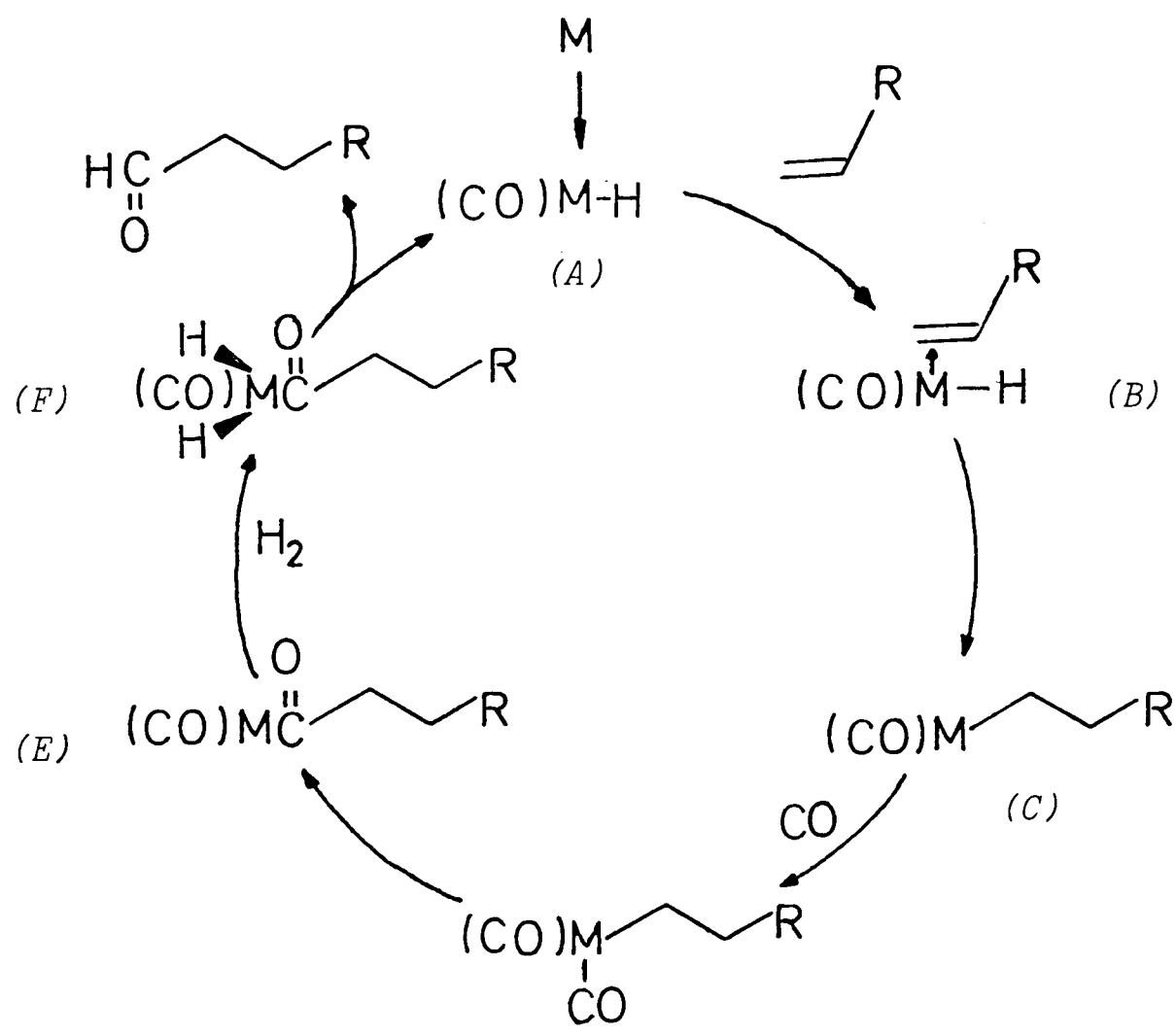


(9) *(10)*

Hydroformylation particularly cobalt and rhodium catalysed reactions has been the subject of some excellent reviews,[33-38] which describe variations in the catalyst, substrate and reaction conditions in detail.

2. *Hydroformylation in relation to Catalysis and Organotransition metal Chemistry*

The conversion of an olefin into an aldehyde requires several sequential steps following initial coordination of alkene. These may be represented as in Scheme I.2.1, and it is pertinent to discuss these in turn.



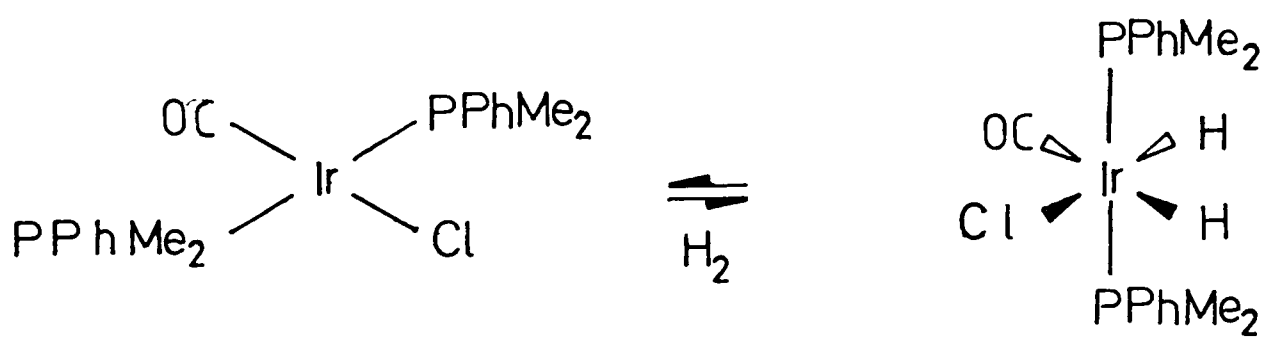
Scheme I.2.1

The detailed reaction pathway involves successive formation of coordinatively saturated and unsaturated intermediates and there are good precedents for each type of complex and their interconversion. The first part of the cycle bears close resemblance to that of homogenous hydrogenation, the difference being that the alkyl intermediate *(C)* is

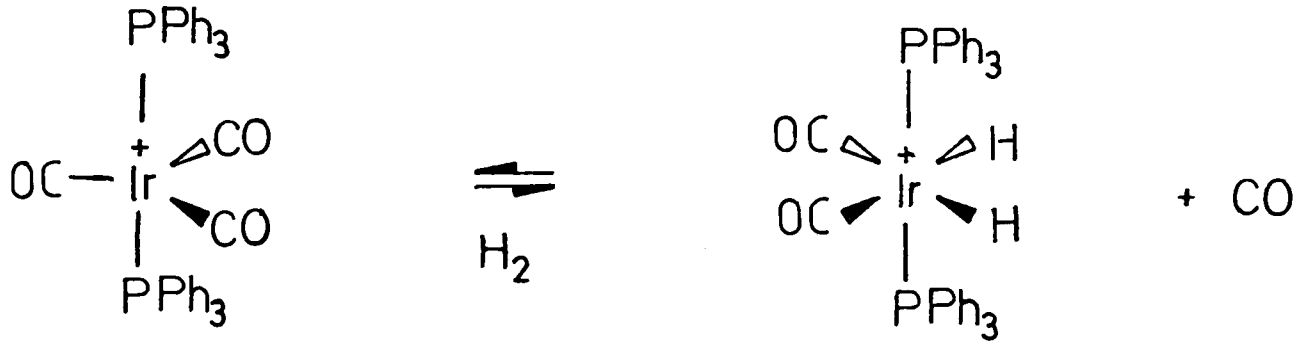
intercepted by carbon monoxide rather than hydride.

(a) Metal hydrides and metal carbonyl hydrides

Square-planar 16-electron phosphine complexes of rhodium and iridium readily add hydrogen in a step which may be reversible or irreversible. Studies of stable complexes have been more extensively carried out for the latter metal and examples due to Vaska and other workers[39,40] include the following:



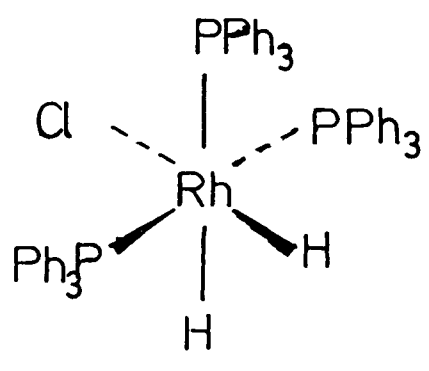
(11) *(12)*



(13) *(14)*

The first example is st specific since only one of the six possible diastereomeric products is f l and illustrates a general tendency to coordinate hydride *trans* to electron-withdrawing π-acidic ligands. The second example requires formal displacement of carbon monoxide by hydrogen and it is likely that this occurs with a prior dissociative step so that the reactive species is an 16-electron unsaturated complex.

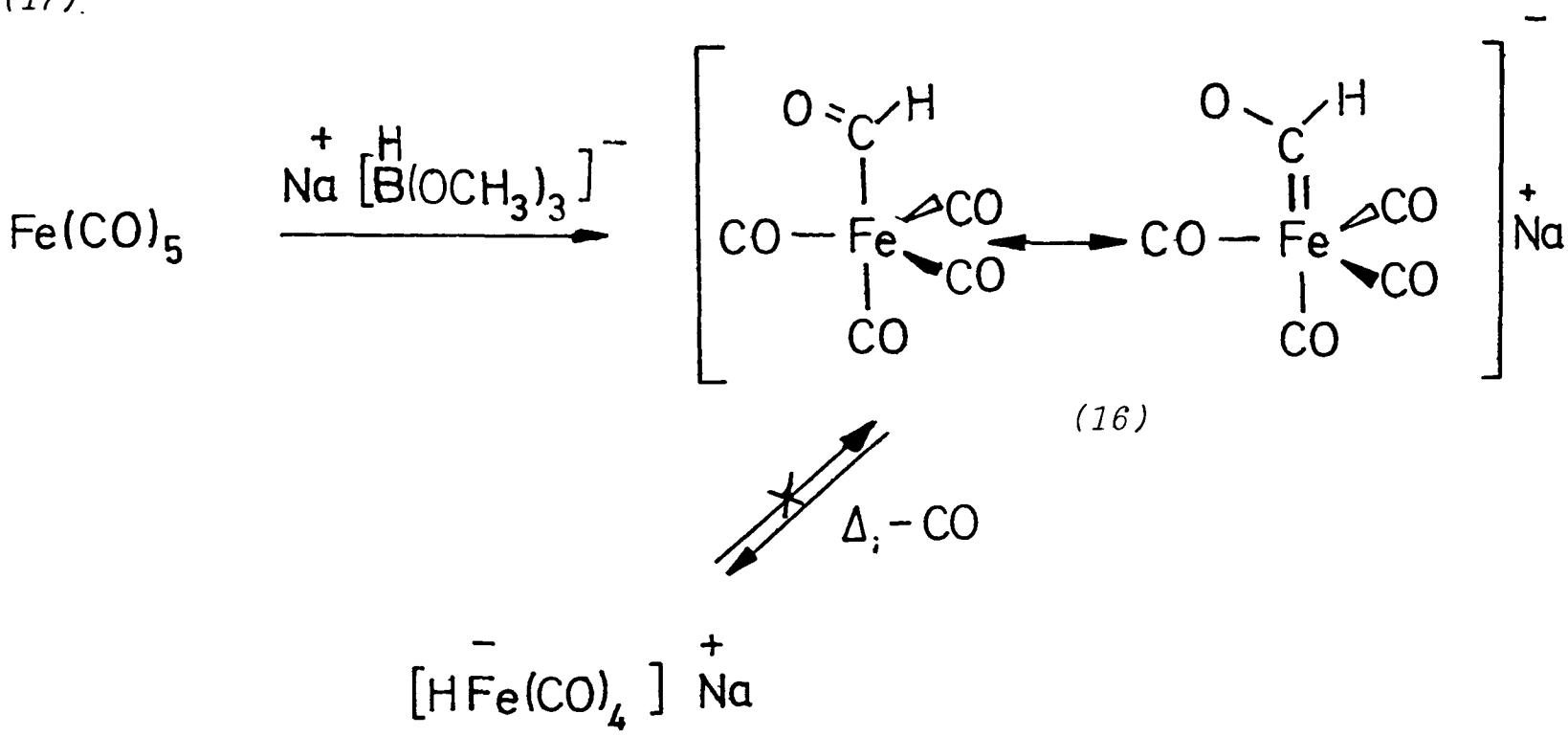
Homogeneous hydrogenation by *tris*-(triphenylphosphine)rhodium (I) chloride has been extensively studied.[29,41] Tolman[42] has prepared the dihydride derivative *(15)* of this complex by oxidative addition of hydrogen and shown that the equatorial triphenylphosphine ligand, labilised by the high *trans*-effect of the hydride, dissociates rapidly at -25^{o}. Subsequent trapping of this co-ordinatively unsaturated species by substrate, for example cyclohexene, is the next step on the reaction pathway. Characteristically monohydridorhodium complexes are involved in hydroformylation whereas both mono- and dihydridorhodium complexes can accomplish hydrogenation.



(15)

Hydroformylation entails metal carbonyls and reaction with hydrogen can produce a carbonyl metal-hydride. These have been widely investigated recently because of an interest in metal-formyls relevant to both hydroformylation and the carbonylation of hydrogen, usually referred to as the Fischer-Tropsch reaction. Other than in special cases the formyl appears to be less stable than the isomeric carbonyl hydride and recent evidence suggests a rapid migration between the two states.[43] Stable formyls are frequently made by the reduction of coordinated carbon monoxide and are characteristically coordinatively saturated with an electron-rich centre. Thus the iron formyl complex *(16)* may be prepared according to Scheme I.2.2 and is kinetically stabilized since the

product formed irreversibly by loss of carbon monoxide is the hydride *(17)*.[43]

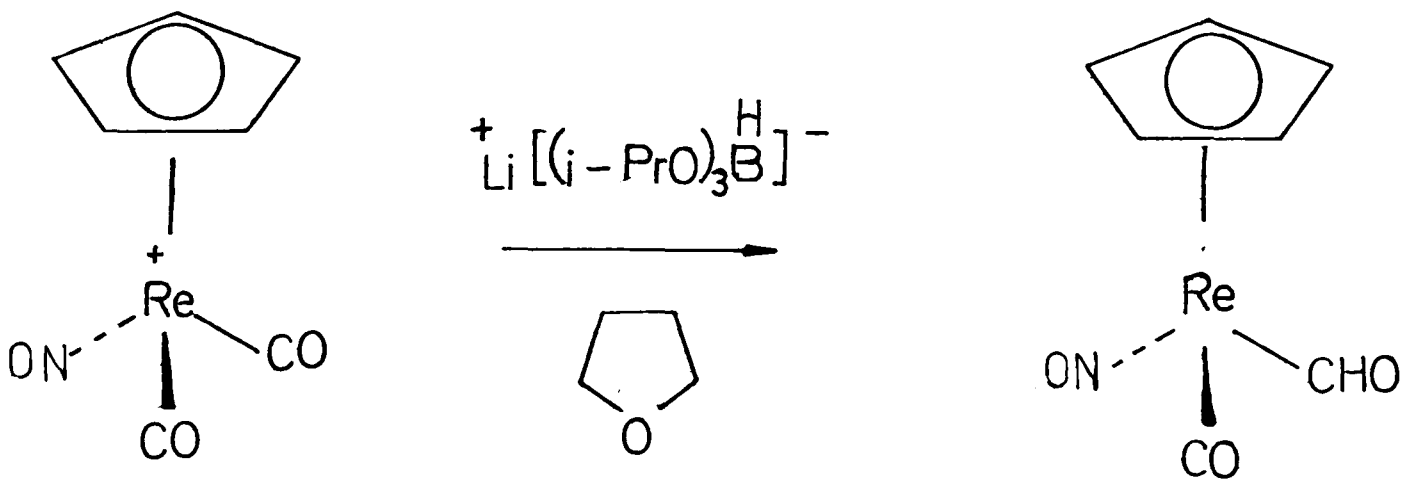


(16)

(17)

Scheme I.2.2

This stability is thought to be due to delocalization of charge on to the formyl-oxygen atom. Later work, also by Casey,[44] has shown that the neutral rhenium formyl complex *(18)* may be prepared by an analogous method.

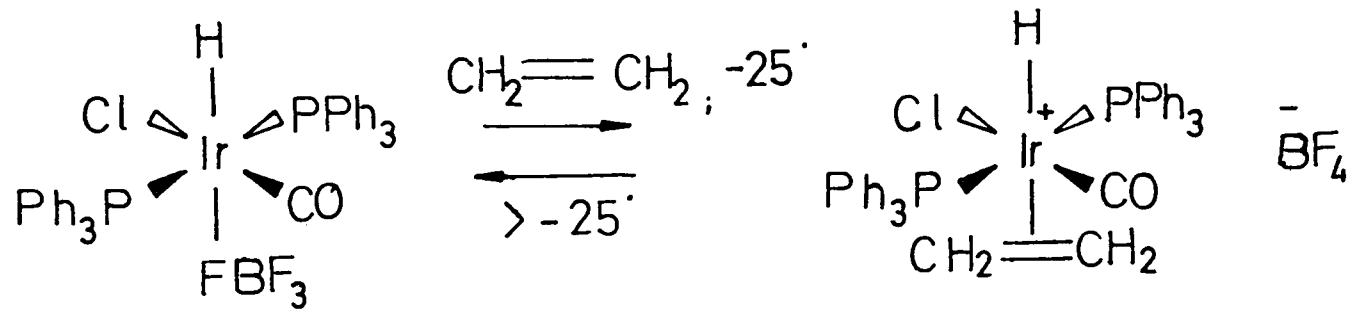


(18)

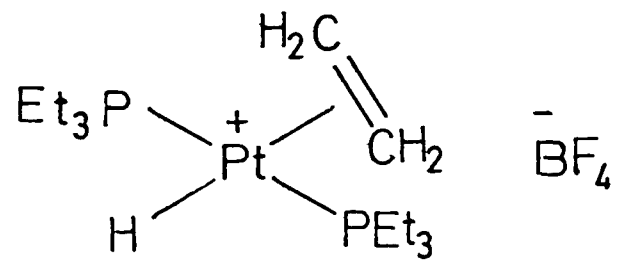
Such evidence as exists suggests that carbonylhydride rather than formyl-metal complexes are prevalent under hydroformylation conditions.

(b) Hydrido-olefin complexes and hydrogen migration to carbon

Stable complexes containing hydride and olefin ligands are relatively rare since intramolecular reaction to give metal-alkyl occurs readily. This pathway is stereochemically precluded in the *trans* complexes *(19)*[45] and *(20)*[46] since the mechanism of alkyl formation



(19)



(20)

involves transfer of hydrogen from the metal to the β-carbon atom in the developing alkyl with *cis* stereochemistry (Figure I.2.1).

Where the ligands are mutually *cis* then reversible isomerization may occur which may be studied by NMR[47,48] or isotopic labelling.[49]

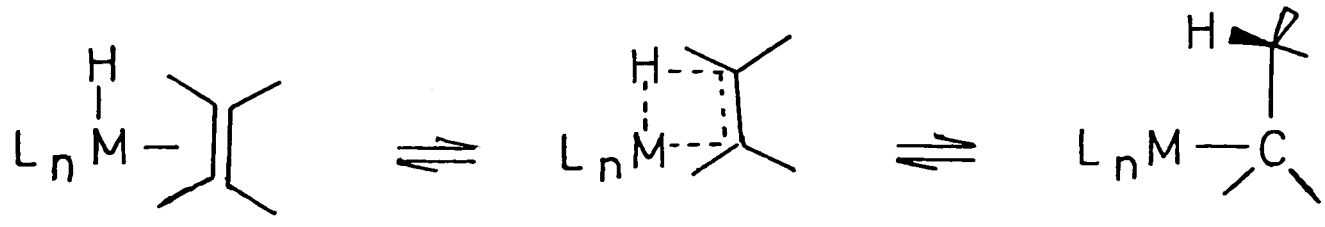
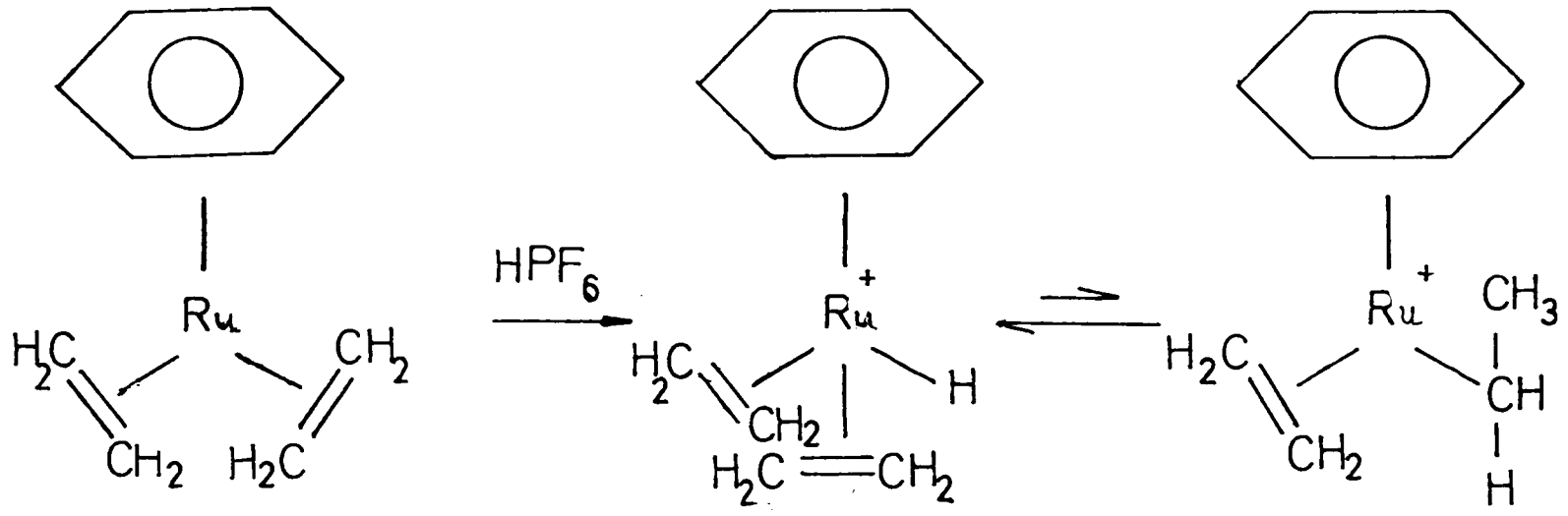


Figure I.2.1

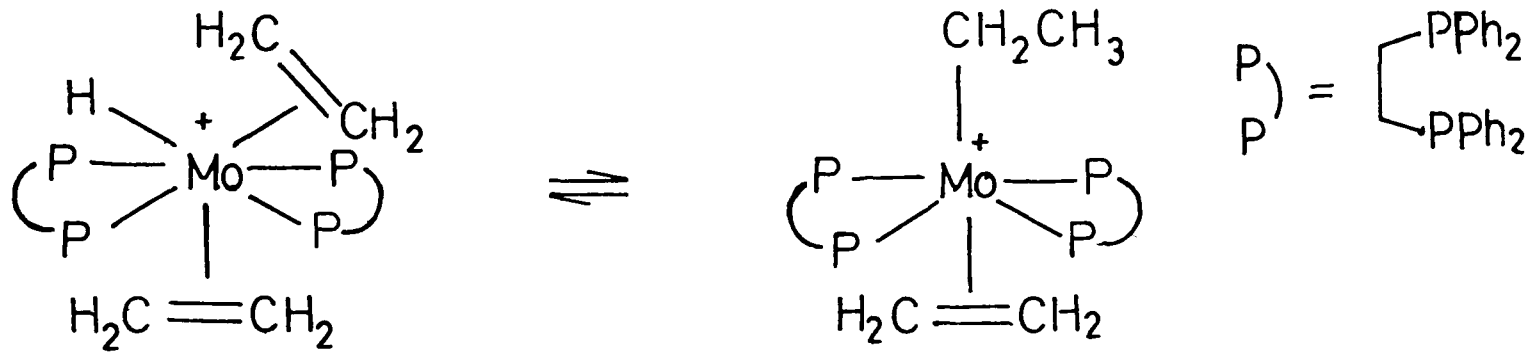
In the ruthenium complex *(21)* equilibration with the alkyl *(22)* is dynamic on the NMR timescale and leads to equivalency of olefinic and hydride protons.



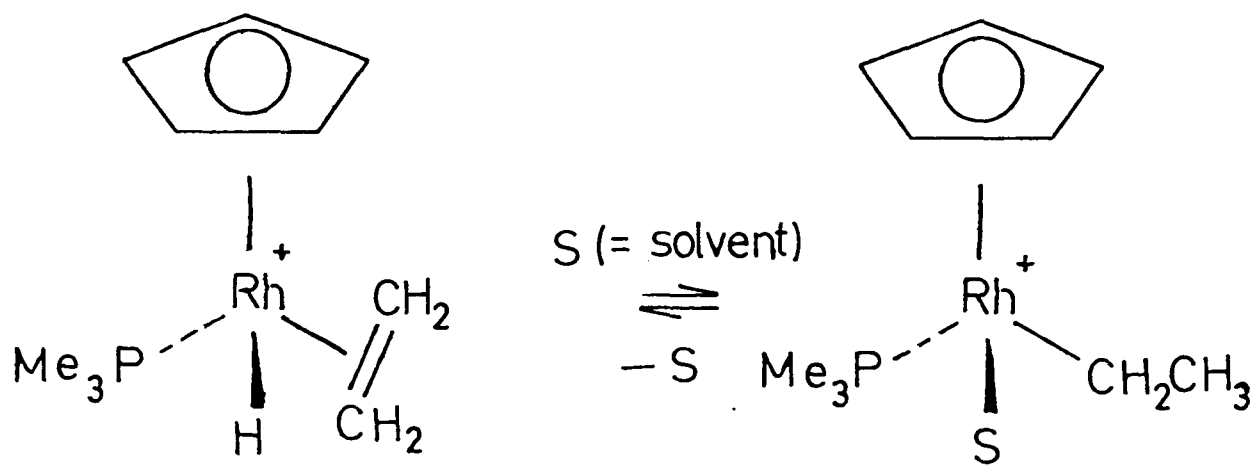
(21) *(22)*

The molybdenum *(23)* and *(24)* and rhodium complexes *(25)* and *(26)* behave similarly.[47,48]

All the hydrido-olefin complexes known are *mono*-hydridic since isomerization of a hypothetical olefinic dihydride gives a hydrido-alkyl. Compounds of this latter type tend to undergo reductive elimination



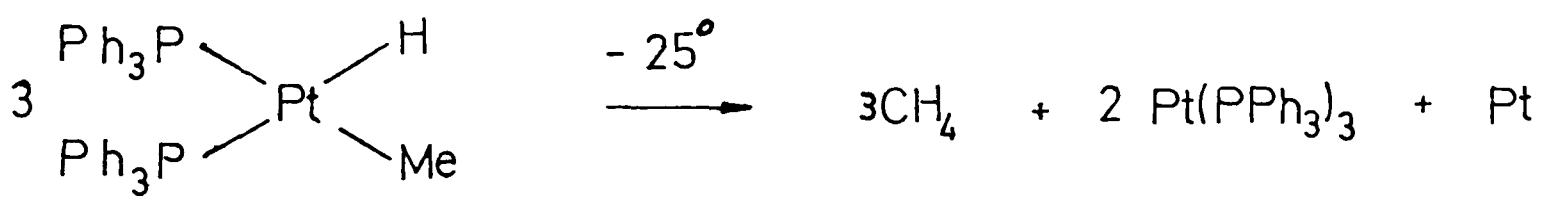
(23) *(24)*



(25) *(26)*

as in the case of *(27)* where methane is eliminated at -25^{o}.[50]

Norton and co-workers[51,52] have studied the decomposition of tetracarbonylhydridomethylosmium *(28)*; although *cis*-hydrido and alkyl ligands are present kinetic studies indicate that the elimination



(27)

proceeds *via* a binuclear pathway (Figure I.2.2). The reluctance to react by a unimolecular path is due to the instability of $Os(CO)_4$.

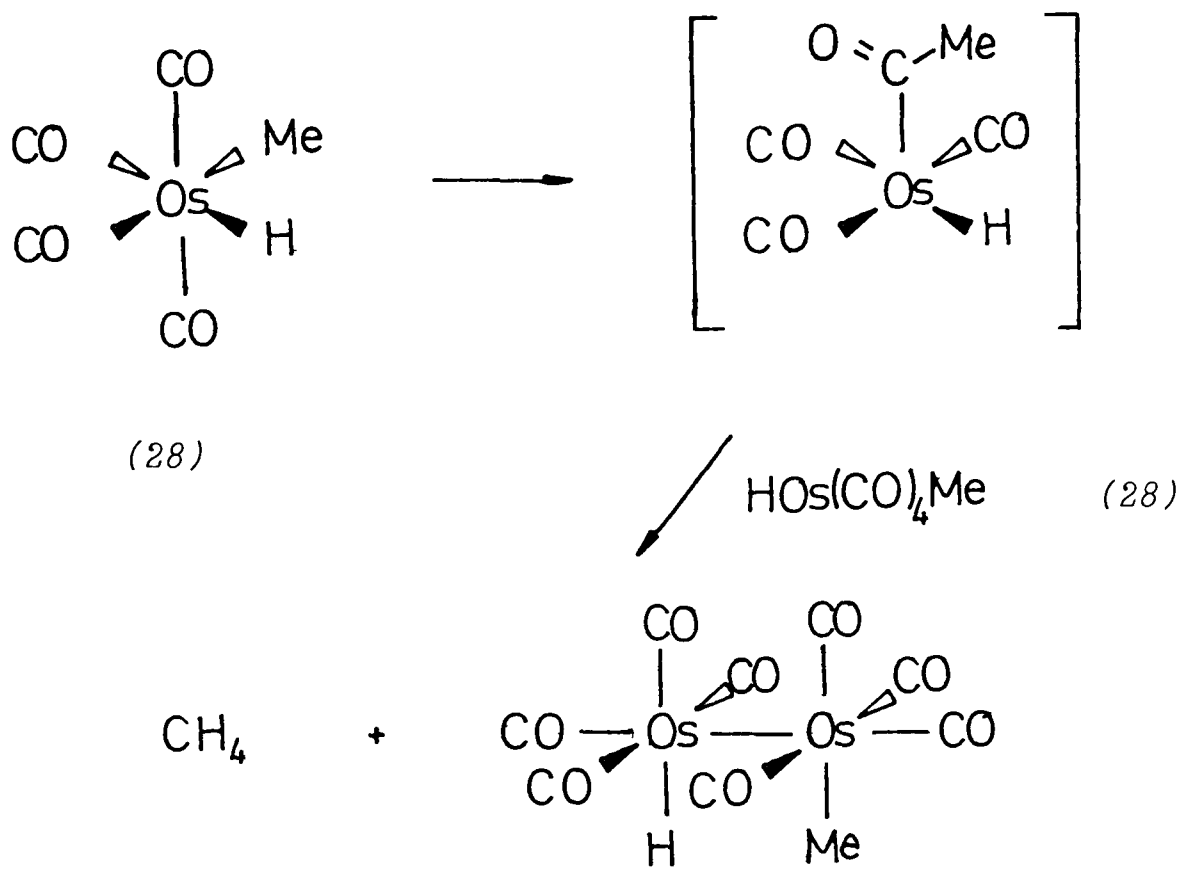
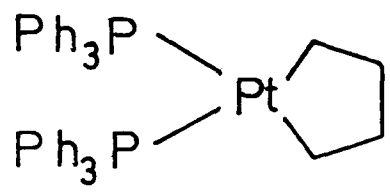


Figure I.2.2.

(c) Stability of metal-alkyls

The reactivity of olefin metal hydrides is mirrored by the lability of metal-alkyls. These may decompose by homolytic fragmentation[53] or more commonly by the reverse of hydride insertion, reverting to the olefin hydride (Figure I.2.1). This can then dissociate a hydride ligand. Most of the detailed mechanistic studies relate to platinum alkyls which are unusually stable and readily handled. It is found that dialkyl complexes are much more reactive than metallocycloalkanes, for example the thermal decomposition of 1,4-tetramethylene *bis*(diphenylphosphino)platinum (II) *(29)* is 10^4 times slower than the corresponding di-*n*-butyl compound *(30)*.[54]



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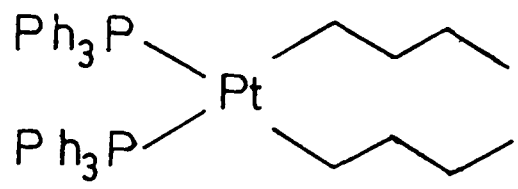
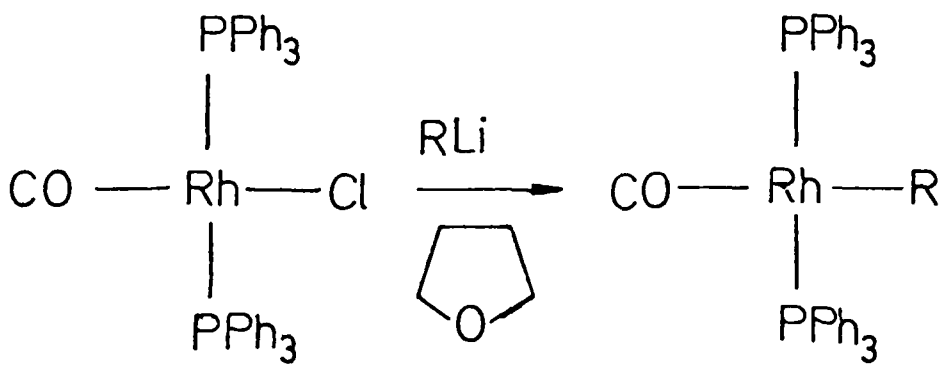


(30)

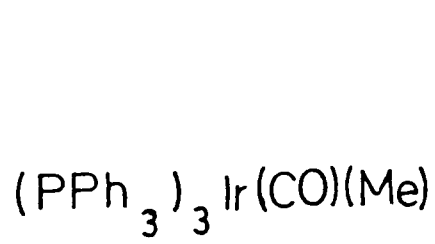
This illustrates the stereoelectronic requirement that the metal carbon and the β-C-H bond should be *syn* co-planar at the transition state.

Whilst iridium alkyls are relatively stable[55] analogous rhodium alkyls are not.[56] The reaction of alkyl-lithium compounds with *trans-bis*(triphenylphosphine)carbonylchlororhodium (I) *(31)* studied by Hegedus[56] produces species *(32)* closely related to hydroformylation intermediates. Here there is infra-red evidence for alkyl metal complex formation, although attempts at isolation are unsuccessful.



(31) *(32)*

ν_{CO} 1980 cm^{-1} 1962 cm^{-1}

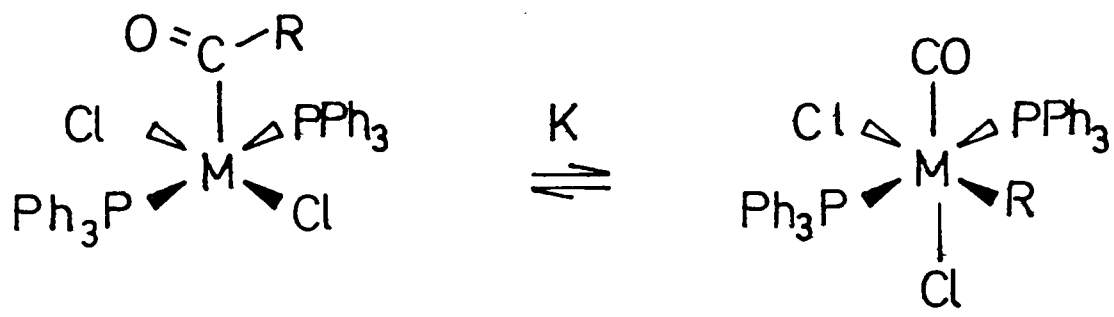


(33)

1945 cm^{-1}[55]

(d) Alkyl-metal carbonyls and metal acyls: the insertion step

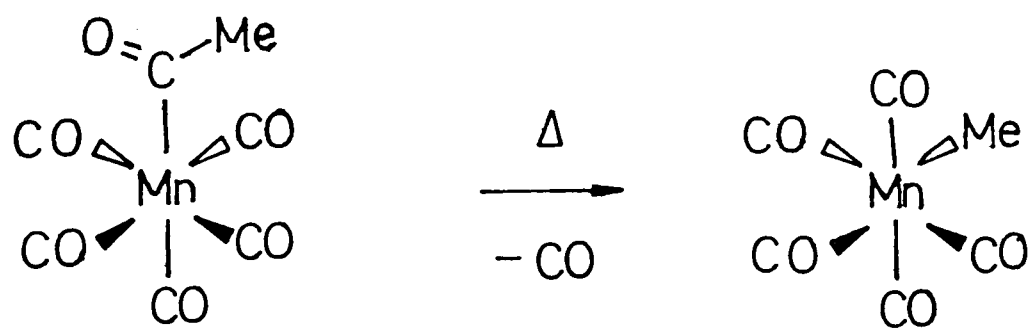
Metal alkyl complexes containing coordinated CO can undergo a rearrangement which formally results from insertion of CO into the metal-carbon bond. In some cases the two species are in an equlibrium whose position can vary with the metal and nature of the associated ligands. Slack *et.al.*[57] have examined the stability with respect to migration of a number of acyl complexes (Figure I.2.3). The equilibrium constants decrease in the order Ir > Rh and CF_3, Ph > Me, suggesting that the metal-alkyl bond strength is a major factor in the value of K.



M = Ir; Rh R = CF_3; Ph; Me

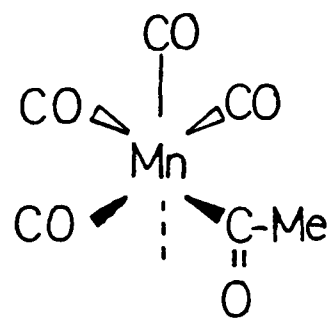
Figure I.2.3

More commonly the acyl complex is a stable, isolable species for example the manganese-acyl complex *(34)* which may undergo thermal rearrangement with concomitant loss of carbon monoxide.[58]



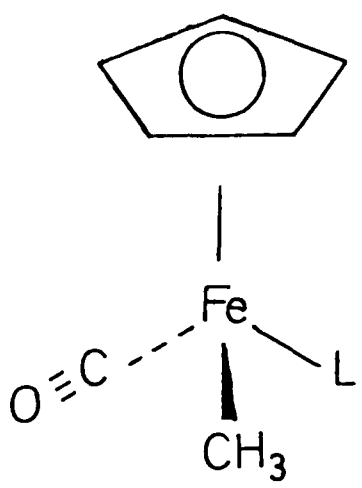
(34) *(35)*

Alkyl migration has been subjected to many mechanistic studies[59] so that the stereochemistry is well established. In normal cases the reaction involves migration of the alkyl groups to a static CO rather than the converse. This particular pathway has been identified for the insertion of carbon monoxide into methylpentacarbonylmanganese *(35)* by using a specifically mono-^{13}CO labelled complex. In addition the insertion step has been shown to require *cis*-coordination of the participating ligands,[58,60] and product distribution from labelling studies indicate it proceeds *via* a coordinatively unsaturated intermediate *(36)*.

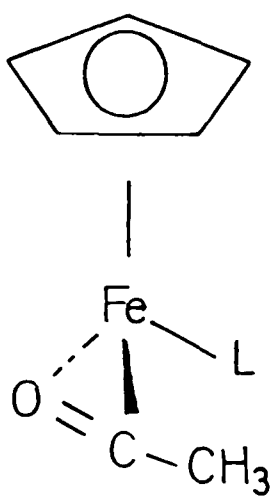


(36)

The possibility also exists of a coordinatively saturated dihaptoacyl complex intermediate rather than the monohapto structure favoured above. A recent example has shown that the optically pure cyclopentadienyl-methyl-iron complex *(37)* undergoes insertion to give the product *(38)* with high stereoselectivity; this is consistent with an η^2-acetyl intermediate *(39)*.[61]



(37)



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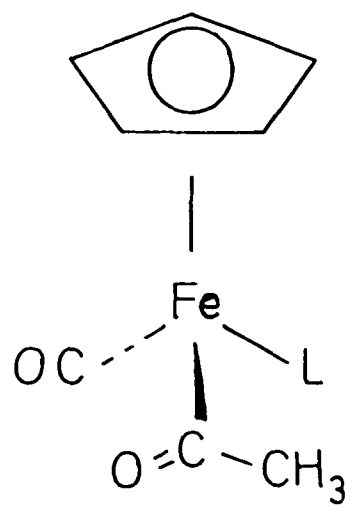
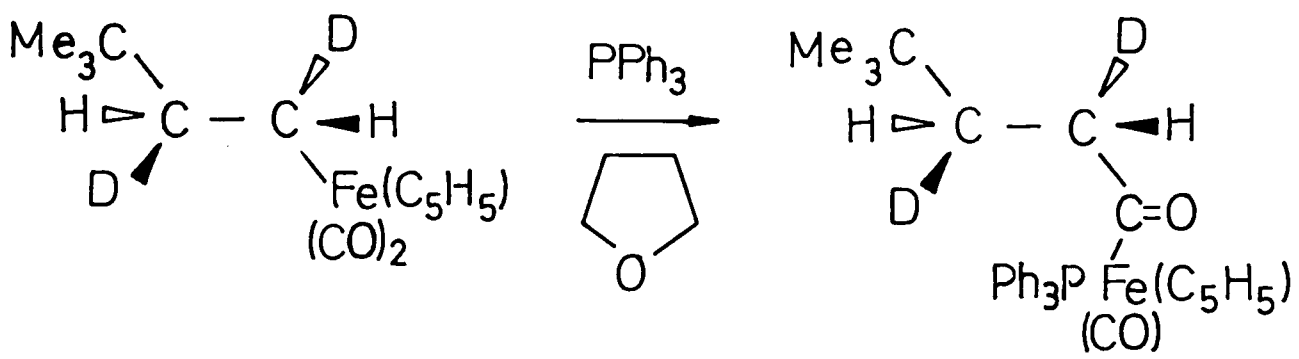


(38)

L = $Ph_2PN(CH_3)-(S)-CH(CH_3)Ph$

The stereochemistry at carbon in an alkyl to acyl migratory insertion has also been established. The evidence overwhelmingly favours retention of configuration at a migratory chiral centre, for example NMR studies have shown[62] that the *erythro*-alkyl-iron complex *(40)* affords the *erythro*-acyl complex *(41)*.

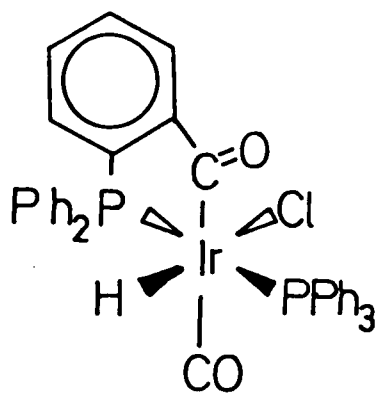


(40) *(41)*

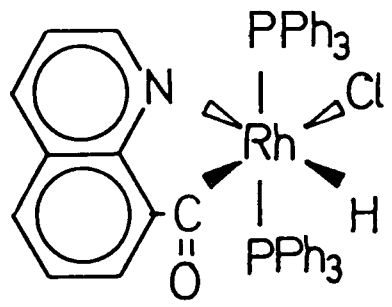
(e) Reductive elimination of acyl hydrides

There are very few examples of acyl-hydrido metal complexes, and the presumption is that they decompose rapidly with elimination of aldehyde. The reverse reaction is known in appropriate cases where a second coordination site is present in the substrate. Examples include the acyl hydride *(42)* prepared by the reaction of (2-formylphenyl)diphenyl phosphine with Vaska's complex[63], *trans-bis*(triphenylphosphine)carbonyl-chloroiridium (I) , and similarly the *cis*-acyl hydride *(43)* from 8-formyl-quinoline and *tris*(triphenylphosphine)rhodium (I) chloride.[64]

It is not clear whether hydrogen is the product-forming reducing agent in rhodium complex catalysed hydroformylation. In the cobalt complex catalysed reaction one possible aldehyde forming step that has been suggested[65] is the reaction of $HCo(CO)_4$ with $RCOCo(CO)_4$; this must

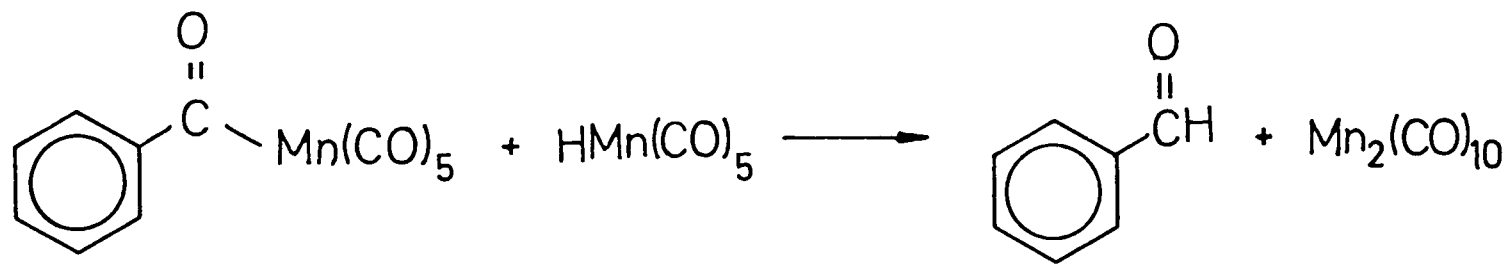


(42)



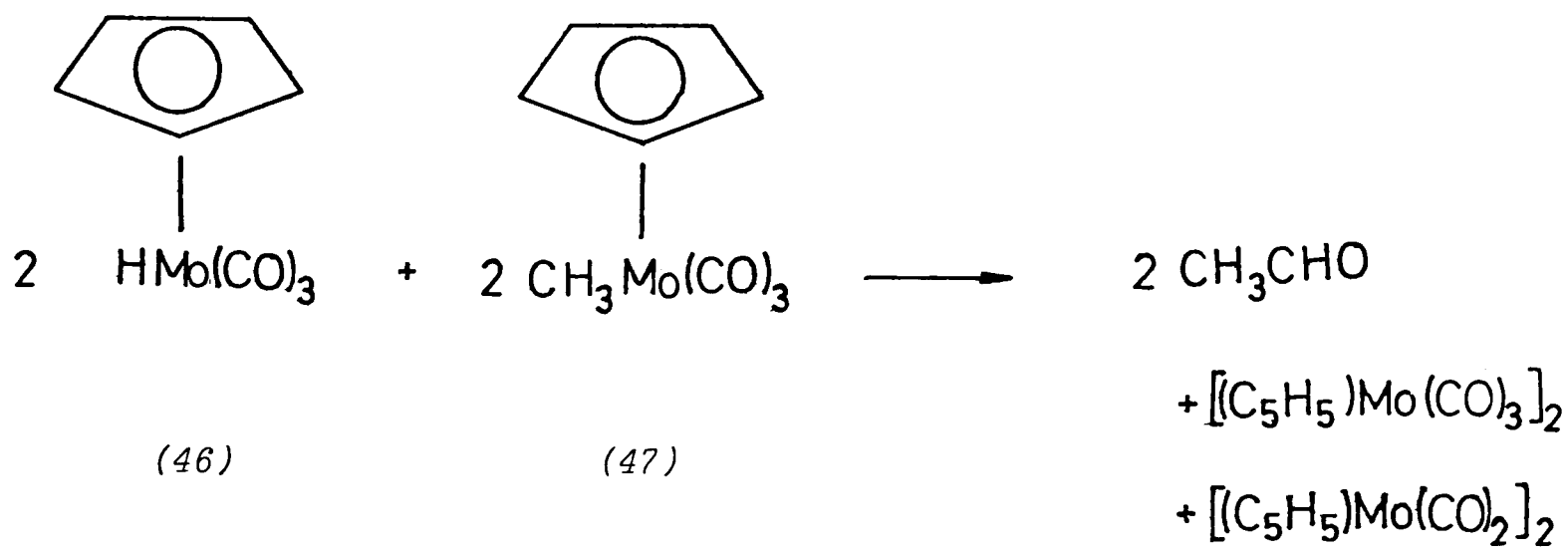
(43)

be the only pathway in the case of stoichiometric hydroformylation. Although similar evidence has yet to be presented for the rhodium catalysed reaction, there are several examples in analogous cases. Gladyz and co-workers[66] have shown that the benzoylmanganese carbonyl complex *(44)* reacts with hydridopentacarbonylmanganese *(45)* to produce benzaldehyde as the only organic product.



(44) *(45)*

Similar work by Bergman *et.al.*[67] has shown that the molybdenum hydride *(46)* and the molybdenum alkyl *(47)* yield acetaldehyde, but no methane, on reaction; kinetic studies are consistent with a mechanism



(46) *(47)*

involving initial isomerization of alkyl to acyl. This in turn is trapped by entry of the metal-hydride into the unsaturated acyl coordination sphere.

3. The mechanism of rhodium catalysed hydroformylation

It is instructive to consider the mechanism of hydroformylation in two sections, separating studies on phosphine-free catalysts from those on phosphine-containing catalysts.

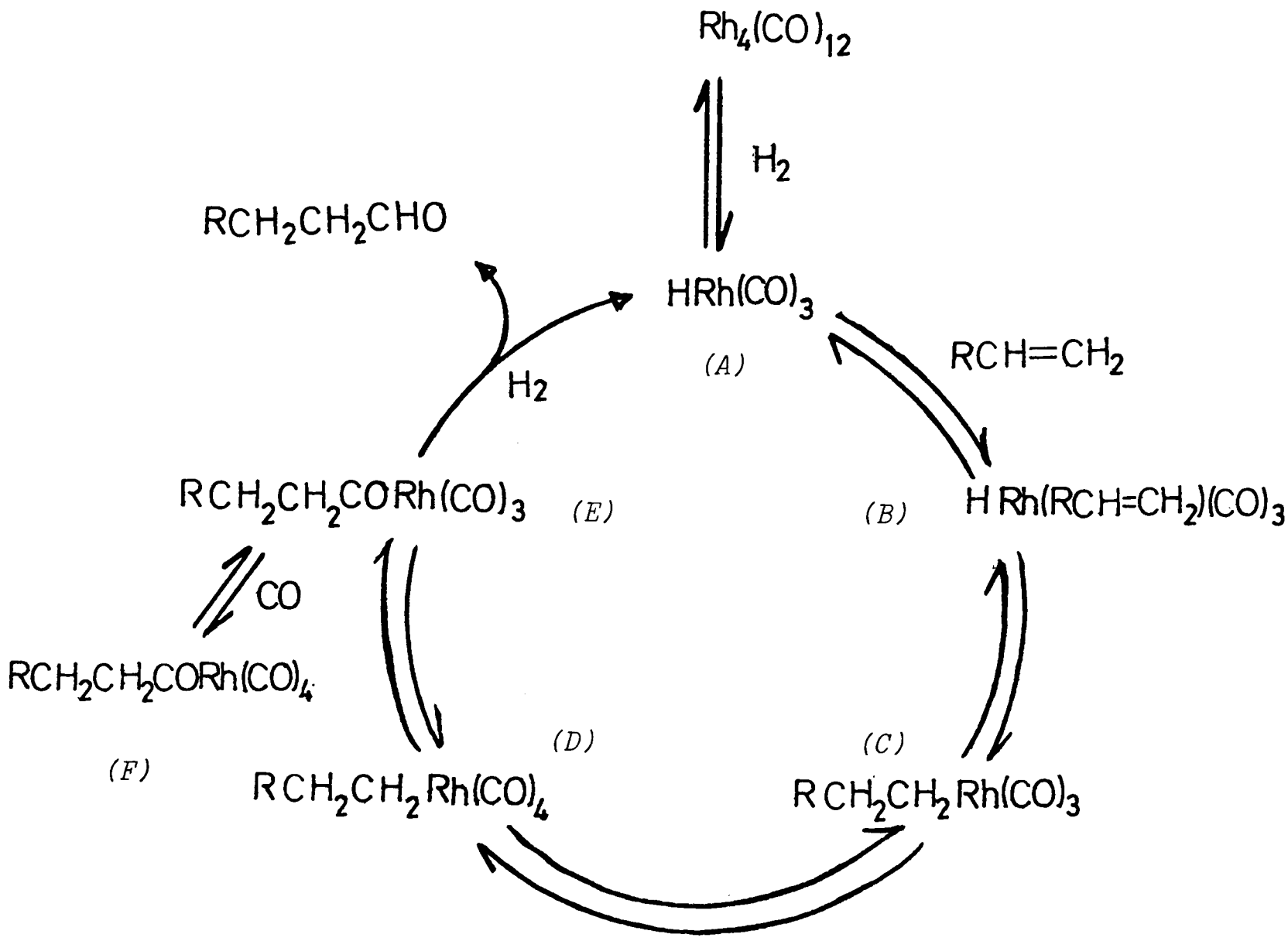
(a) Hydroformylation catalysed by rhodium carbonyl complexes

Unlike cobalt, rhodium does not form insolable mono- or dinuclear homoleptic carbonyl complexes. The simplest stable carbonyls are cluster complexes $Rh_4(CO)_{12}$ and $Rh_6(CO)_6$, based respectively on a tetrahedral and octahedral framework of rhodium atoms.

The reaction of dodecacarbonyltetrarhodium with hydrogen, carbon monoxide and a terminal olefin has been studied by a number of workers; typical reaction conditions are 75^{o}, 150 atmospheres and 1:1 hydrogen to carbon monoxide mixtures.[68] Marko and co-workers have examined the kinetics of this system and presented a mechanism consistent with their results (Figure I.3.1) which requires a reactive mono-nuclear intermediate.

The reaction pathway is essentially that indicated in Scheme I.2.1. Initial trapping of the coordinatively unsaturated complex $HRh(CO)_3$ *(A)* by olefinic substrate is followed by olefin insertion into the metal-hydride bond which gives the alkylhydride *(C)*. Carbon monoxide-induced alkyl migration leads to formation of an acyl-rhodium intermediate *(E)* which can eliminate aldehyde by oxidative addition of hydrogen.

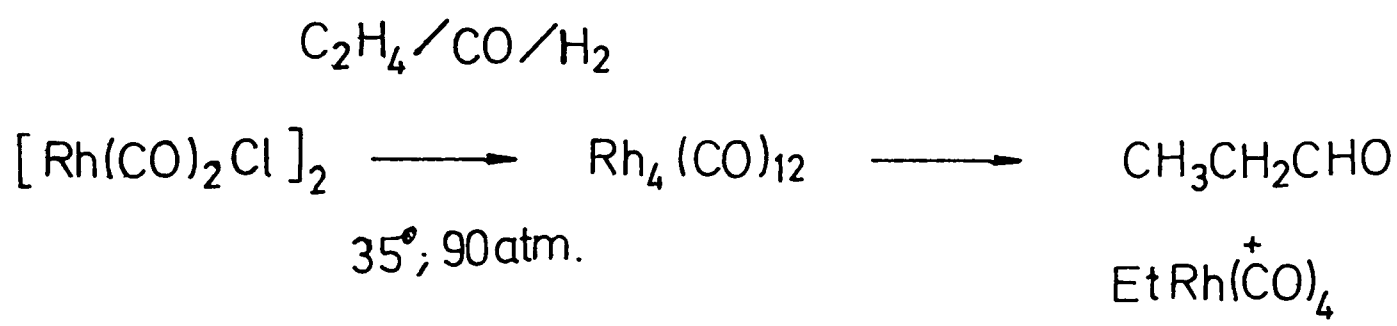
The kinetic studies[68] suggest that the majority of the rhodium is transformed to the relatively stable acyl-complex *(F)* and the rate determining step is the reaction of *(E)* with hydrogen. There exists some direct spectroscopic evidence as to the nature of some of the intermediates *(A)* to *(E)*: King *et.al.*,[69] using high pressure infra-red



$$\frac{d[RCH_2CH_2CHO]}{dt} = K\,[RCH{=}CH_2]^{0}[Rh][P_{H_2}][P_{CO}]^{-1}$$

Figure I.3.1

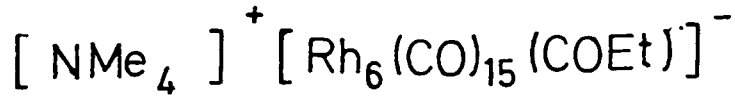
spectroscopy, consider that $EtRh(CO)_4$ *(48)* [analogous to *(D)*] can be identified under certain conditions (Scheme I.3.1).



(48)

Scheme I.3.1

In similar studies employing heptene Marko[68,70] has identified the acyl-derivative *(F)*. Indirect evidence in favour of acyl rhodium complexes is provided by Chini *et.al.*.[71] Using similar reaction conditions to those of King they were able to isolate the acylated cluster-complex *(49)* on addition of a tetra-alkylammonium salt.



(49)

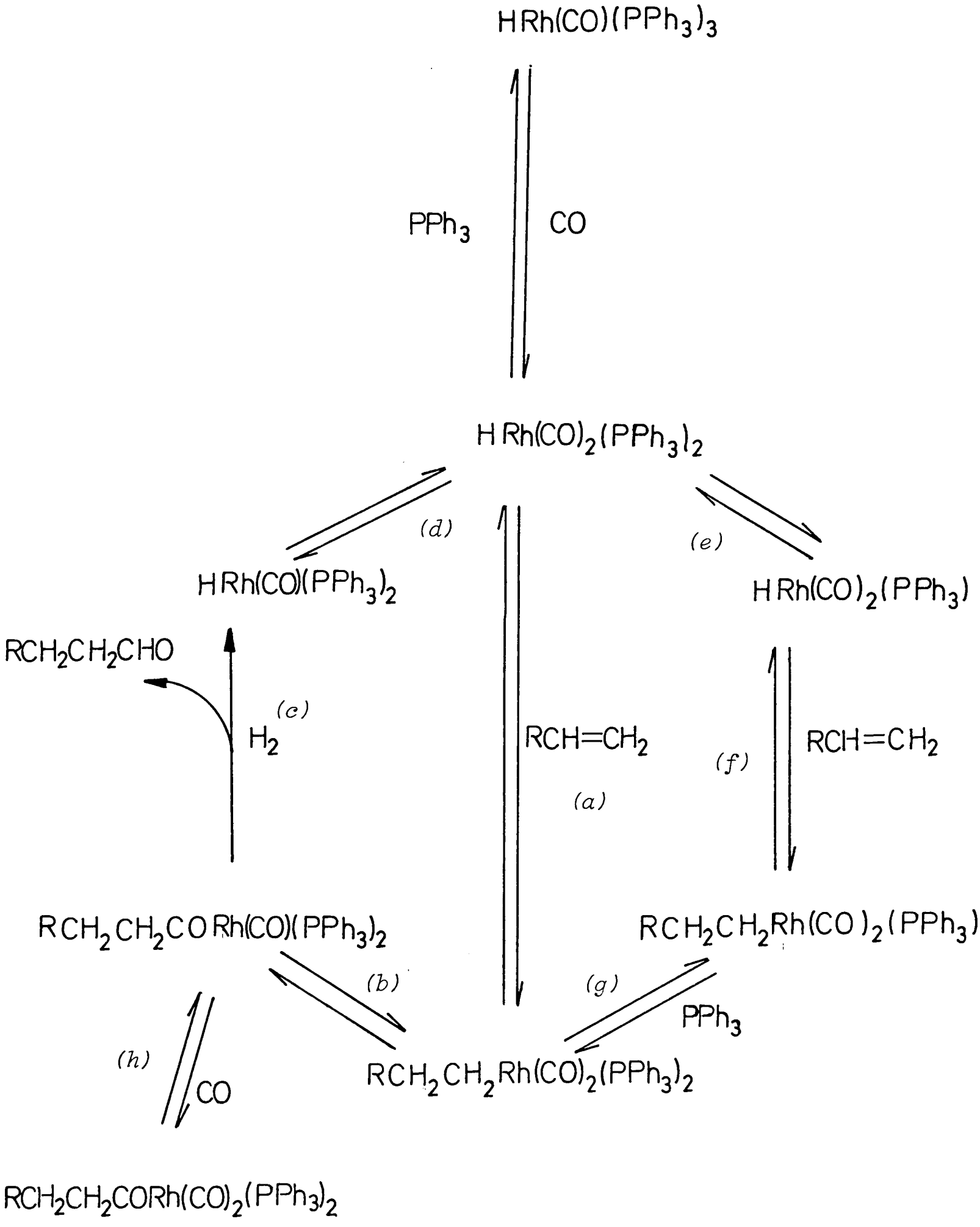
Some pertinent observations have been made in the analogous octacarbonyldicobalt catalysed reaction, particularly the fate of various labelled substrates. Investigations using α-^{14}C-propene[72] and 4-$[^2H]_3$-but-1-ene, 5-$[^2H]_3$-pent-1-ene and 6-$[^2H]_3$-hex-1-ene at high[73] and low[74] pressures have been carried out by Piacenti *et.al.*. Examination of label distribution in recovered starting material and aldehyde products

suggests that isomerization does not take place *via* a σ-bonded alkylcobalt complex but *via* an olefinic carbonyl hydride. The fact that the step forming isomeric aldehydes precedes the formation of alkyl-cobalt carbonyl intermediates has been confirmed by some other work of Piacenti. Both unlabelled[75,76] and labelled[77] alkyl- and acyl[78]-cobalt carbonyl complexes, prepared *in situ* or independently, react under hydrogen and carbon monoxide to produce aldehydes; isomerization was shown *not* to occur under these conditions. It is not clear whether a similar rhodium olefinic hydride intermediate is involved in the $Rh_4(CO)_{12}$ catalysed reaction.

(b) Phosphine modified rhodium catalysed reaction

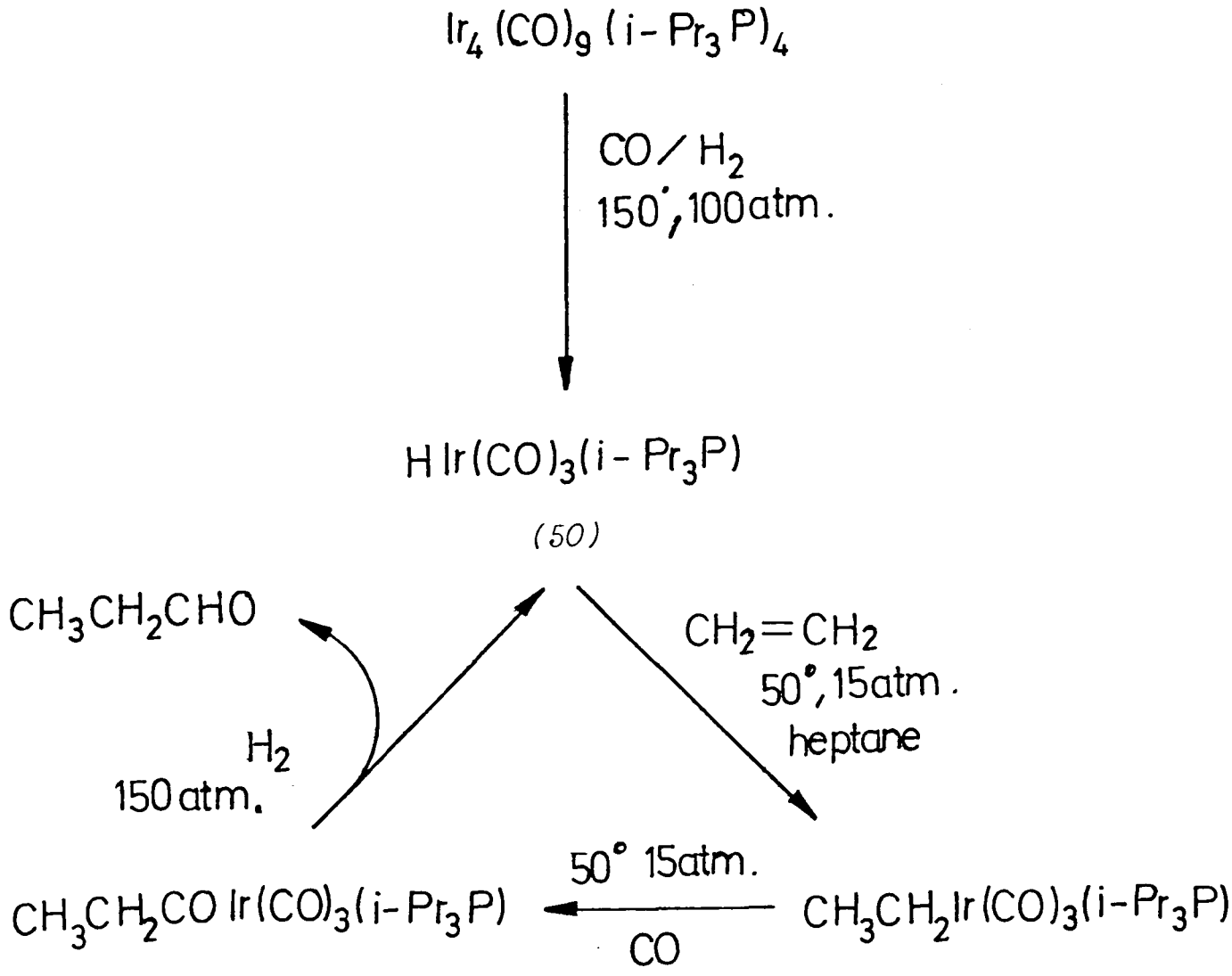
The complex hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) was prepared over 15 years ago[79] and has been well characterized. Its role in hydroformylation is much less well defined however; the original mechanistic studies were performed by Wilkinson and co-workers[16,18] under mild reaction conditions and little of significance has been added since. The major reaction pathway for the formation of *n*-aldehyde as suggested by Wilkinson is summarized in Scheme I.3.2.

The individual reaction steps are those identified in Scheme I.2.1 although two possible pathways may be important depending on catalyst concentration. Steps (a)-(d) represent the associative mechanism whereas steps (e)-(g) and (b)-(d) the dissociative mechanism. Wilkinson inferred from kinetic studies (especially relating to rhodium catalyst concentration) and also from the effect of excess phosphine that, at rhodium concentrations lower than *ca.* 6×10^{-3} mol l^{-1}, the dissociative pathway predominates whereas at higher concentrations the associative pathway is important.[18]


HRh(CO)(PPh3)3
PPh3
CO
HRh(CO)2(PPh3)2
(d)
(e)
HRh(CO)(PPh3)2
HRh(CO)2(PPh3)
RCH2CH2CHO
(c)
H2
RCH=CH2
(a)
(f)
RCH=CH2
RCH2CH2CORh(CO)(PPh3)2
RCH2CH2Rh(CO)2(PPh3)
(b)
(g)
PPh3
(h)
CO
RCH2CH2Rh(CO)2(PPh3)2
RCH2CH2CORh(CO)2(PPh3)2

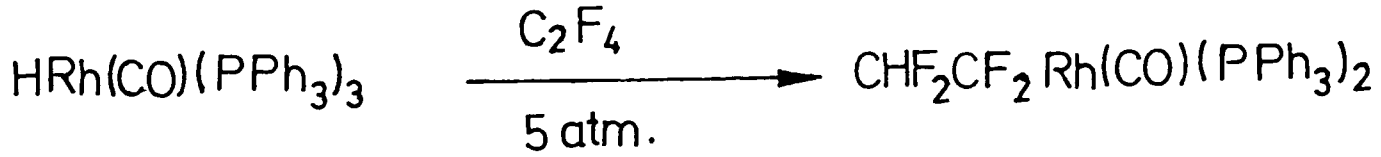
Scheme I.3.2

There are very few examples of the direct observation of reaction intermediates. Whyman[80] however has conducted a very elegant study into the stoichiometric hydroformylation of propene with an iridiumphosphine complex *(50)* (Scheme I.3.3) and identified analogous reaction intermediates by high pressure infra-red spectroscopy.



Scheme I.3.3.

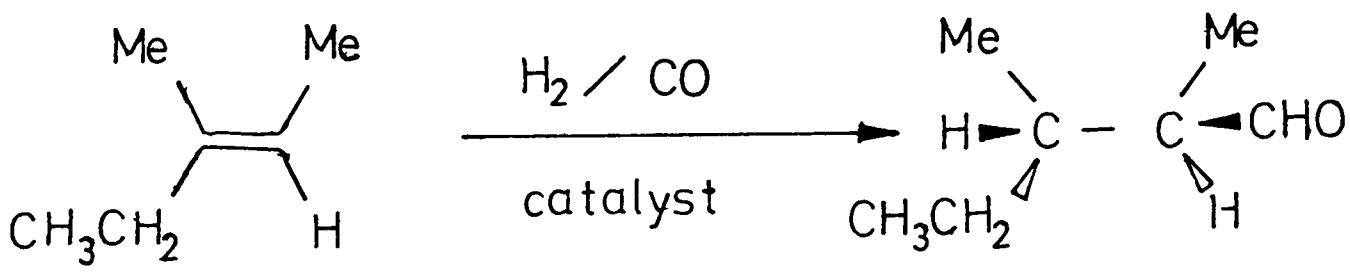
Other evidence comes from related infra-red and in some cases NMR studies of rhodium complexes.[81] Hydridocarbonyl*tris*(triphenylphosphine)-rhodium (I) reacts with tetrafluoroethylene to give the alkylrhodium complex *(51)* which can be isolated and has *trans*-triphenylphosphine ligands.



(51)

Reaction with carbon monoxide produces only the tricarbonyl analogue of *(51)* and not an acyl complex; this presumably reflects the relatively high σ-bond strength of the metal-alkyl. When a mixture of carbon monoxide and ethylene is used in place of tetrafluoroethylene, no intermediates are isolable but an intermediate acyl-complex may be tentatively identified by IR and NMR spectroscopy.

Indirect evidence on the mechanism of hydroformylation is provided by Pino and co-workers[82] who have examined the stereochemistry of the reaction. Isomeric pentenes were hydroformylated with Wilkinson's catalyst and the products shown to arise from a formal *cis*-1,2-addition of *H* and *CHO*. Thus *(E)*-3-methylpent-2-ene *(52)* yields *threo*-2,3-dimethyl-pentanal *(53)*.



(52) *(53)*

Sanger[83] examined the effect on hydroformylation reactivity of adding *cis*-chelating phosphines to solutions of hydridocarbonyl*tris*-(triphenylphosphine)rhodium (I). Equimolar or greater quantities had a much more powerful retarding effect than equivalent amounts of

triphenylphosphine. This was attributed to the necessity of a *trans*-phosphine rhodium complex at some stage in the reaction, which is precluded when *cis*-chelated complexes are involved.

At an industrial level, rhodium complex-catalysed hydroformylation has been subjected to extensive kinetic measurements, and computer modelling of the reaction pathway. This work is comprehensively summarised in a recent review.[38]

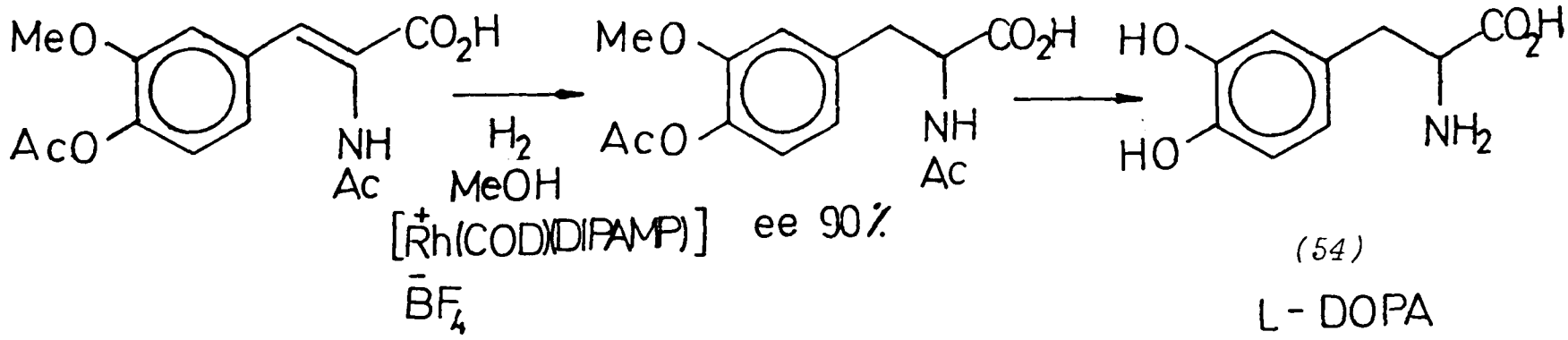
CHAPTER II - RESULTS AND DISCUSSION

CHAPTER II - RESULTS AND DISCUSSION

The aims of this project were threefold, and these are outlined below:

(a) Investigation of potentially *trans*-chelating biphosphines as their rhodium complexes in hydroformylation

Numerous examples of *cis*-chelating biphosphines exist and their involvement in catalysis and organometallic chemistry has been well studied. Asymmetric *cis*-biphosphine rhodium complexes are interesting; these catalyze the hydrogenation of prochiral olefinic substrates to give useful chiral products. For example L-DOPA (*54*), prescribed for Parkinsons' disease, is prepared *via* a chelating *bis*(diphenylphosphino-ethane)rhodium complex and shown below:[84]



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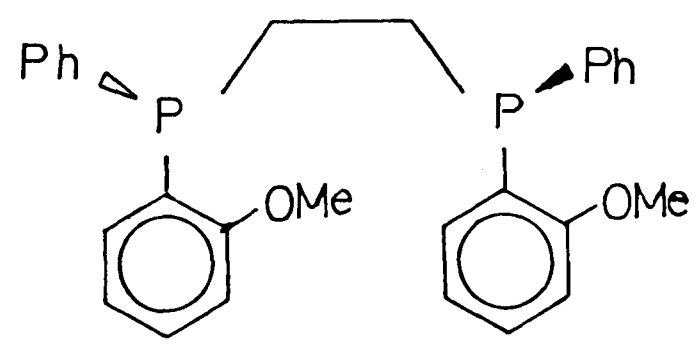
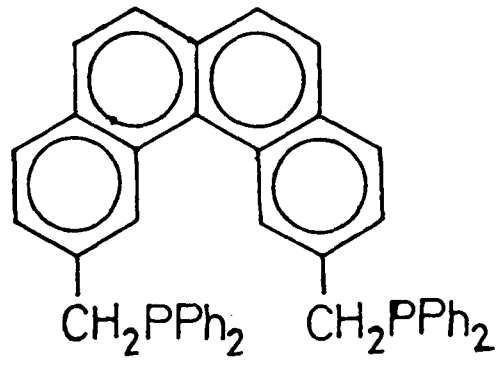


Many of the common catalytic reactions, including hydroformylation, olefin isomerization and decarbonylation require a series of intermediates

in which a pair of phosphines remain *trans*-coordinated. This suggests that *trans*-chelating biphosphines will be of some interest in catalysis. Examples of biphosphines which are exclusively *trans*-chelating are rare. Venanzi and co-workers[85] have recently prepared the biphosphine *(55)*; this adopts *trans*-phosphine coordination in rhodium *(56)* and iridium *(57)* square planar complexes. Although the biphosphine *(55)* has been



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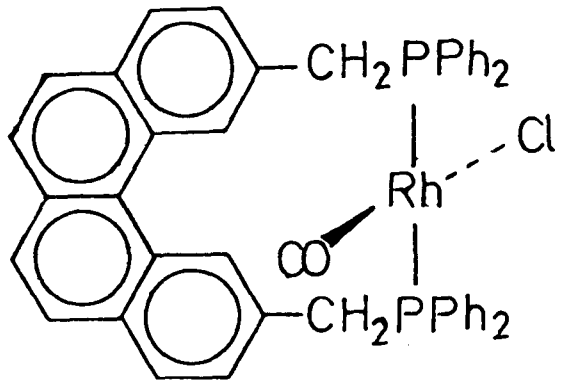

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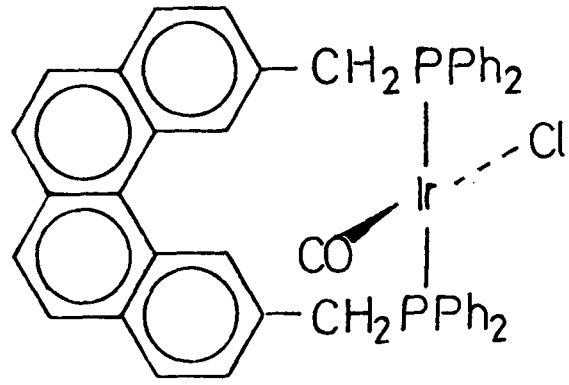


(57)

named TRANSPHOS because of its' chelating ability, there are examples in platinum chemistry of *cis*-phosphine *(55)* substituted complexes.[86]

The intention was to prepare a series of biphosphines with the ability to effect *trans*-coordination and investigate their rhodium complexes under catalytic conditions, and the ways in which they might modify hydroformylation.

(b) Investigation of the reaction of hydrogen and/or carbon monoxide with rhodium-phosphine complexes in solution

Heteronuclear NMR techniques, particularly the observation of phosphorus-31 nuclei, permit the identification of catalytic intermediates in solution. With new biphosphines in hand, it was intended that their rhodium complexes with hydrogen and/or carbon monoxide be examined. This allows a comparison of hydrogenation and hydroformylation and enables the distinction between *cis*- and *trans*-coordination to be made.

(c) A study of the mechanism of olefin hydroformylation with particular reference to the identification of reactive intermediates

The hydroformylation mechanism proposed by Wilkinson (see Chapter I, section 1.3 page 26) is over ten years old, but there is little substantial evidence regarding the structure of intermediates, although analogous iridium chemistry has been well studied.[80] Both alkyl- and acyl-iridium complexes were identified using high pressure infra-red spectroscopy. The lack of direct evidence in rhodium chemistry encouraged a systematic investigation, with the intention of defining the reactive intermediates by NMR spectroscopy.

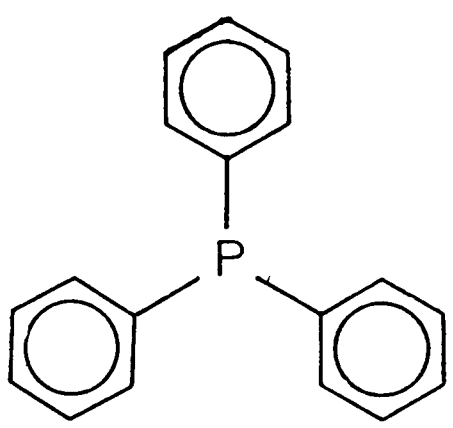
In the remainder of this Chapter, section 1 describes phosphine and rhodium complex preparations, section 2 the characterization of reaction complexes by NMR and section 3 the mechanistic study of olefin hydroformylation. Section 4 comprises catalytic studies both at atmospheric pressure and by autoclave techniques.

II.1 Synthesis of Phosphines and their Rhodium Complexes

1.1. *Synthesis of mono- and biphosphines*

(a) Mono-phosphines

Triphenylphosphine *(58)* was obtained from Aldrich and a single recrystallization from ethanol gave pure material. 2-Methoxyphenyldiphenylphosphine *(59)* was a gift from Dr. B Murrer and Hoffman's method[87] *via* tetraphenylphosphonium bromide *(60)* gave 5-phenyl-5*H*-dibenzophosphole *(61)* (Scheme II.1.1).



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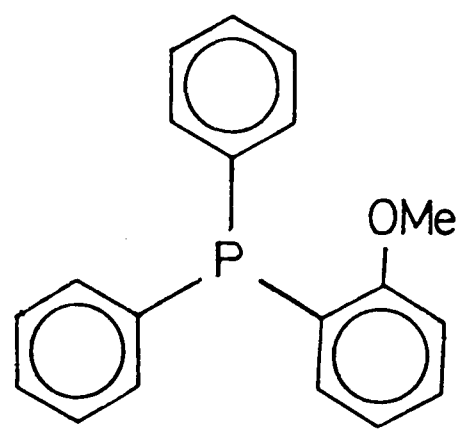

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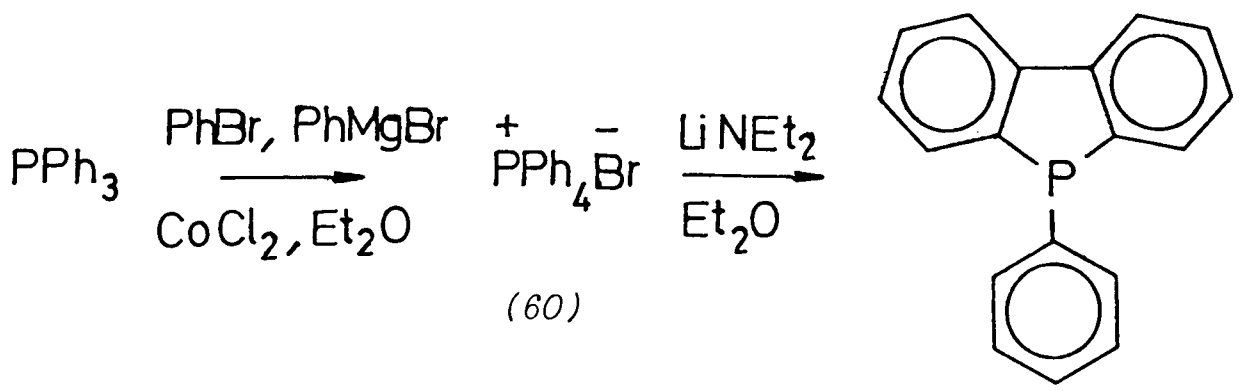


(60)

(61)

Scheme II.1.1.

(b) Biphosphines

Three criteria for *trans*-chelation at rhodium may be defined. Firstly the interphosphine distance must be large enough for *trans*-substitution on a rhodium atom to become possible. In typical complexes[88-91] the rhodium-phosphorus distance is 2.3 angstroms and this requires that a

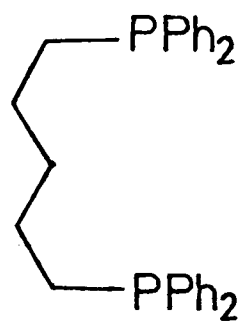
trans-chelate complex has two phosphorus nuclei 4.6 angstroms apart. Molecular models show that in permethylene biphosphines $R_2P(CH_2)_nPR_2$ n must be greater than four to fulfil this requirement. Even if the first condition is met, *cis*-chelation can still occur. In order to prevent this a substituent may be introduced into the middle of the carbon chain, enabling weak and reversible binding to rhodium and preventing hydride abstraction from the interphosphine chain. Furthermore *trans*-chelation is encouraged, even though the chain is flexible.

An alternative approach which meets these criteria is to link the biphosphine termini with a rigid backbone, suitably designed to permit the coordination of reagents and substrate without undue steric repulsion.

On the basis of the first two criteria phosphines *(62)* to *(66)* were prepared (the first named for comparison purposes) and their chemistry is described in detail later. Since the ligand *(55)* prepared by Venanzi and co-workers[85] is flexible, and also constrains coordination of other species, a different approach, which meets the third criterion, was taken. Phosphine *(67)* is more rigid because the methylene groups are remote from the site of complexation and less free to act as a molecular hinge. Molecular models show that there is sufficient space to coordinate hydride or carbonyl ligands in the orthogonal plane.

Syntheses

1,5-*Bis*(diphenylphosphino)pentane *(62)* was obtained from Strem Ltd., but all other biphosphines and precursors were prepared by the author. It has previously been established that nucleophilic displacement by diphenylphosphide anion proceeds in greater yields when mesylate rather than tosylate is the leaving group.[92] For this reason it was decided to prepare biphosphines from dialcohols *via* mesylates where appropriate.



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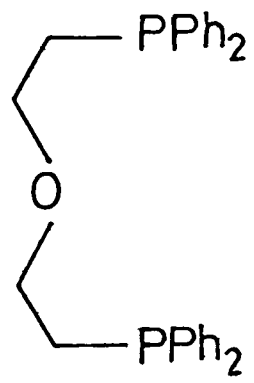

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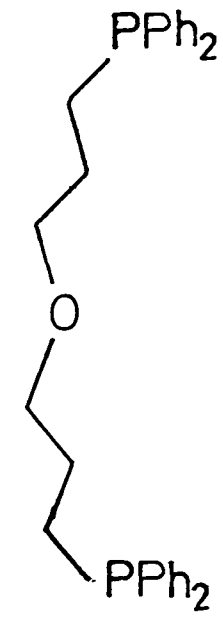

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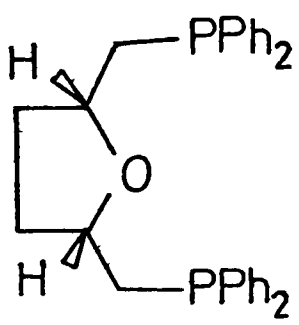

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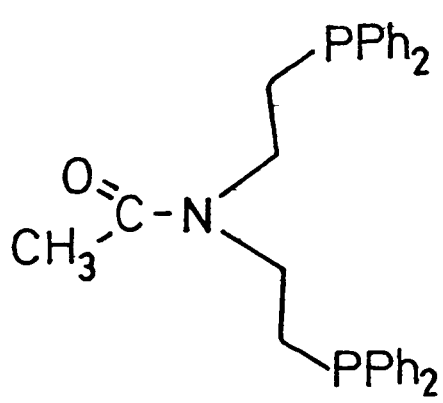

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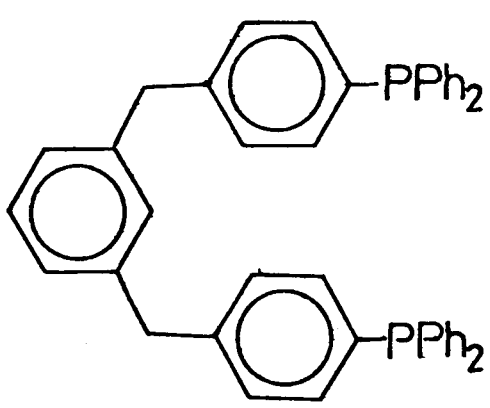
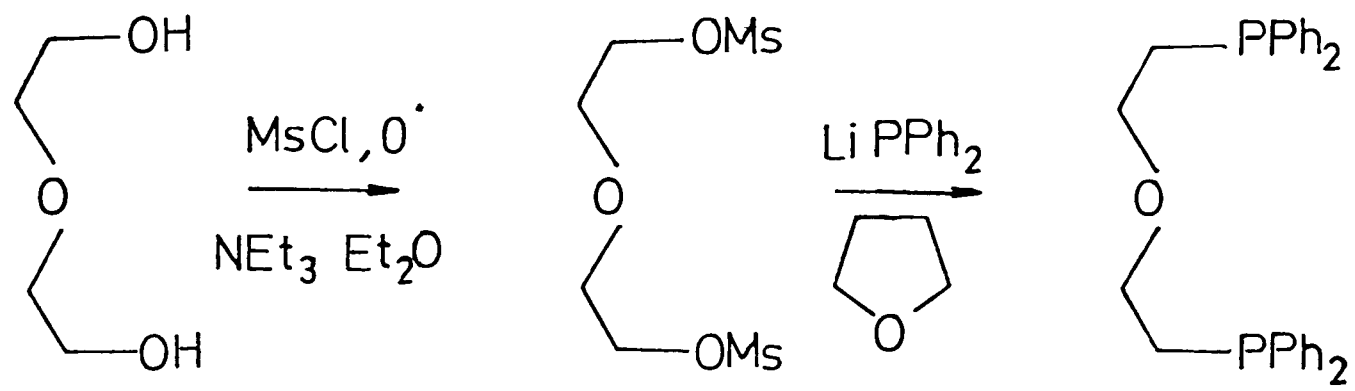


(67)

Synthesis of 1,5-*bis*(diphenylphosphino)-3-oxapentane *(63)* was achieved in two steps from 3-oxapentane-1,5-diol *(68)* (Scheme II.1.2).

The last step is the crucial phosphination reaction mentioned above; best yields were obtained when the dimesylate *(68)* was added to a solution of lithium diphenylphosphide in tetrahydrofuran at -78°. The phosphine *(63)* was isolated as an oil and could not be induced to crystallize, even over a long period of time.

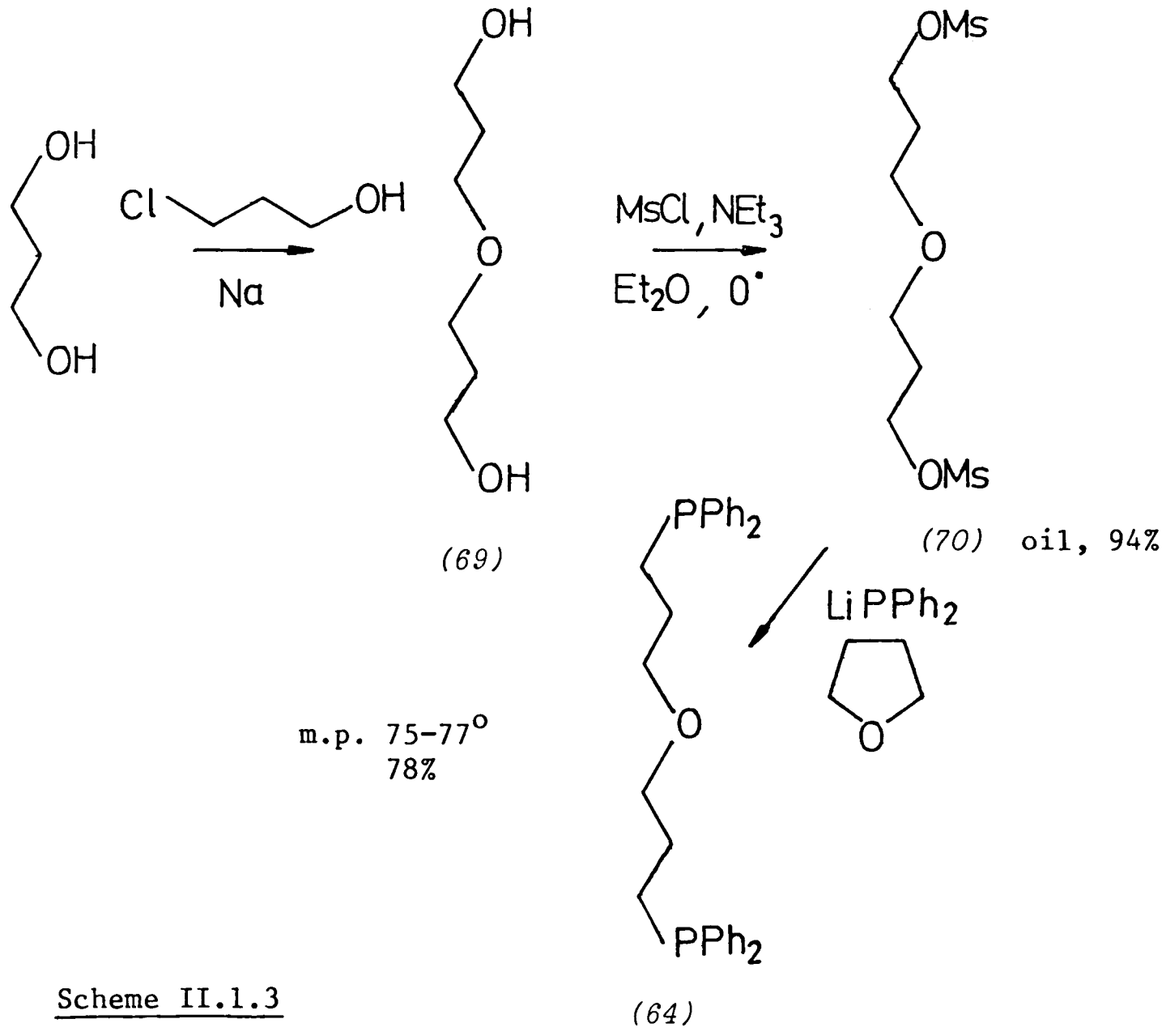


(68) m.p. 58-59°

(63) oil, 93%

Scheme II.1.2

The homologue *(64)* was made in a similar manner *via* 4-oxaheptane-1,7-diol *(69)* (Scheme II.1.3).



(69)

(70) oil, 94%

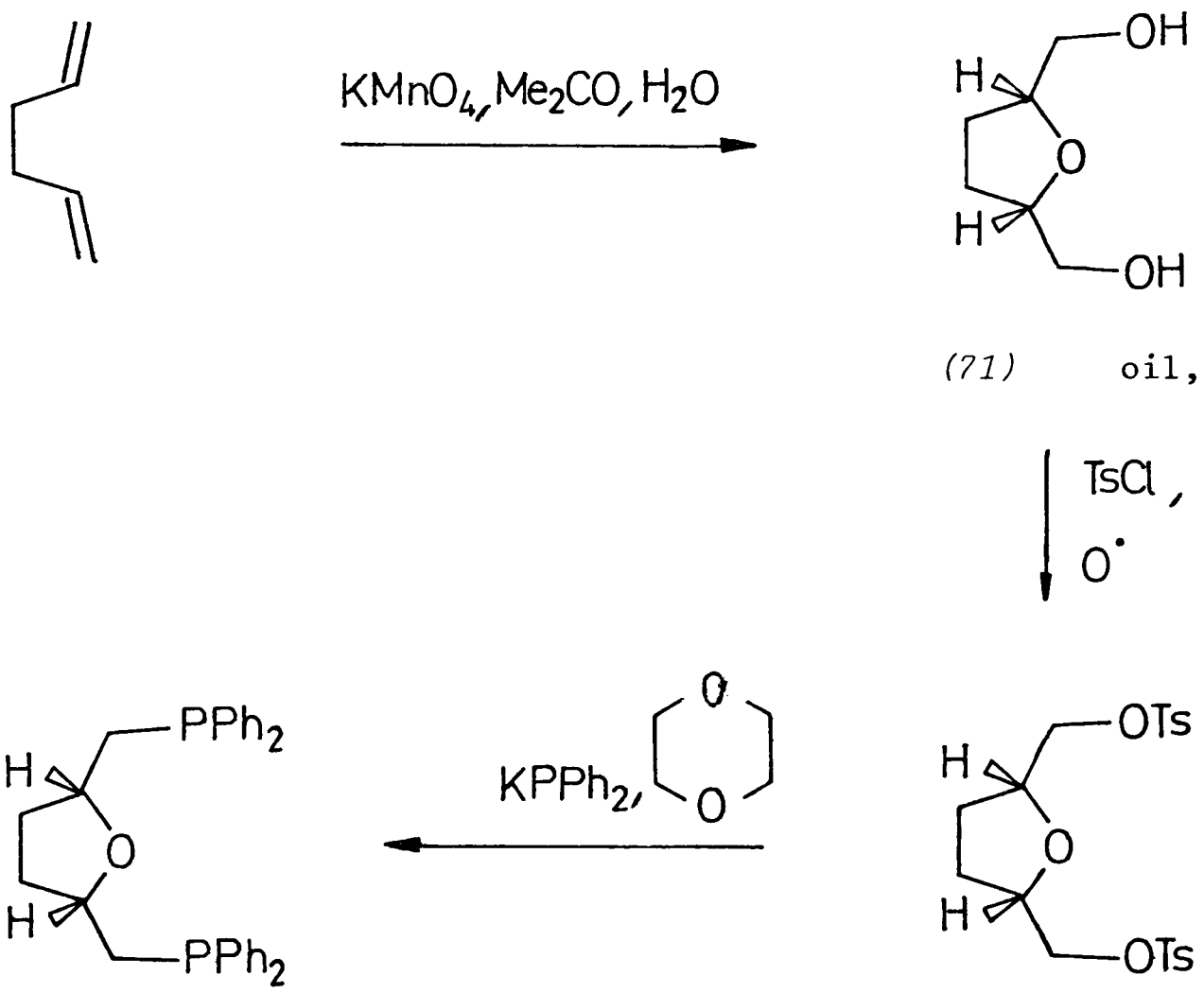
m.p. 75-77°
78%

Scheme II.1.3

(64)

Recrystallization of the phosphine *(64)* from methanol gave analytically pure material.

A more rigid analogue of phosphine *(63)* was prepared from *cis*-2,5-dihydroxymethyltetrahydrofuran *(71)*, the product of permanganate oxidation of hexa-1,5-diene. A variant in procedure was the preparation of its ditosylate *(72)* and subsequent reaction with potassium diphenylphosphide (Scheme II.1.4). Previous work[93] has shown that cleavage of triphenylphosphine by sodium-potassium alloy produces a reagent more effective in the displacement of tosylate groups.



(71) oil, 43%

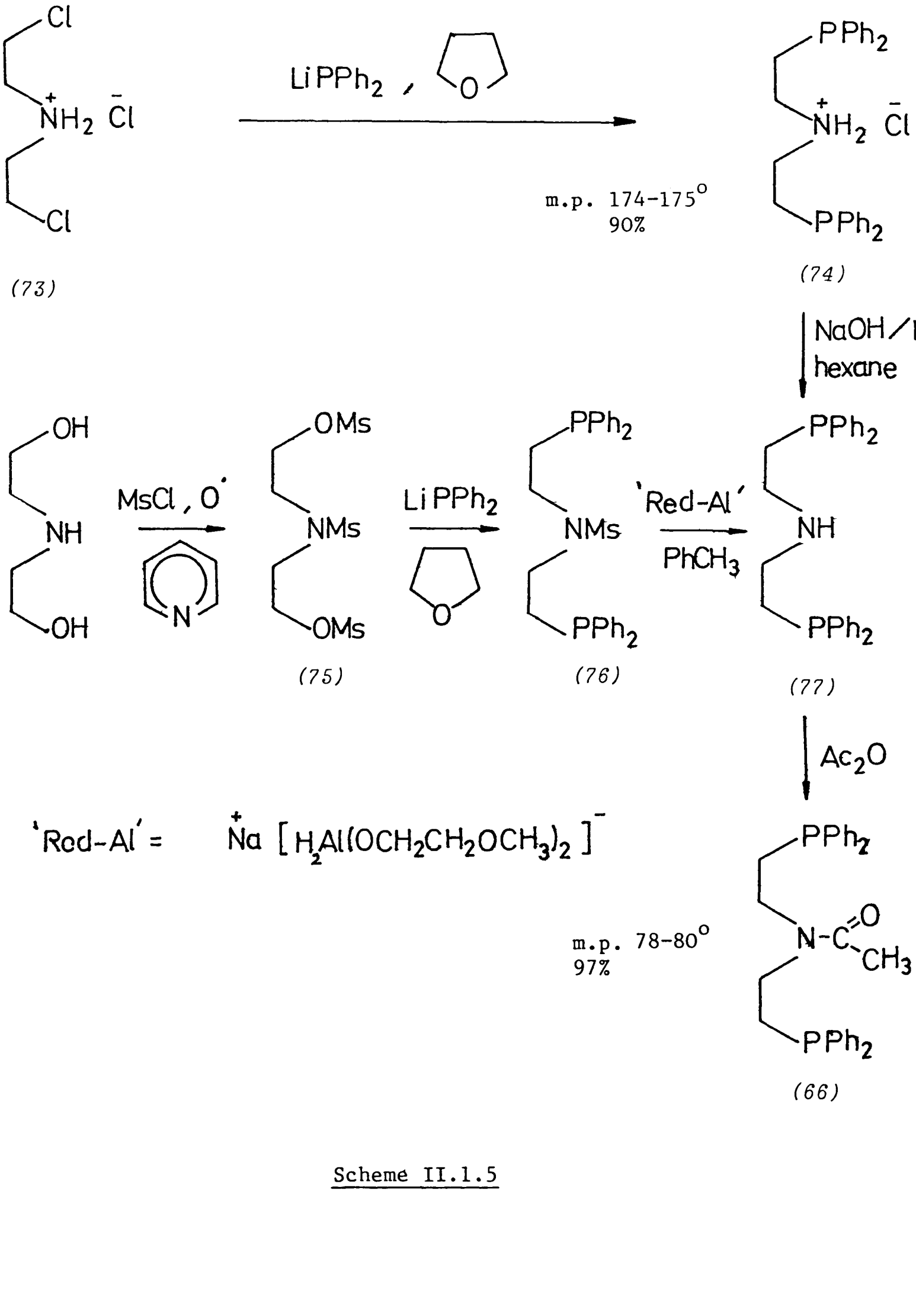
(65) m.p. 63-4°, 94%

(72) m.p. 130-2°, 33%

Scheme II.1.4

Two independent approaches were used to prepare the N-acetyl-3-azapentane-biphosphine *(66)*, summarized in Scheme II.1.5. The first method was that of Whitesides[94] and was employed because of the ready availability of

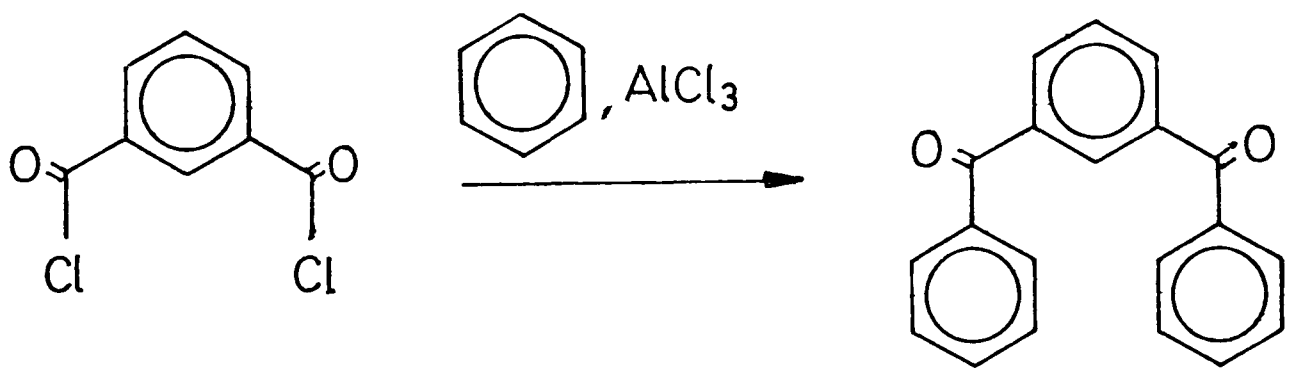
3-aza-1,5-dichloropentane hydrochloride *(73)*. The feasibility of the second route was investigated because of its' potential flexibility. In each case *N*-acetylation of the aminophosphine *(77)* was effected by acetic anhydride.



(73) *(74)* *(75)* *(76)* *(77)* *(66)*

Scheme II.1.5

A rigid biphosphine *(64)* was also prepared. It had been shown that the reaction of isophthaloyl chloride *(78)* with benzene under Friedel-Crafts conditions produced 1,3-dibenzoylbenzene *(79)* in high yield.[95] In an analogous manner isophthaloyl chloride *(78)* was reacted

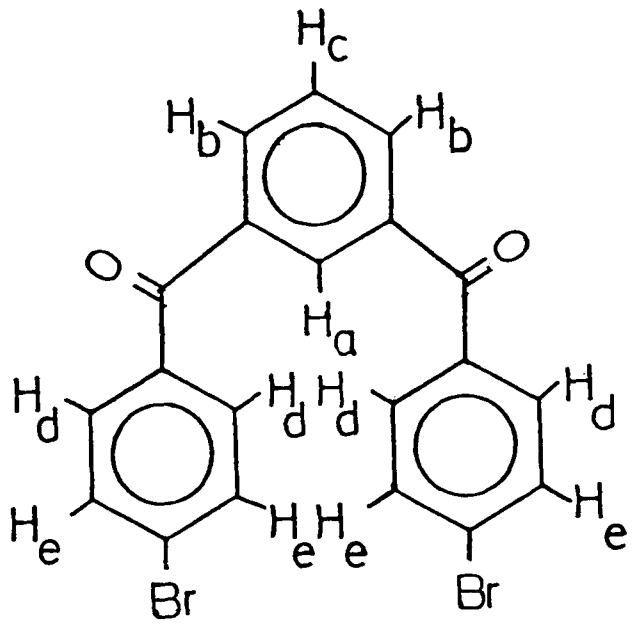


(78) *(79)*

with bromobenzene in presence of aluminium trichloride, with the intention of producing the *p,p'*-disubstituted isomer *(80)* a suitable precursor for phosphine *(67)*. The reaction proceeded smoothly in bromobenzene as solvent at a temperature of 80°, with formation of a dark red solution. The isolated product was shown by spectroscopic means to be a 3:1 mixture of the required compound *(80)* and another isomer (possibly *81*) since mass spectroscopy is consistent with a single molecular mass for the parent ion. The ^{1}H-NMR of the crude product and purified major isomer separated by thin layer chromatography are illustrated in Figure II.1.1. Friedel-Crafts acylations are irreversible with the result that kinetically favourable products can be formed; this is to be contrasted with Friedel-Crafts alkylations where thermo-

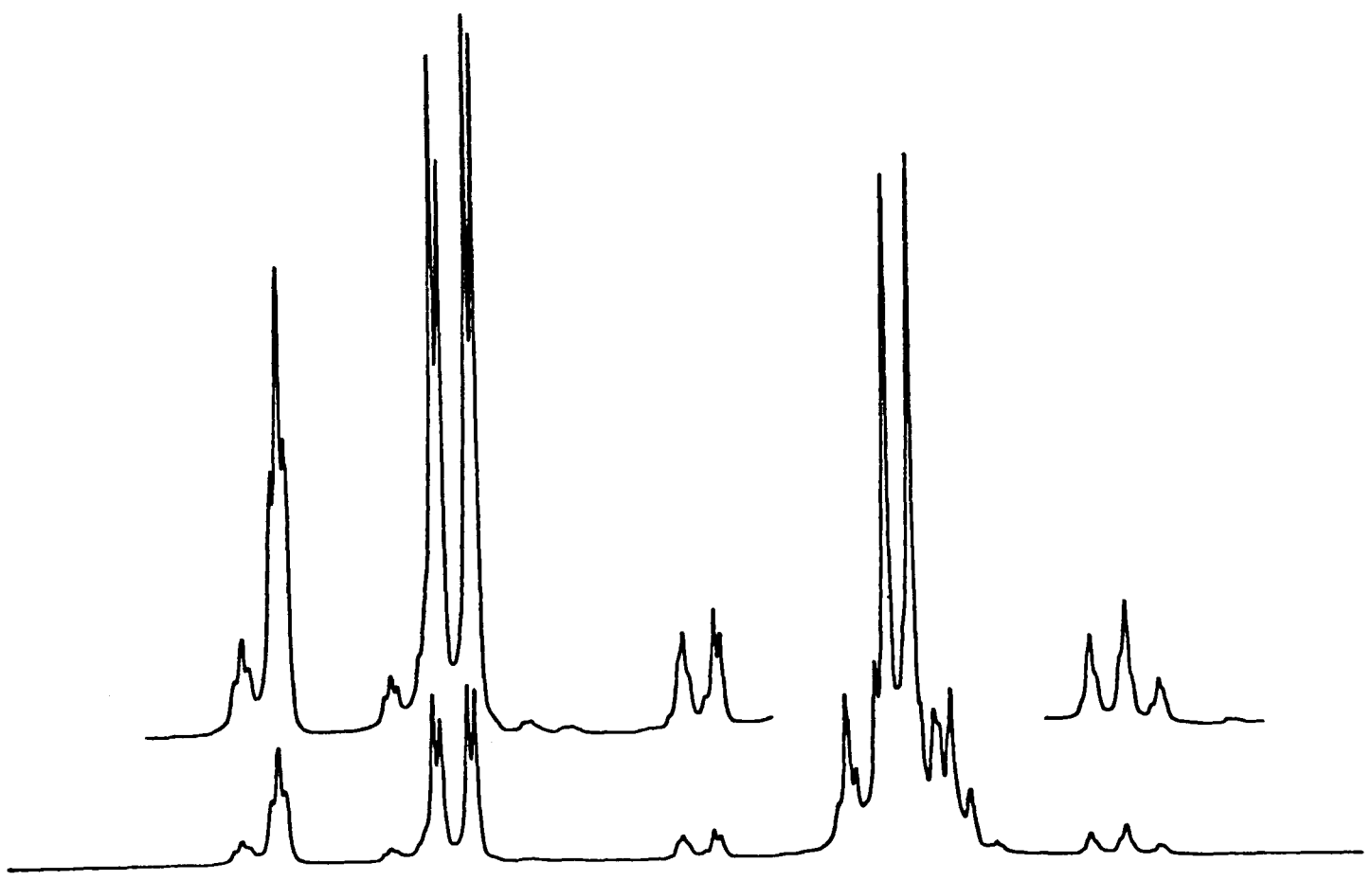
Figure II.1.1

^{1}H-NMR (300 MHz) of the products from the reaction of isophthaloyl dichloride with bromobenzene

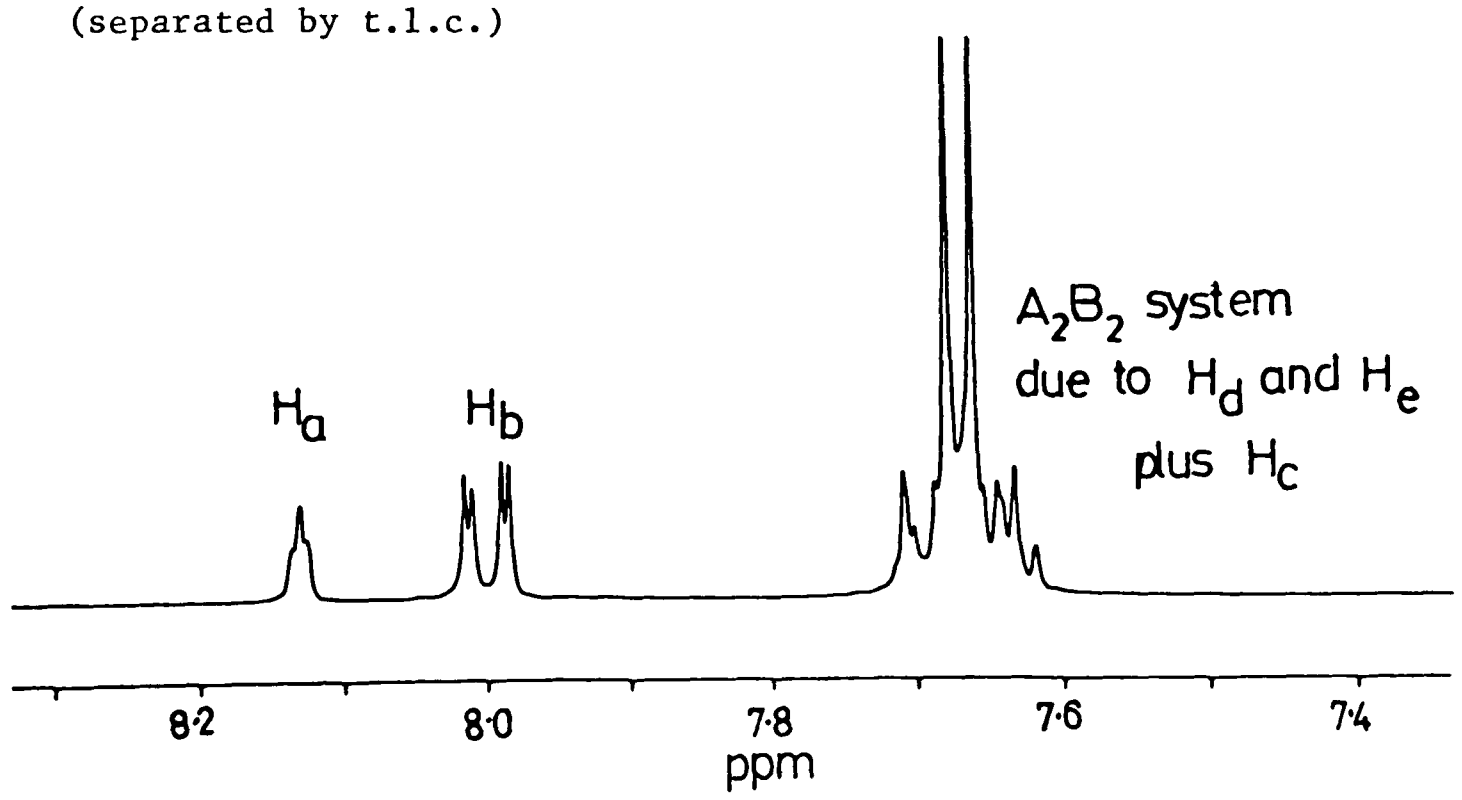


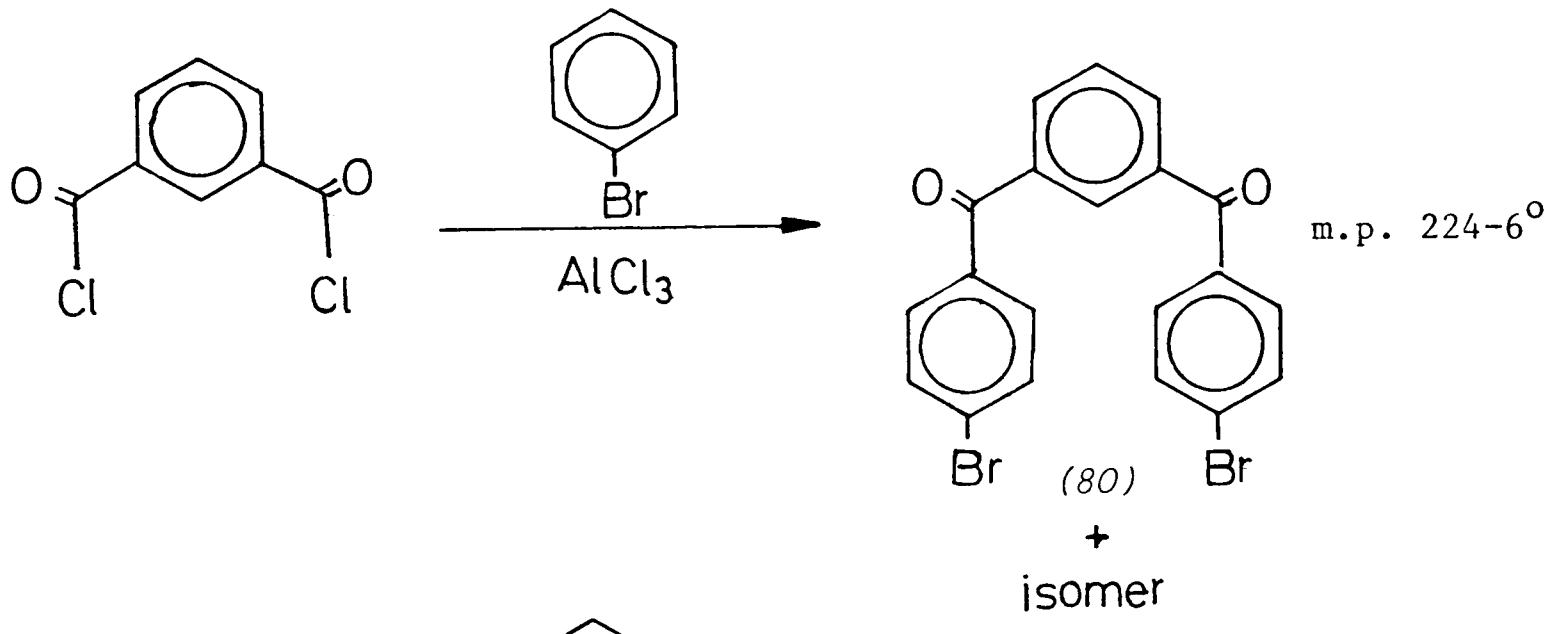
(80)

(a) Crude mixture



(b) Major Isomer
(separated by t.l.c.)

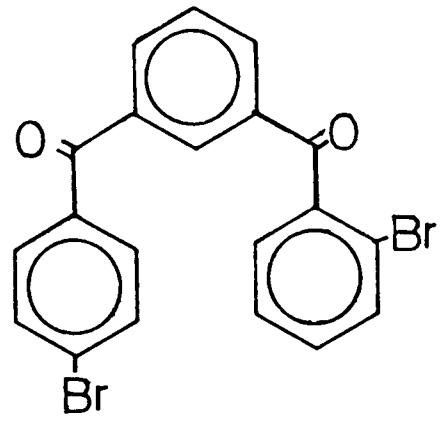




(80)

+

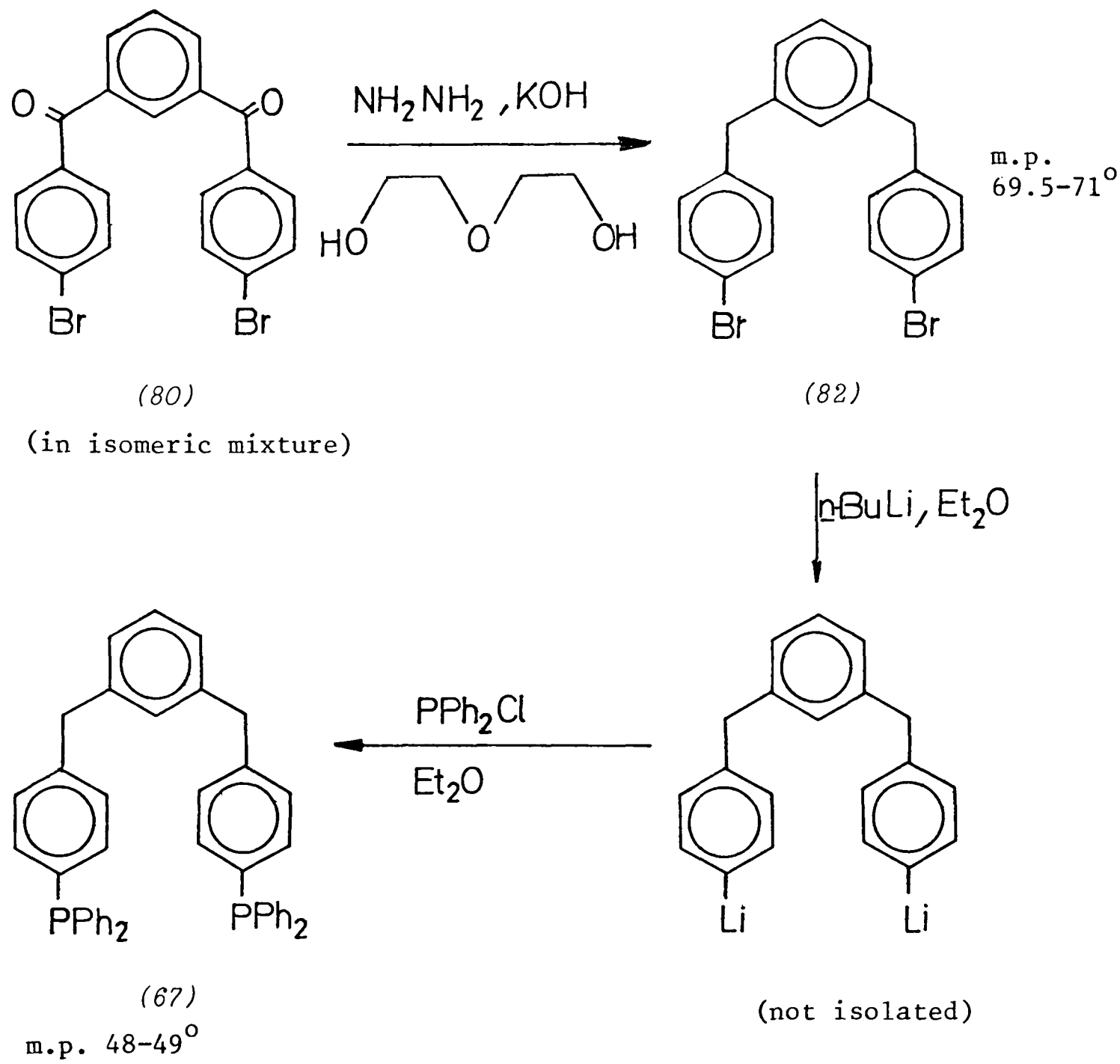
isomer



(81)

dynamically favourable products prevail under suitable reaction conditions. The acylation was also carried out in nitrobenzene as solvent, and although yields were comparable, difficulty in separation of the solvent from products was encountered.

Attempts at large-scale purification of the diketone *(80)* proved fruitless. The crude mixture was subjected to Wolff-Kischner reduction[96] and a pure sample of 1,3-(4-bromobenzyl)benzene *(82)* was separated by fractional crystallization. Conversion of the dilithioderivative, from reaction of compound *(82)* with *n*-butyl lithium, into the phosphine *(67)* was achieved by reaction with chlorodiphenylphosphine using a standard method.[97] Scheme II.1.6 summarizes the synthetic pathway. Separation by flash chromatography caused the phosphine to crystallize.



(80)

(in isomeric mixture)

(82)

(67)

m.p. 48-49°

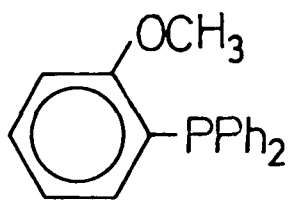
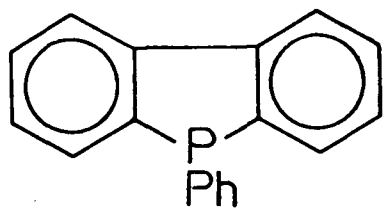
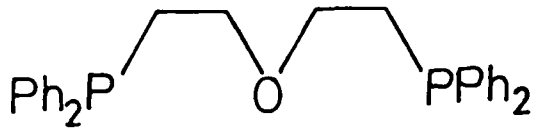
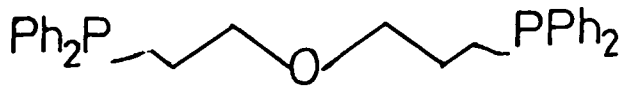
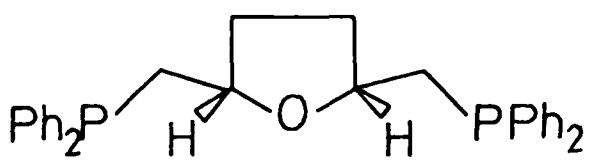
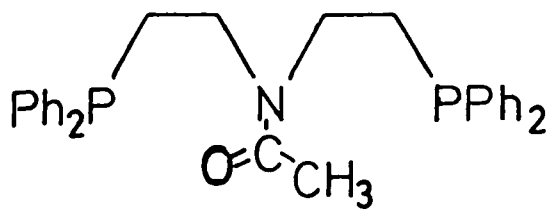
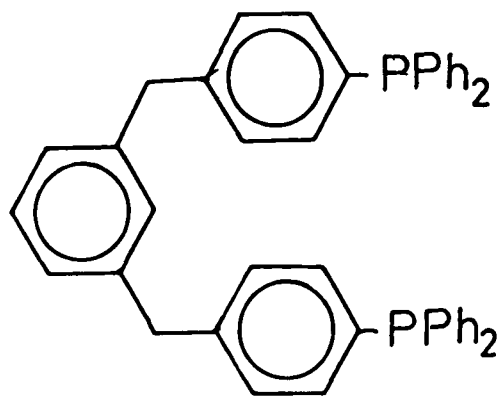
(not isolated)

Scheme II.1.6

In each case the phosphine was fully characterized by ^{1}H and ^{31}P-NMR and (for new compounds) elemental analysis. Table II.1.1. gives ^{31}P-NMR data on phosphines prepared and used in the course of this project.

Table II.1

Phosphine chemical shift data from ^{31}P-NMR analysis relative to external H_3PO_4

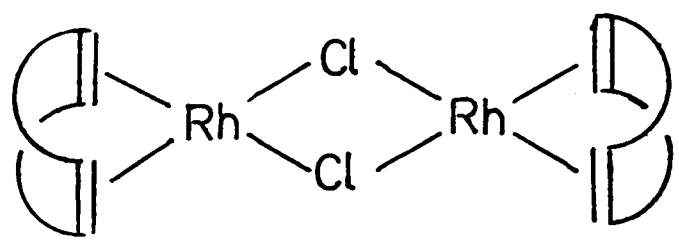
Phosphine		$\delta(CH_2Cl_2)$ppm
(58)		- 4.7
(59)		- 15.5
(61)		- 9.5
(62)		- 15.6
(63)		- 20.9
(64)		- 15.0
(65)		- 23.5
(66)		- 19.3 and - 20.5
(67)		- 5.4

1.2. *Organorhodium Complexes*

The starting material for the synthesis of all rhodium complexes was rhodium trichloride trihydrate, provided on loan from Johnson-Matthey Ltd.

Crabtree and Felkin[98] reported that hydroformylation could be carried out by *bis*(triphenylphosphine)cycloocta-1,5-dienerhodium(I) hexafluorophosphate in benzene in the presence of triethylamine. This affords a simple entry into biphosphine-derived catalysts, and therefore the corresponding rhodium diolefin complexes of *(62)* to *(67)* were prepared by standard methods. As an additional advantage the reaction products of these complexes with hydrogen in methanol are model systems for establishing the *trans*-chelating ability of biphosphines - this is discussed in Chapter II, section 2.

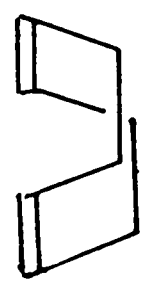
Diene complexes *(83)a*[99] and *(83)b*[100] were prepared according to published procedures.



(83)

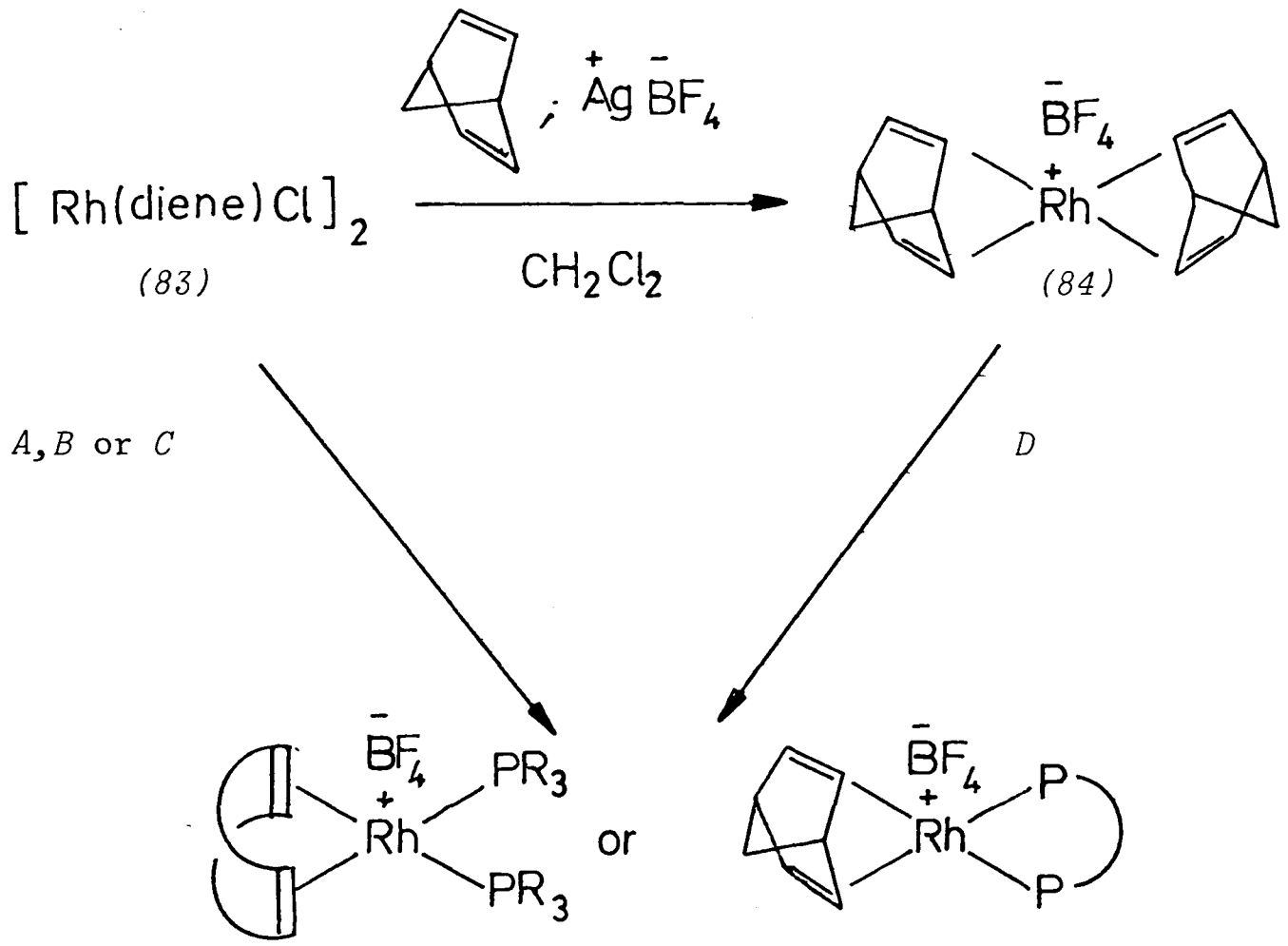
a

b



The cationic *bis*(bicyclo[2.2.1]hepta-2,5-diene)rhodium tetrafluoroborate complex *(84)* was prepared by the method of Green, Kuc and Taylor.[101]

Four procedures were used in the synthesis of bicyclo[2.2.1]hepta-2,5-diene-*bis*(monophosphine) and bicyclo[2.2.1]hepta-2,5-diene(biphosphine) cationic rhodium complexes [compounds *(85)* to *(94)*] (Scheme II.1.7), and Table II.1.2 contains detailed NMR-spectral data pertaining to the isolated complexes.



A: $2PPh_3$, $NaBF_4$, H_2O, CH_2Cl_2.

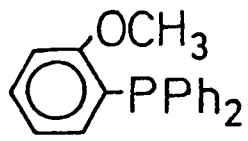
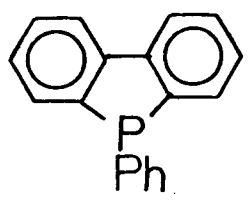
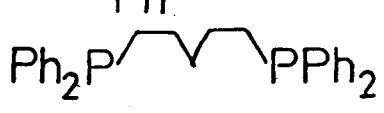
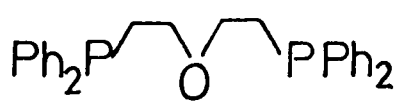
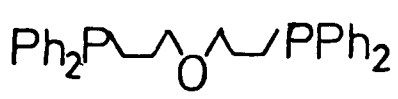
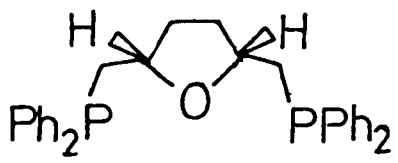
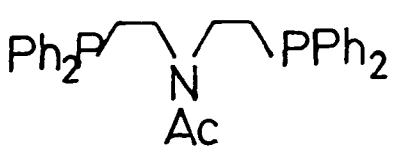
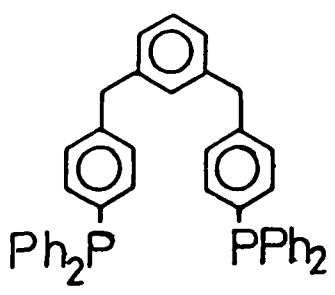
B: *(i)* P⌒P, MeOH *(ii)* $NaBF_4$, H_2O.

C: P⌒P, $AgBF_4$, Me_2CO.

D: $2PR_3$ or P⌒P, CH_2Cl_2.

Scheme II.1.7

Table II.1.2

Diolefin-Phosphine rhodium complex	Phosphine	Method of Preparation (see Scheme II.1.7)		^{31}P NMR $\delta(CH_2Cl_2)$ ppm	$J_{P,Rh}$ Hz
(85)[a]	PPh_3	*(58)*	*A,D*	31.0	156
(86)[b]	PPh_3	*(58)*	*A*	27.7	144
(87)[a]		*(59)*	*D*	24.8	156
(88)[a]		*(61)*	*D*	22.0	152
(89)[a]		*(62)*	*C*	16.7	152
(90)[a]		*(63)*	*D*	18.1	156
(91)[a]		*(64)*	*D*	22.3	154
(92)[a]		*(65)*	*B*	15.0	154
(93)[a]		*(66)*	*D*	28.8 and 19.2[c]	154 ($J_{P,P}$ 35 Hz)
(94)[a]		*(67)*	*D*	29.2	156

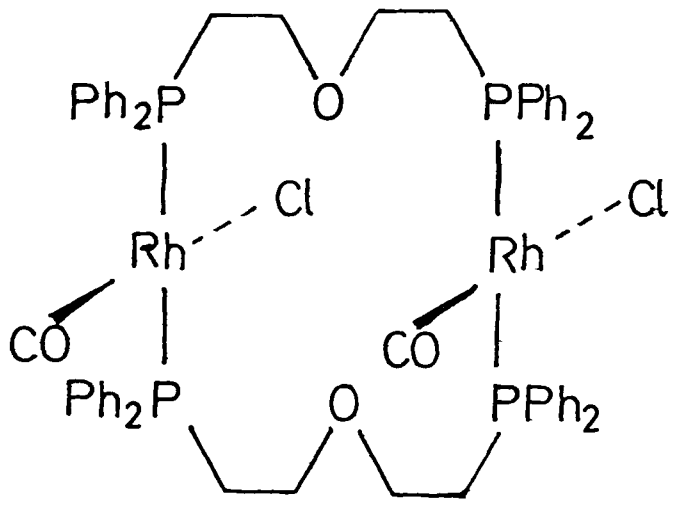
[a] Bicyclo [2.2.1] hepta-2,5-diene complex

[b] Cycloocta-1,5-diene complex

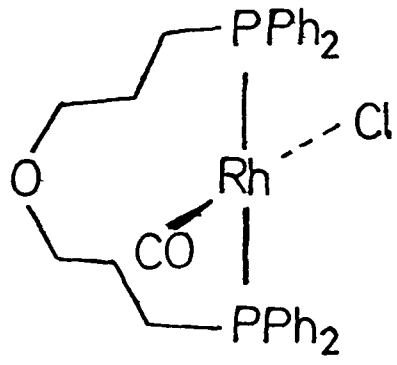
[c] Rhodium coupled AB quartet

[new complexes possess full spectral and analytical data, see Experimental section]

Chlorocarbonylbiphosphinerhodium complexes provide a test of *trans*-chelating ability. The phosphinoether *(63)* forms a dimeric species *(95)* on reaction with di-μ-chlorotetra(carbonyl)dirhodium(I) *(96)* whose X-ray structure has been determined.[102] Unusually the homologue forms a monomeric species *(97)* of similar constitution to that desired from the rigid biphosphine *(67)*, also a mononuclear species *(98)* [*m/e* = 765 by field desorption mass spectrometry *i.e.* $\underline{M}^+$ - CO] with no evidence of dimer. Molecular models indicate that the 9-atom chain of biphosphine *(64)* can readily coordinate to mutually *trans*-positions without any steric strain. The phosphinoamide *(66)* forms a rhodium carbonyl complex *(99)*, in an analogous manner, with ^{31}P-NMR chemical shift and coupling constant and infra-red carbonyl band similar to those of complex *(95)*. (Scheme II.1.8). The rhodium carbonyl complex precursor *(96)* was readily synthesized from rhodium trichloride trihydrate by reaction with carbon monoxide at 100°.[103] *Bis*-(triphenylphosphine)-carbonylchlororhodium(I) *(100)* was prepared according to a published procedure[104] for comparison purposes.



(95)



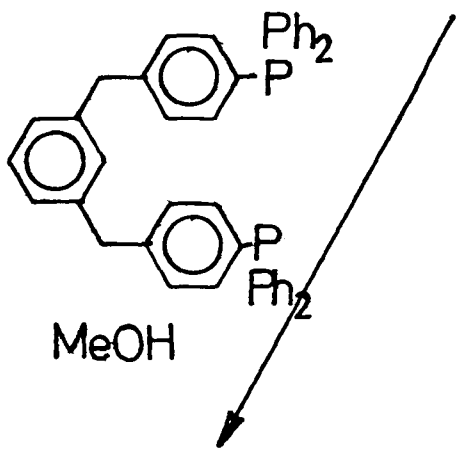
(97) ν_{CO} 1965 cm^{-1}

$Ph_2P(CH_2)_2O(CH_2)_2PPh_2$
MeOH

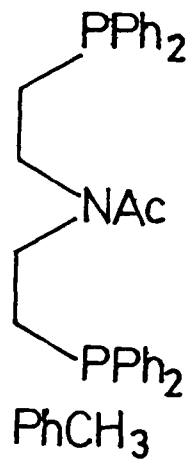
$Ph_2P(CH_2)_3O(CH_2)_3PPh_2$
MeOH

$[RhCl(CO)_2]_2$

(96)

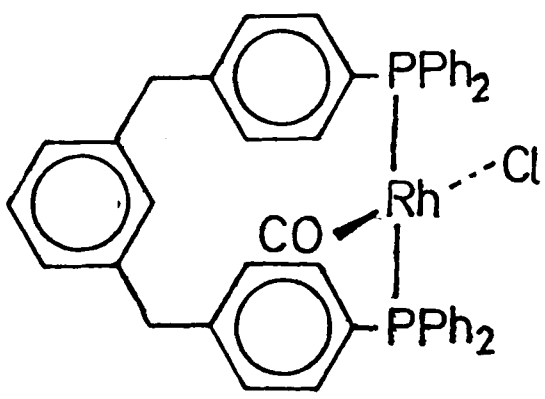


MeOH



$PhCH_3$

PPh_3
$PhCH_3$

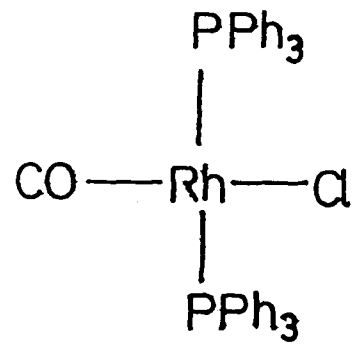


(98)

ν_{CO} 1965 cm^{-1}

(99)
light-yellow complex

ν_{CO} 1970 and 1620 cm^{-1}



(100)

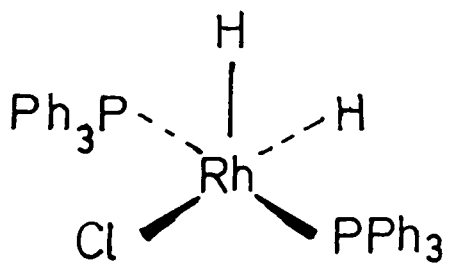
ν_{CO} 1960 cm^{-1}

Scheme II.1.8

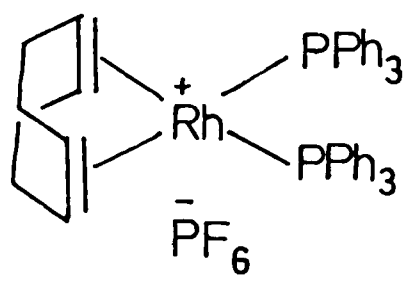
II.2 NMR Characterization of Reaction Solutions

The addition products formed by the reaction of hydrogen or carbon monoxide with rhodium phosphine complexes may have important roles in catalysis. For example chloro*tris*(triphenylphosphine)rhodium (I) is employed in the hydrogenation of α-olefins but the complex itself almost certainly is not the catalytic species. Recent results[42] indicate that hydrogen addition and phosphine dissociation precede olefin coordination; this suggests that the species reactive towards olefins is complex *(101)*.

Hydroformylation is more complex since both hydrogen and carbon monoxide must be coordinated during the catalytic cycle. Wilkinson has shown that a number of rhodium-phosphine species are formed on reaction of hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) with a 1:1 mixture of hydrogen and carbon monoxide, the identification of these complexes rests chiefly on infra-red spectral evidence.[16] Other types of rhodium-phosphine complexes have been examined as hydroformylation catalysts. For example the cationic diolefin complex *(102)*, in the presence of triethylamine is effective for the conversion of 1-hexene into *n*-heptanal.[98] No attempt was made to identify possible reaction intermediates, although



(101)

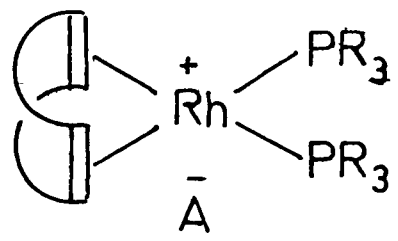


(102)

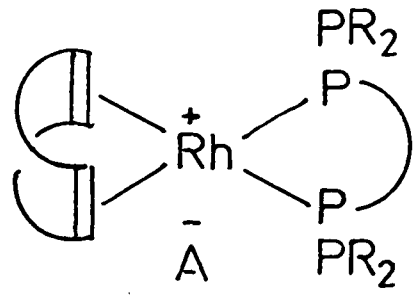
hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) was isolated by the evaporation of catalytic solutions containing added triphenylphosphine. *Trans-bis*(triphenylphosphine)carbonylchlororhodium has been employed in hydroformylation and normally catalysis is preceded by an induction period which is reduced in the presence of triethylamine.[17] Addition of excess triphenylphosphine allows hydrido-carbonyl*tris*(triphenylphosphine) rhodium (I) to be isolated. Thus different procatalysts may lead to similar or identical catalytic species under hydroformylation conditions.

2.1. *Reaction of diolefin rhodium tetrafluoroborates with hydrogen in methanol*

For the reaction of complexes of type *(103)* and *(104)* with hydrogen it is most pertinent to examine monophosphine and chelating biphosphine rhodium complexes separately.



(103)



(104)

Reaction solutions were examined principally by phosphorus-31 NMR spectroscopy and secondly by ^{1}H-NMR. Phosphorus-rhodium coupling constant values are highly dependent on the nature of Rh-P bonds which in turn are influenced by the presence of other ligands ligated to the metal centre.

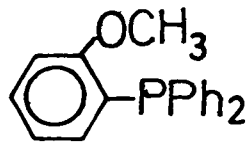
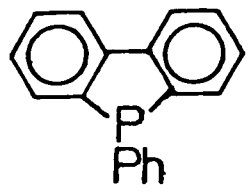
(i) Monophosphines

The spectral data pertaining to the hydrogenation products of complexes *(85)* to *(88)* is recorded in Table II.2.1.

Bicyclo [2.2.1] hepta-2,5-diene *bis*(triphenylphosphine)rhodium (I) tetrafluoroborate *(85)* reacted with hydrogen to form the dihydride *(105)*, whose ^{31}P-NMR spectrum shows a characteristic $J_{P,Rh}$ coupling constant of *ca.* 120 Hz, typical of *trans*-phosphorus coordination. On standing under argon a second species becomes apparent and this is the solvate complex *(106)* (Figure II.2.1). In this latter compound the $J_{P,Rh}$ coupling constant is *ca.* 200 Hz indicating phosphorus coordinated to

Table II.2.1

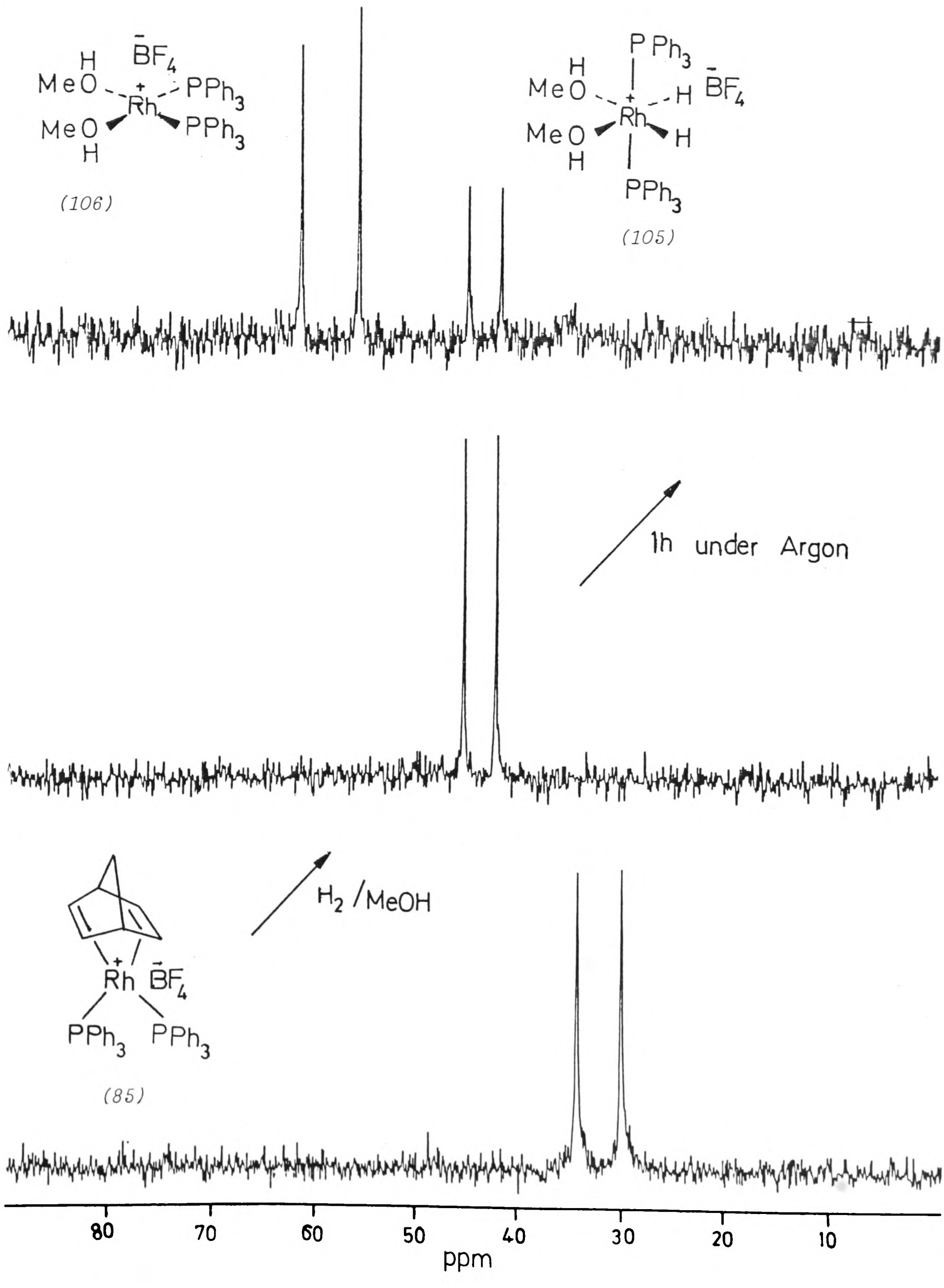
^{31}P- and ^{1}H-NMR of hydrogenated solutions of *bis*(monophosphine)rhodium complexes in methanol

Rhodium Phosphine Complex		^{31}P NMR				^{1}H NMR		
		Methanol Solvate		Dihydride		Hydride region		
		δ(ppm)	$J_{P,Rh}$(Hz)	δ(ppm)	$J_{P,Rh}$(Hz)	δ(ppm)	$J_{H,P}$	$J_{H,Rh}$Hz
(85)	PPh_3	57.1	207	41.8	120	-22.5	17	25
(86)								
(87)		Not Observed		37.2	120	-22.1	16	28
(88)		48.4	194	34.8	118	-21.7	17	23

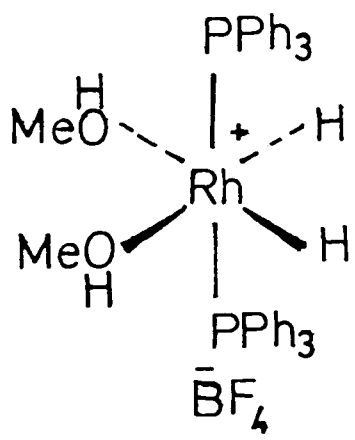
rhodium with a *trans*-oxygen atom. Strong electronegative σ-donors such as alcohols increase the relative contribution of σ-bonding in the *trans*-P-Rh bond leading to higher coupling constant values; thus P-Rh bonds

Figure II.2.1

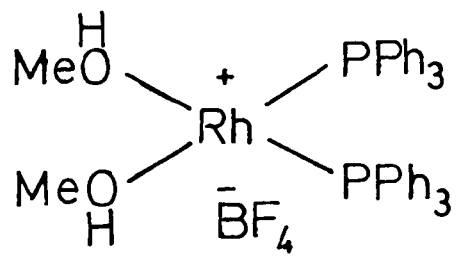
The Hydrogenation of Bicyclo [2.2.1] heptadiene *bis*(triphenylphosphine)-rhodium (I) tetrafluoroborate *(85)* in methanol monitored by ^{31}P-NMR spectroscopy.



trans to π-acidic olefins have lower $J_{P,Rh}$ values of *ca.* 150 Hz. The generality of *ca.* 200 Hz coupling constant values for solvate complexes and *ca.* 120 Hz for dihydride complexes analogous to compounds *(106)* and *(105)* has been established in a large number of cases.[105-111]



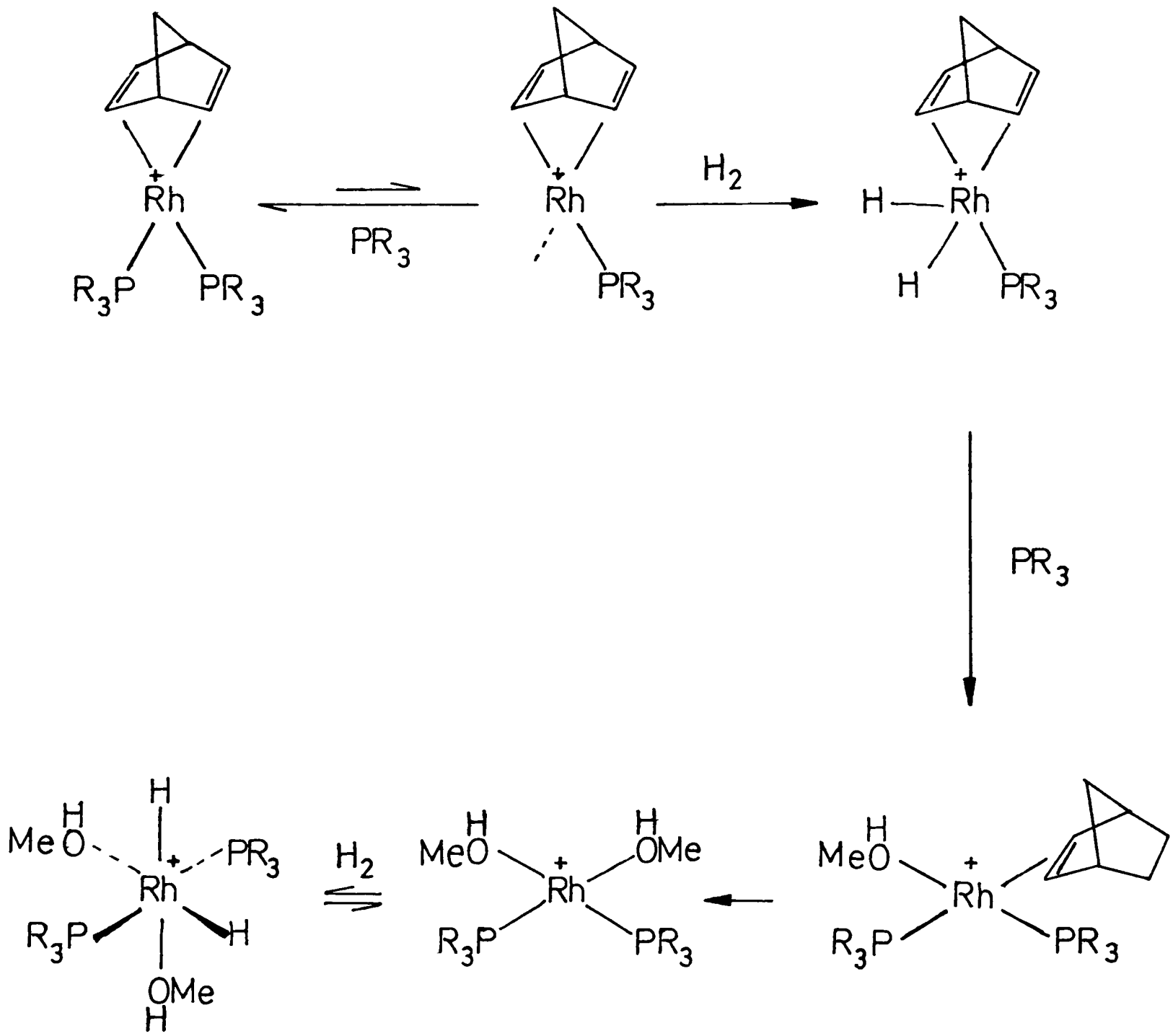
(105)



(106)

The dihydride *(105)* had previously been observed[105] but it had been assumed that triphenylphosphine normally preferred *trans*-chelation and did not form solvates. Complex *(106)* may well be oligomeric[92] since decomposition of the dihydride *(105)* decreases rapidly with increasing concentration. At the lowest concentration investigated (0.01 M) hydrogenation of complex *(85)* produced solely the dihydride *(105)*, and the spectrum did not change on standing. At a concentration of 0.025 M observations similar to those above were made, but the second species *(106)* became evident on removal of hydrogen from the reaction solution. When a solution of 0.05 M concentration was hydrogenated, both species *(105)* and *(106)* were observed immediately and complex *(106)* was formed exclusively on standing.

The reaction of hydrogen with cationic rhodium-phosphine complexes of type *(103)* had previously been investigated by a number of other workers [111] and the course of the reaction (Scheme II.2.1) is thought to be as shown below:

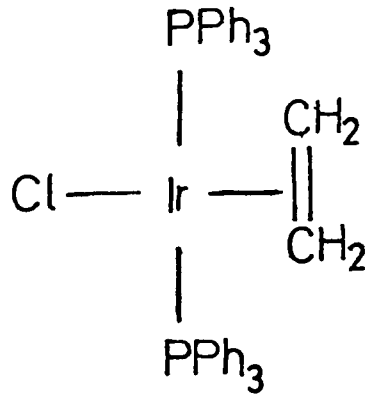


Scheme II.2.1

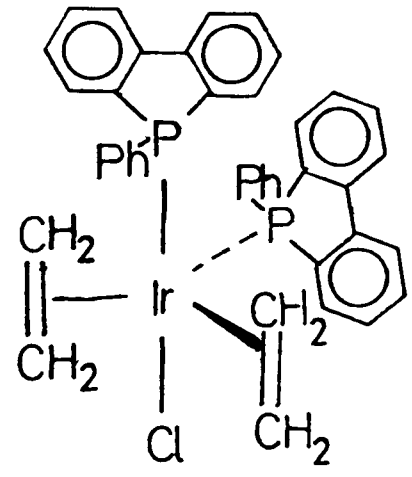
Several examples of cationic dihydridorhodium complexes exist, and in some cases isolation and full characterization is possible.[105] The involvement of oxygen in the rhodium coordination environment of solvate

complexes has been established by Stults and co-workers using extended X-ray absorption fine structure techniques (EXAFS).[112]

The equilibrium between dihydride and solvent complexes (Scheme II.2.1) appears to be dependent on the nature of the phosphine (PR_3). For example when the 5-phenyl-5*H*-dibenzophospholediolefin complex *(88)* was hydrogenated, both solvate and dihydride complexes were observed under conditions where the triphenylphosphine complex *(85)* gave only dihydride. This unexplained preference for *cis*-phosphole ligands has been noted in iridium chemistry.[113] Dichlorotetra(ethylene)diiridium reacts with triphenylphosphine to give the square planar *trans-bis*(triphenylphosphine) complex *(107)*; the similar reaction employing 5-phenyl-5*H*-dibenzophosphole in place of triphenylphosphine produces a 5-coordinate



(107)



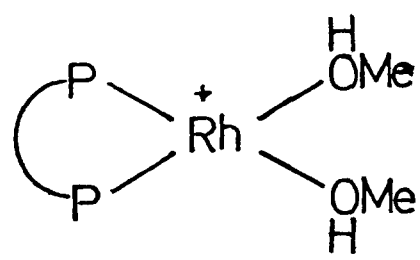
(108)

iridium complex *(108)* with *cis*-phosphole ligands. The remaining *bis*-(monophosphine)diolefin complex examined was complex *(87)*, which contained 2-methoxyphenyldiphenylphosphine *(59)* ligands and only gave rise to a dihydride complex on reaction with hydrogen. This selectivity may be due

to unfavourable inter-ligand Ph-Ph repulsions destabilizing the solvate complex with respect to oxidative addition of hydrogen.

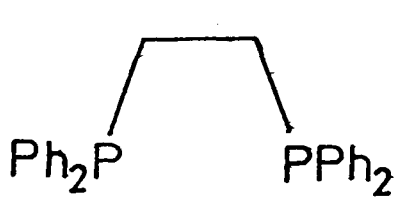
(ii) Chelating biphosphines

There are several examples of biphosphines which form medium ring chelates to rhodium and thus only produce solvate complexes *(109)* of the type shown below:

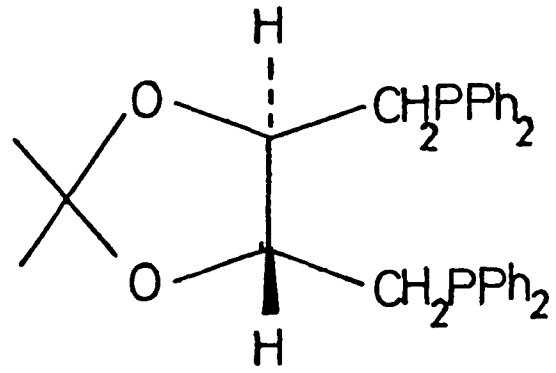


(109)

Halpern and co-workers [106] were the first to observe that 1,2-*bis*(diphenylphosphino)ethane *(110)* has a rhodium solvate which shows no affinity for hydrogen. Similar behaviour is exhibited by the asymmetric phosphine *(111)* which forms a seven ring chelate at rhodium.[108]



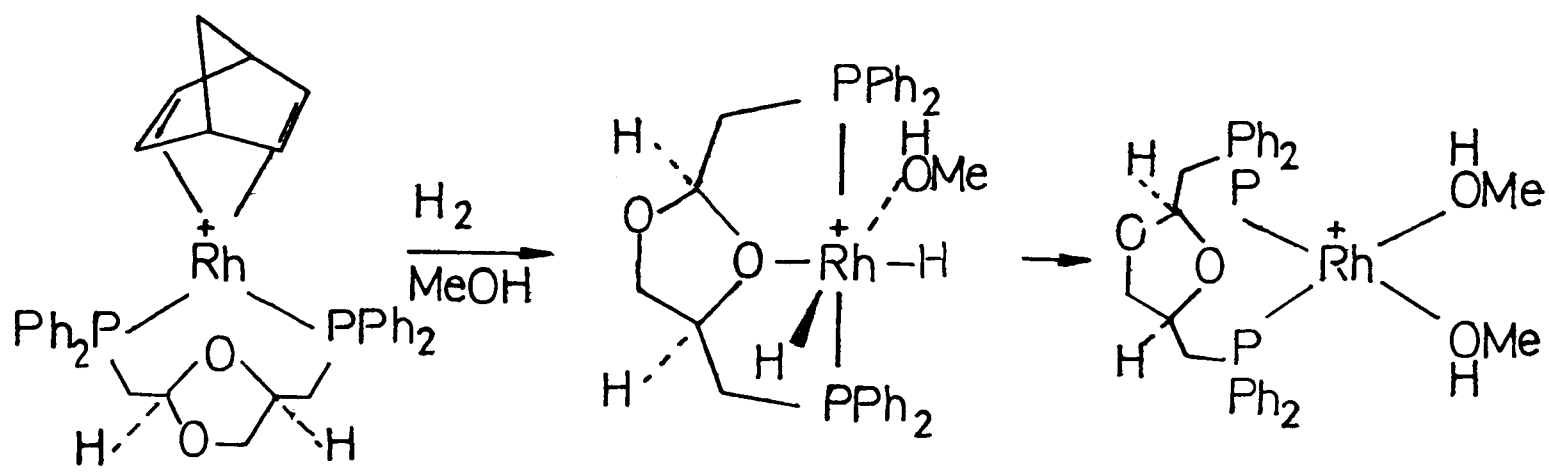
(110)
(DIPHOS)



(111)
(DIOP)

Examples of *trans*-chelate rhodium dihydrides are scarce. The sugar derived biphosphine rhodium diolefin complex *(112)* gives the *trans*-phosphine

dihydride *(113)* on reduction with hydrogen, although on standing under argon this is converted to a solvent adduct *(114)* of the type described above.[114] Both of these complexes may be observed under conditions of hydrogenation.

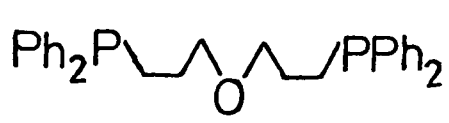
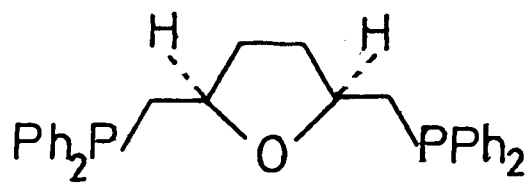
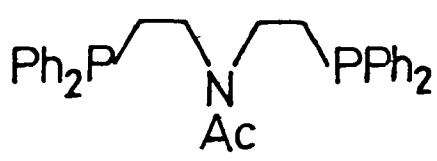
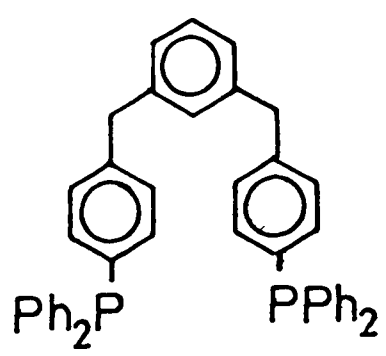


(112) *(113)* *(114)*

The rhodium complexes of biphosphines *(62)* to *(67)* were subjected to treatment with hydrogen in methanol and the products analysed by ^{1}H- and ^{31}P NMR spectroscopy (see Tables II.2.2 and II.2.3). In all cases, exposure of the solution to hydrogen and agitation discharged the characteristic orange colour of the diene complex in *ca.* 20 seconds. Bicyclo [2.2.1] hepta-2,5-diene-1,5-*bis*(diphenylphosphino)pentane rhodium (I) tetrafluoroborate *(89)* was investigated first and its reaction with hydrogen in methanol produced a ^{31}P-NMR spectrum more complex than was observed in earlier cases. Monitoring the reaction by this latter technique shows that two species were formed initially, a complex *(115)* with a $J_{P,Rh}$ coupling constant characteristic of a solvent adduct (202 Hz) and a second complex *(116)* of coupling constant 132 Hz. Further hydrogenation produced a new species *(117)* (consistent with a dihydride structure) with concurrent decrease in the amount of complex *(116)*.

Table II.2.2.

^{31}P NMR spectra of biphosphinerhodium (I) complexes in methanol

Diolefin Complex	Phosphine	Methanol Solvate		Dihydride	
		δ(ppm)	$J_{P,Rh}$(Hz)	δ(ppm)	$J_{P,Rh}$(Hz)
(89)		39.4	202	33.0	118[a]
(90)		Not Observed		45.1	120
(91)		47.9	204	31.7	118[b]
(92)		Not Observed		48.1	119
(93)		51.7 and 46.2 ($J_{P,P}$ 64 Hz)	202 and 200	Not Observed	
(94)		Not Observed		40.2	120

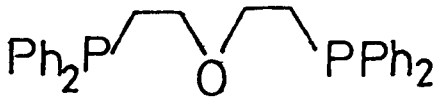
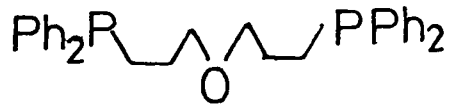
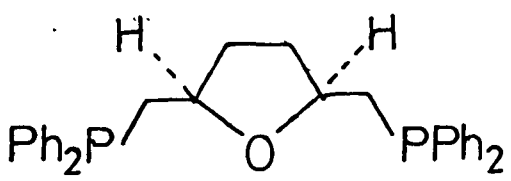
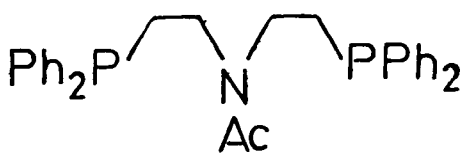
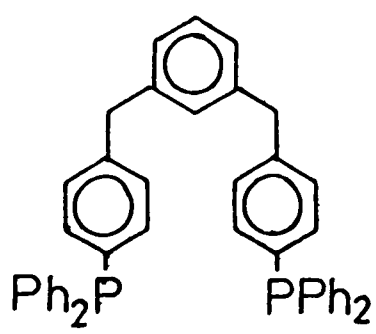
[a] The initial hydridic species is a monohydride formed by C-H insertion, δ 51.6 ppm $J_{P,Rh}$ 132 Hz.

[b] Final hydridic product. The other hydridic products formed initially are δ 34.3 $J_{P,Rh}$ 118 Hz and δ 34.7 $J_{P,Rh}$ 118 Hz.

Table II.2.3

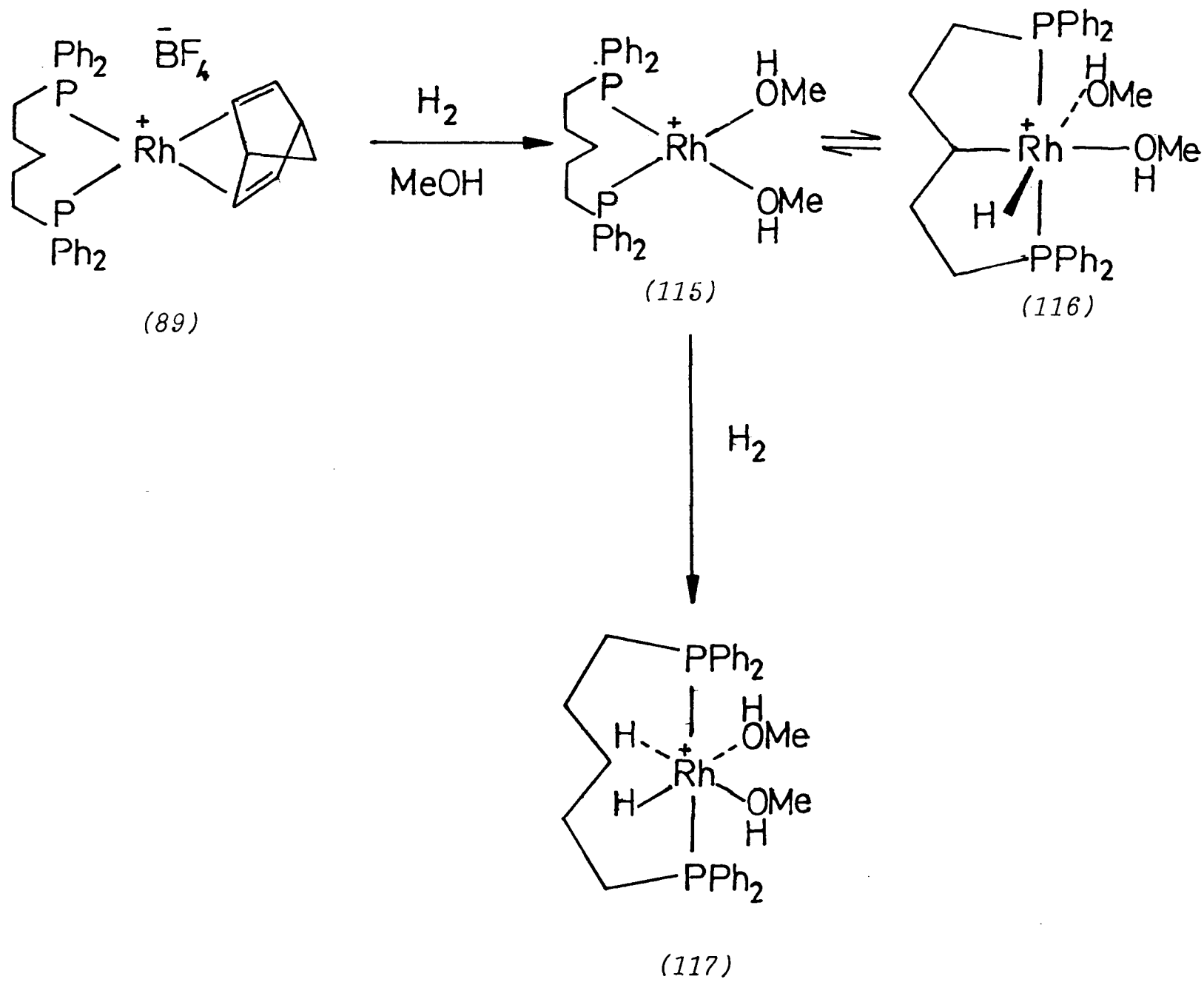
^{1}H-NMR spectra of biphosphine rhodium (I) complexes

in methanol-d_4

Diolefin Complex	Phosphine	Dihydride δ(ppm)	$J_{H,P}$	$J_{H,Rh}$	$J_{H,H}$
(89)		-22.9	11	32	-[b]
(90)		-19.2 and -21.6	14	27	14
(91)		-21.9 and -22.3	14	28	14[a]
(92)		-18.7 and -21.8	13	26	13
(93)		Not Observed			
(94)		-22.5	multiplet		

[a] Final hydridic product. The other hydridic products formed initially are δ-22.8 ppm $J_{H,P}$ 18 Hz, $J_{H,Rh}$ 25 Hz and δ -22.6 ppm $J_{H,P}$ 15 Hz, $J_{H,Rh}$ 25 Hz; [b] C-H insertion product δ 22.5, $J_{P,Rh}$ 31.7 Hz, $J_{H,P}$ 11 Hz.

Monitoring the hydrogenation by ^{1}H-NMR gives more specific information (Figure II.2.2). The initial single high-field hydridic species *(116)* which shows phosphorus and rhodium couplings is gradually replaced by a second species *(117)*, with similar coupling constants, at higher field. If the reduction is carried out with deuterium in place of hydrogen this second species *(117)* is not observed but the first *(116)* is unaffected. The NMR spectra of complexes *(115)* to *(117)* are consistent with the structures presented in Scheme II.2.2.



(89) *(115)* *(116)*

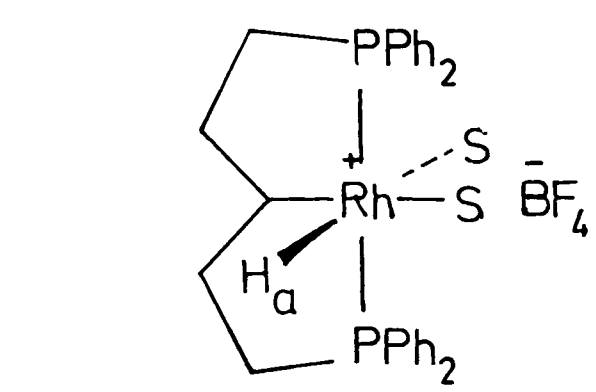
(117)

Scheme II.2.2

Since the two phosphorus atoms of complex *(116)* are equivalent it is likely to be the product of insertion at the γ-carbon atom of the chain. Complexes *(115)* and *(116)* are always formed together in comparable amounts

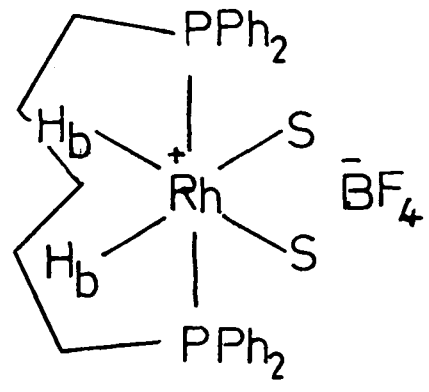
Figure II.2.2

The reaction of bicyclo[2.2.1]hepta-2,5-diene-1,5-*bis*(diphenylphosphino)-pentanerhodium(I) tetrafluoroborate *(89)* with (A) hydrogen and (B) deuterium in methanol monitored by ^{1}H-NMR spectroscopy.

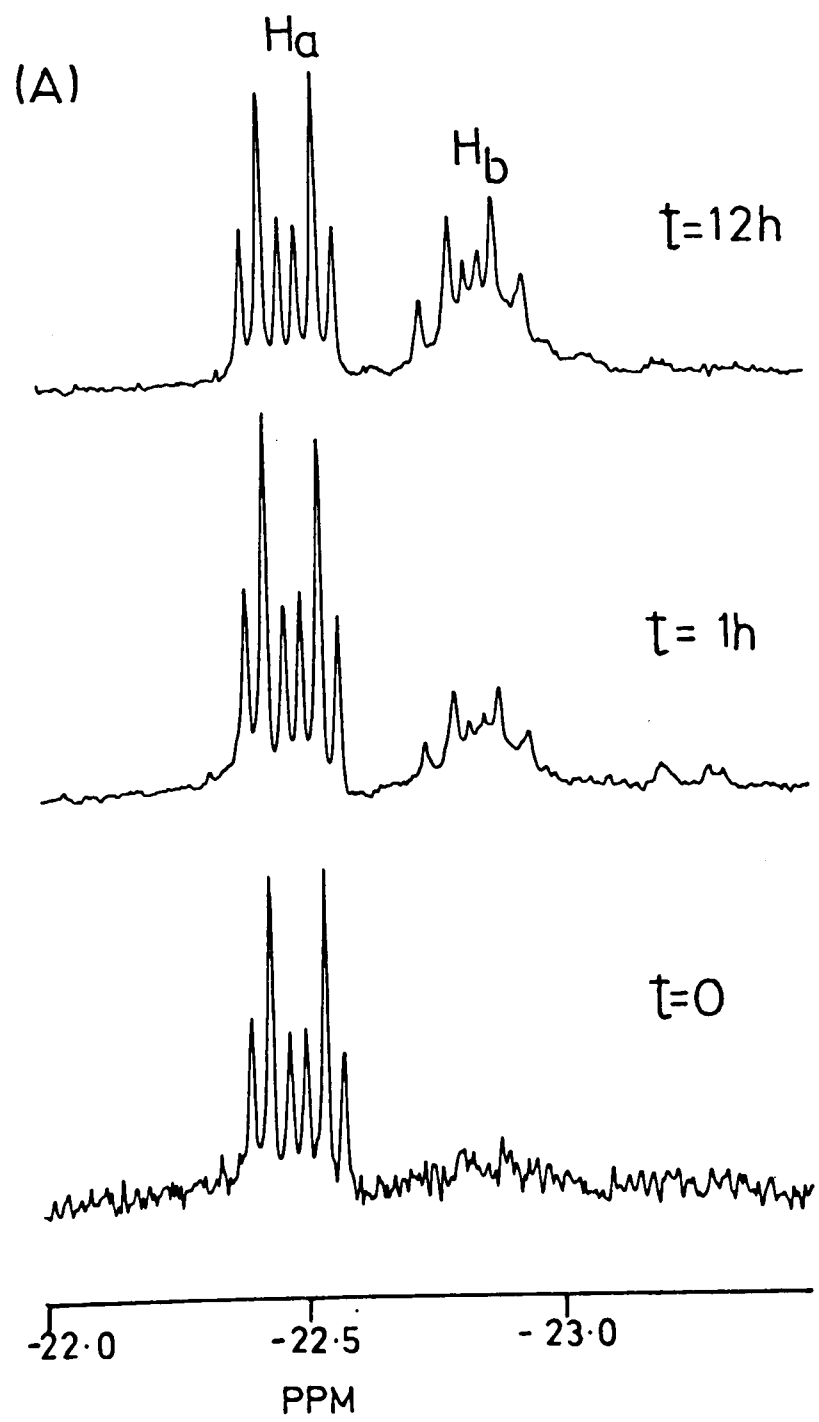


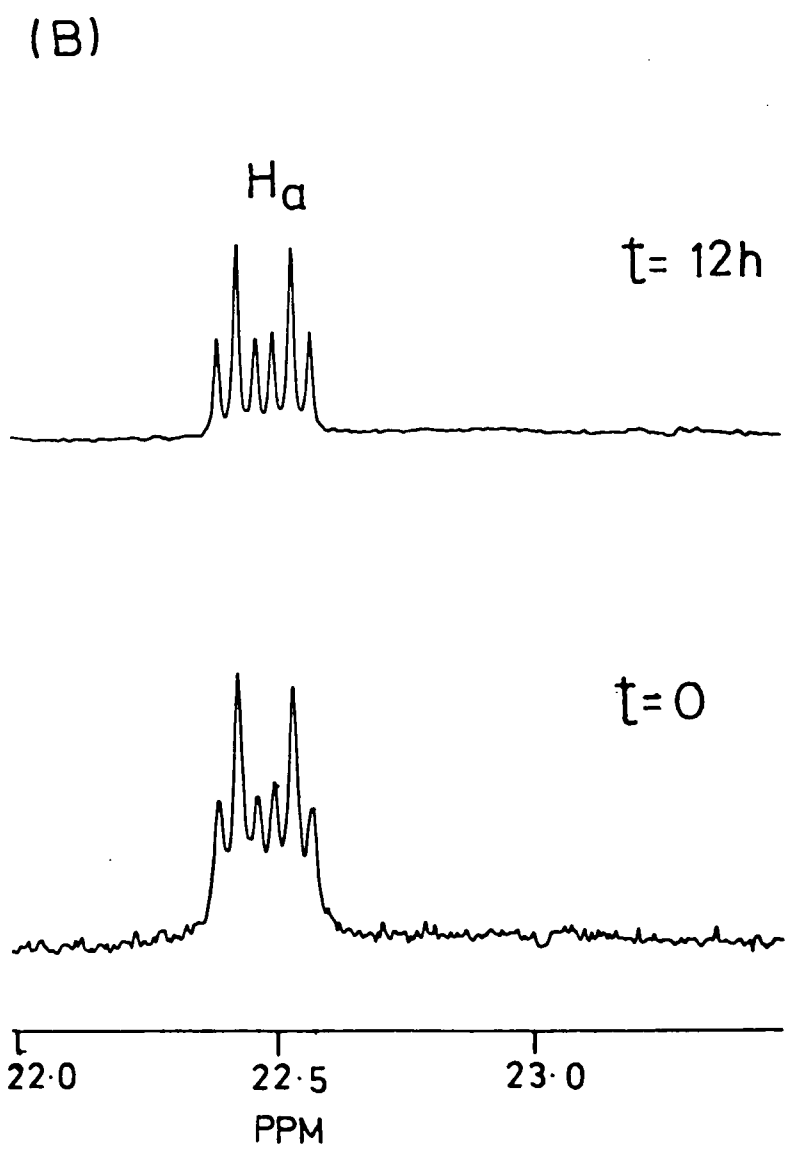
(116)

(S= MeOH)



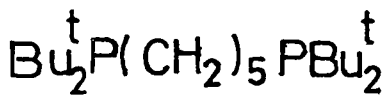
(117)



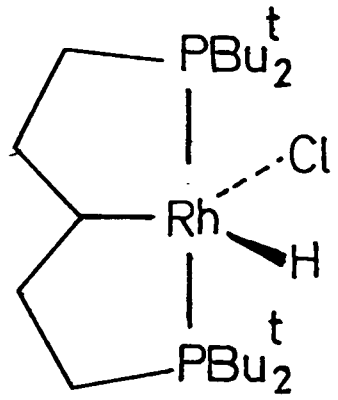


and disappear simultaneously, and thus they must be in rapid equilibrium. The CH insertion is likely to form and break down by a stereospecific process because reduction by deuterium and regeneration of the diolefin complex *(89)* by addition of norbornadiene does not incorporate deuterium into the interphosphine chain (shown by field desorption mass spectroscopy).

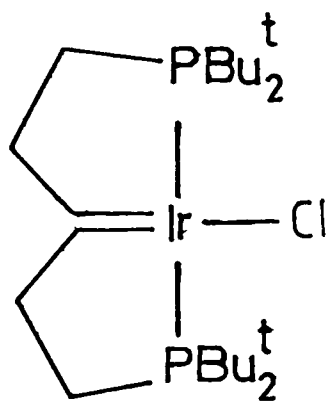
There are several examples of alkane activation reactions particularly in rhodium and iridium chemistry. For example, using 1,5-*bis*(di-*t*-butylphosphino)pentane *(118)* complexes *(119)* and *(120)* have been characterized.[115] Dehydrogenation preceded by alkane activation has been observed in the formation of the rhodium complex *(121)* by Bennett and co-workers.[116]



(118)



(119)



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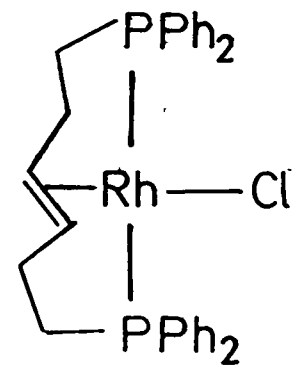


(121)

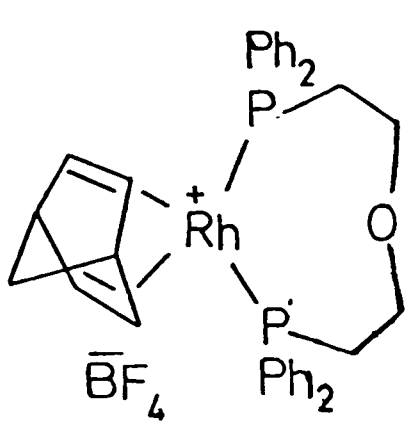
The hydrogenation of bicyclo[2.2.1]hepta-2,5-diene-1,5-*bis*(diphenylphosphino)-3-oxapentane rhodium (I) tetrafluoroborate *(90)* was investigated

by ^{31}P-NMR and showed only one species *(122)*, attributed to a dihydride complex, which persisted on standing under hydrogen or argon. Temperature dependence of the two high-field hydridic signals (by ^{1}H-NMR) was observed (Figure II.2.3); only at the lowest temperature recorded (253^{o}K) can chemical shifts and $J_{H,H}$, $J_{H,P}$ and $J_{H,Rh}$ coupling constants be obtained. On warming the fine structure is lost and line-broadening occurs. The fact that two hydridic signals with the same H-H coupling of 14 Hz are observed suggests that (at 253^{o}K) the interchain oxygen atom is bound to rhodium. The hydride (H_b) is *trans* to solvent and occurs at the normal chemical shift of -21.6 ppm whereas the hydride (H_a) *trans* to chain-oxygen is at lower field (-19.2 ppm). Changes take place in the CH_2 regions of the spectrum overthe same temperature range which are more difficult to interpret. The temperature dependence of the ^{1}H-NMR spectra can be explained by a mechanism involving decoordination and recoordination of solvent. Reduction of the diolefin complex *(90)* by hydrogen deuteride [generated by the reaction of methanol with lithium aluminium deuteride] gives hydride signals (253^{o} K) with chemical shifts very similar to those of complex *(122)*, but the H-H coupling is absent (Figure II.2.4). In this latter case two isomeric hydride-deuteride complexes *(123)* and *(124)* are formed analogous to *(122)*.

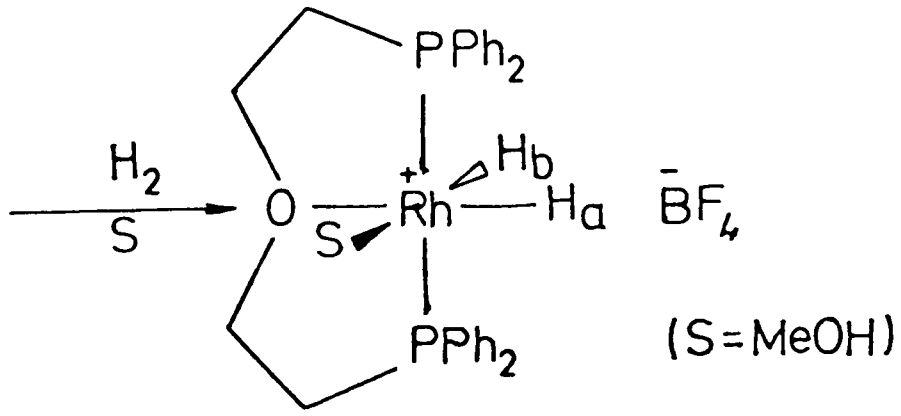
Hydrogenation of bicyclo[2.2.1]hepta-2,5-diene-*cis*-2,5-*bis*(diphenylphosphinomethyl)tetrahydrofuran rhodium (I) tetrafluoroborate *(92)* in methanol showed similar behaviour to that of the acyclic analogue *(90)* above. Only one species, a dihydride *(125)* was identified by ^{31}P-NMR and the temperature dependence of the high-field hydride signals by ^{1}H-NMR is shown in Figure II.2.5.

Figure II.2.3.

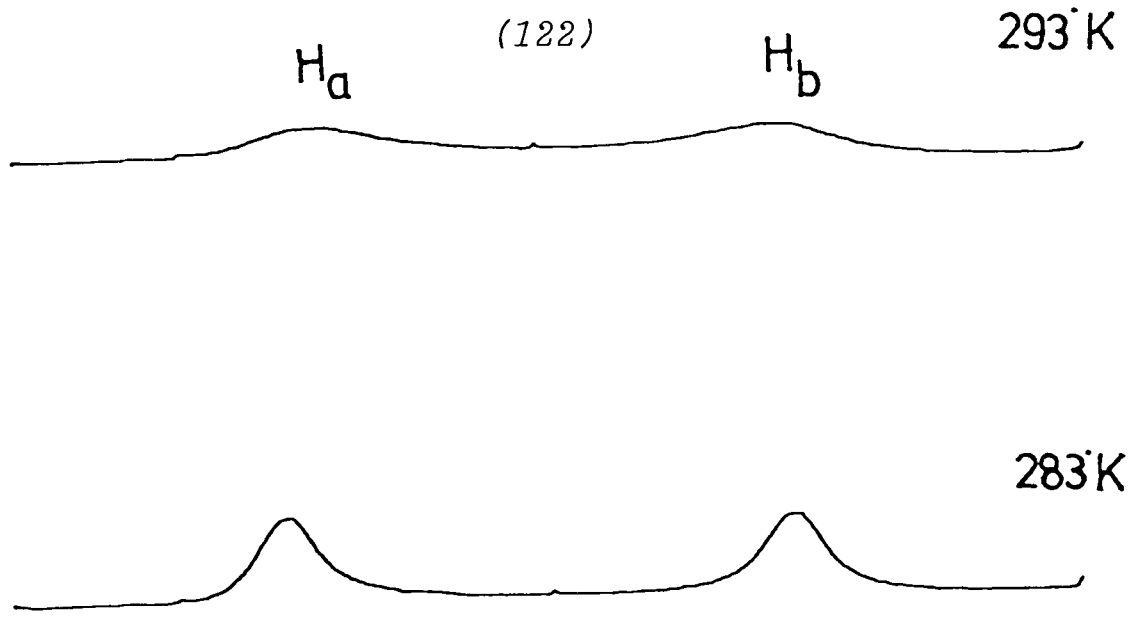
Reduction of rhodium-diolefin complex *(90)* in methanol, monitored by ^{1}H-NMR



(90)



(122)



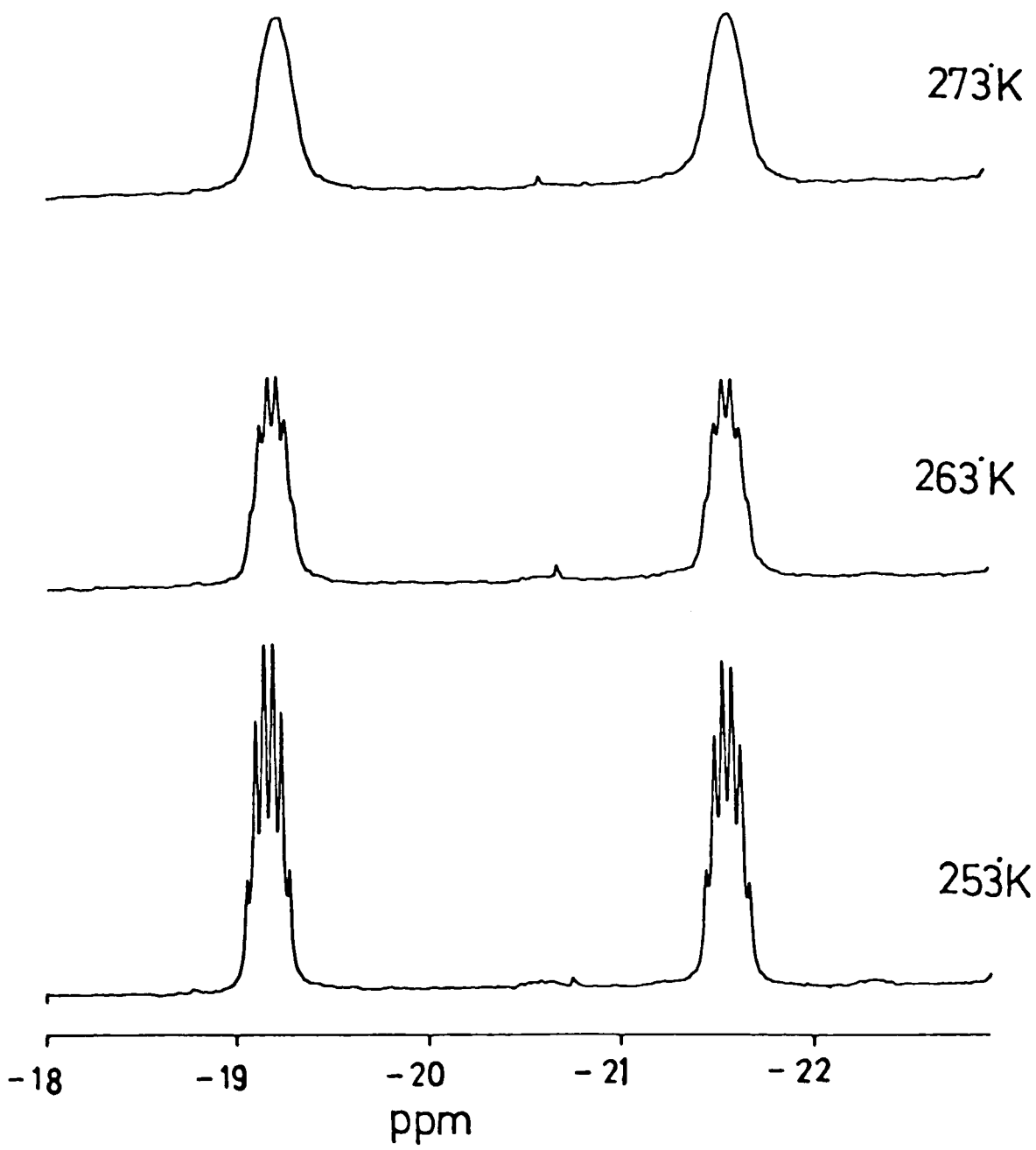
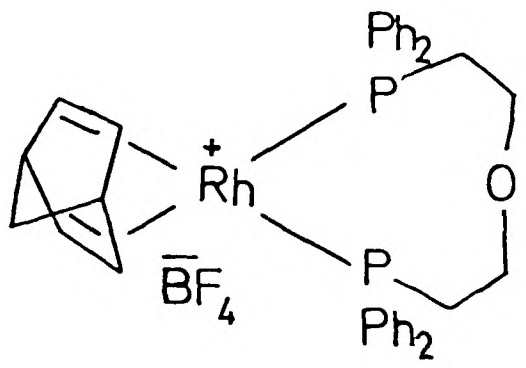


Figure II.2.4

Reduction of rhodium-diolefin complex *(90)* by (a) hydrogen deuteride and (b) hydrogen in methanol, monitored by ^{1}H-NMR



(90)

(a) HD or (b) H_2 → MeOH

(a) *(123)*, *(124)*

(b) *(122)*

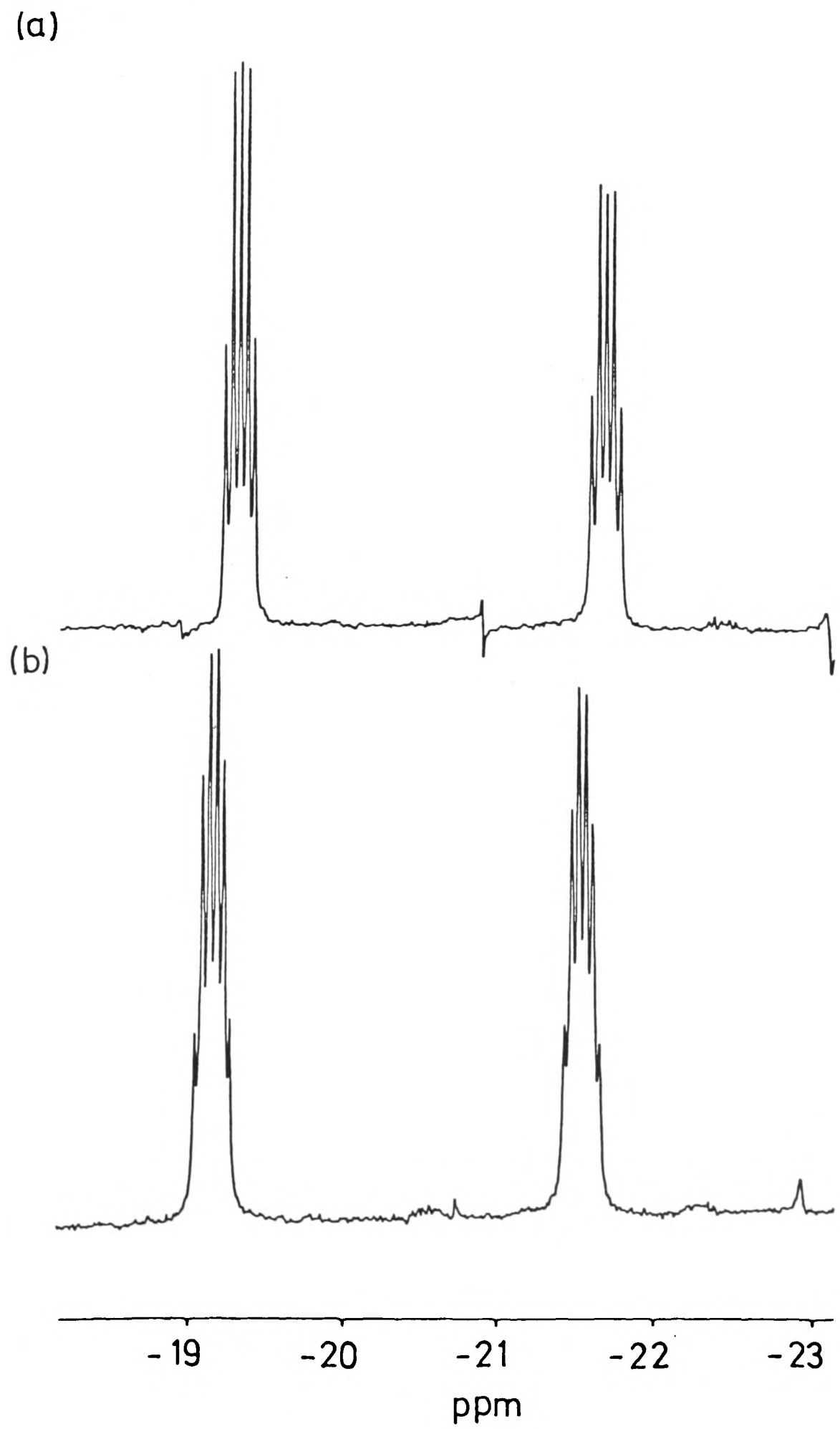
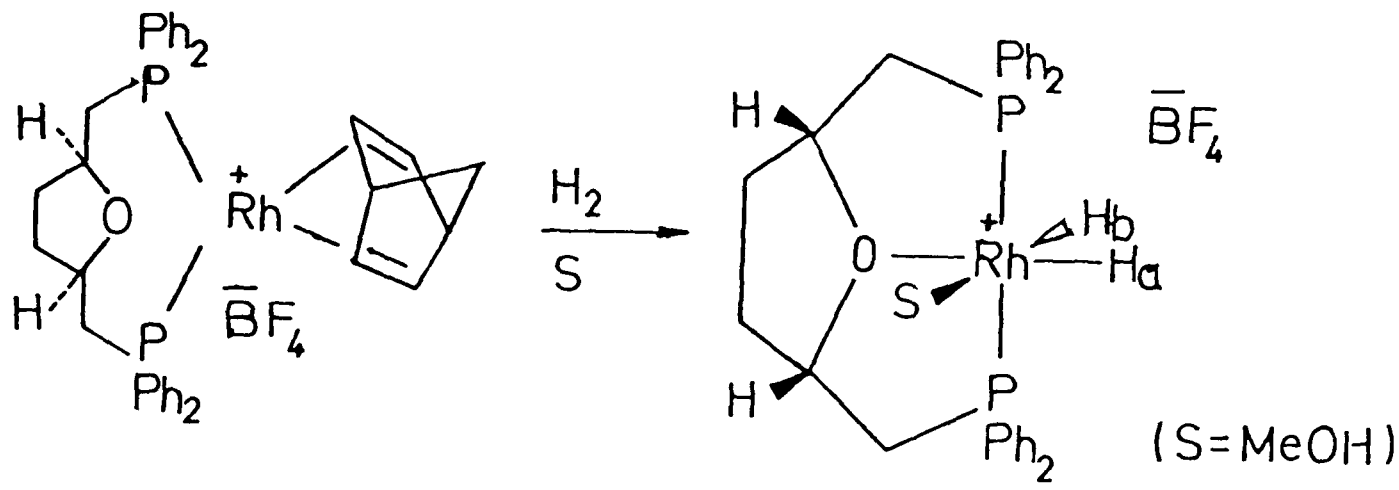


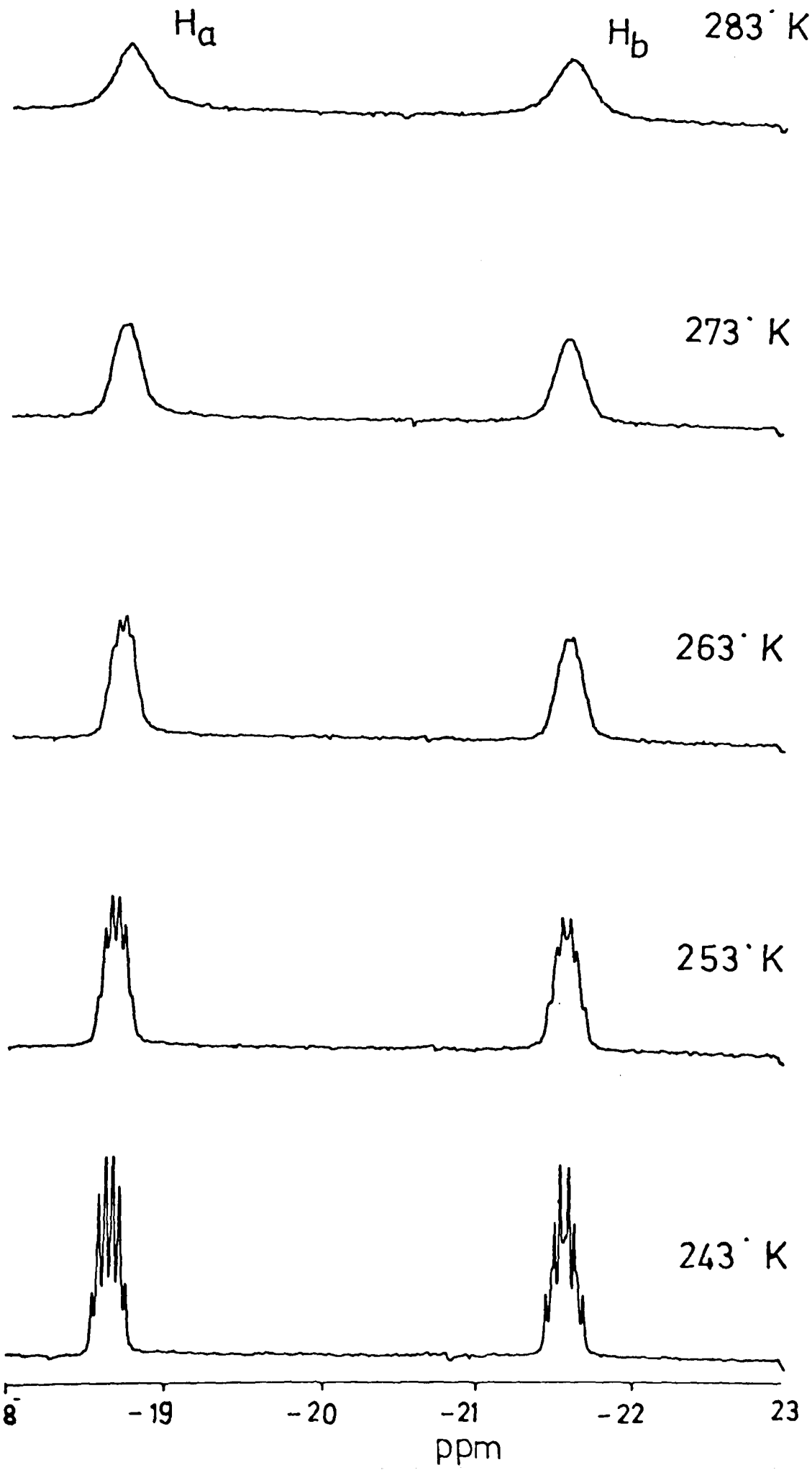
Figure II.2.5

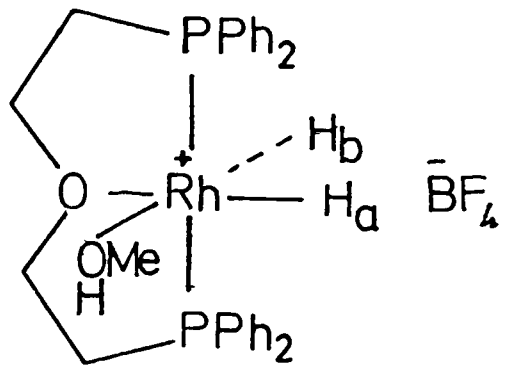
Reduction of rhodium diolefin complex *(92)* in methanol, monitored by ^{1}H-NMR



(92)

(125)a

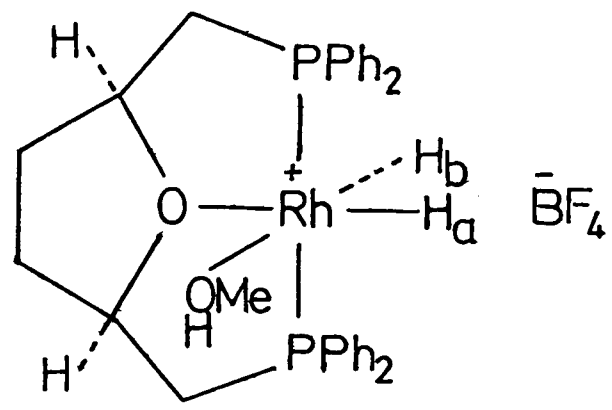




(122)

(123) H_a = D, H_b = H in *(122)*

(124) H_a = H, H_b = D in *(122)*

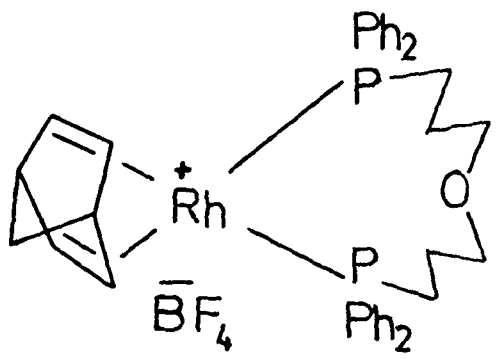


(125)b

Hydrogenation of the homologous biphosphine complex *(91)* was similarly investigated. Four species were observed by ^{31}P-NMR (Figure II.2.6) in experiments at differing time intervals. Initially the spectrum consists of a major dihydridic species *(127)* ($J_{P,Rh}$ 118 Hz) and minor amounts of a solvate complex *(126)* ($J_{P,Rh}$ 204 Hz; possibly oligomeric) and a further two species *(128)* and *(129)* with identical coupling constants and similar chemical shifts to those of the complex

Figure II.2.6

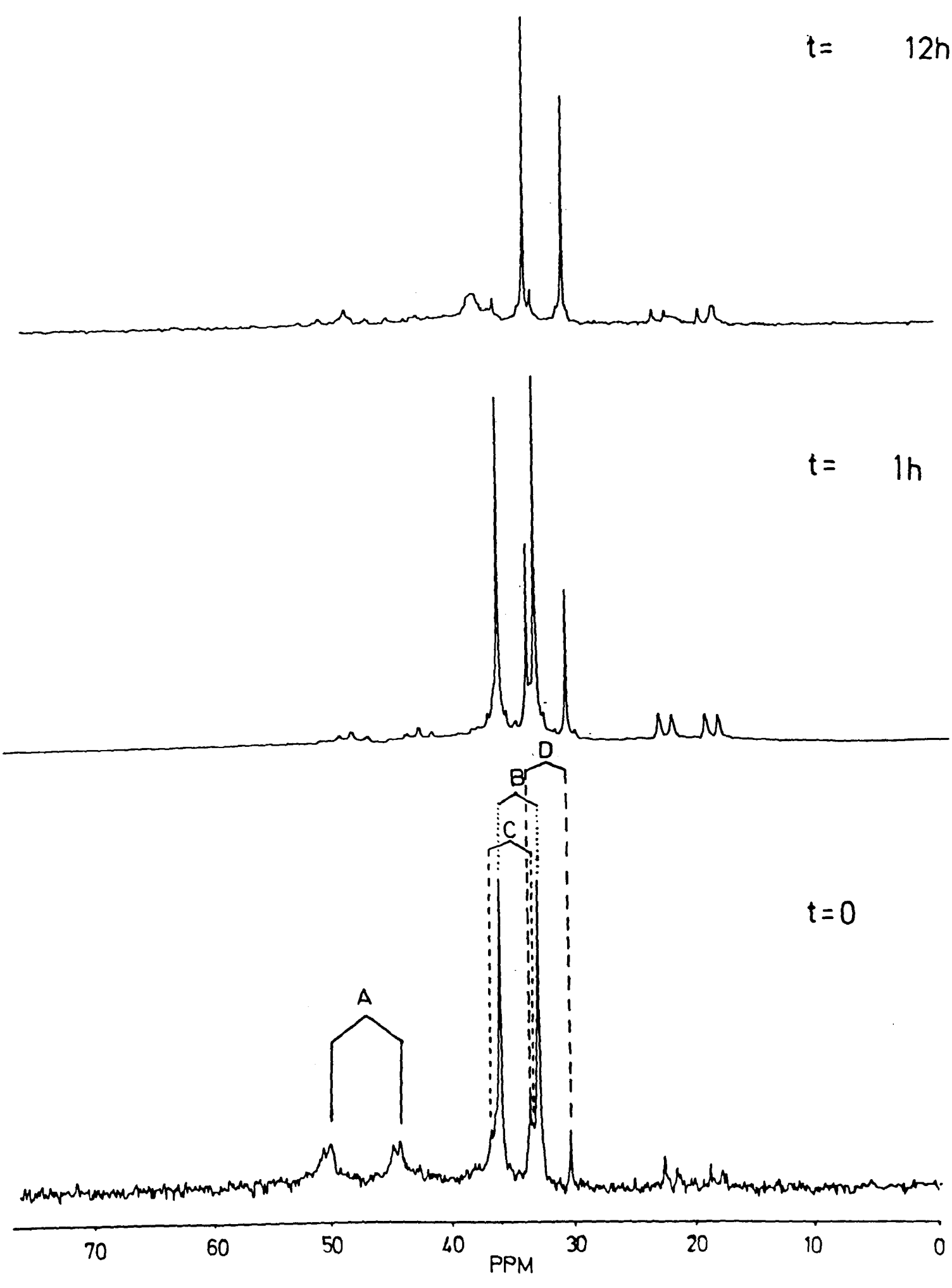
Reduction of rhodium diolefin complex *(91)* in methanol, monitored by ^{31}P-NMR



(91)

H_2 / MeOH

A = *(126)*
B = *(127)*
C = *(128)*
D = *(129)*



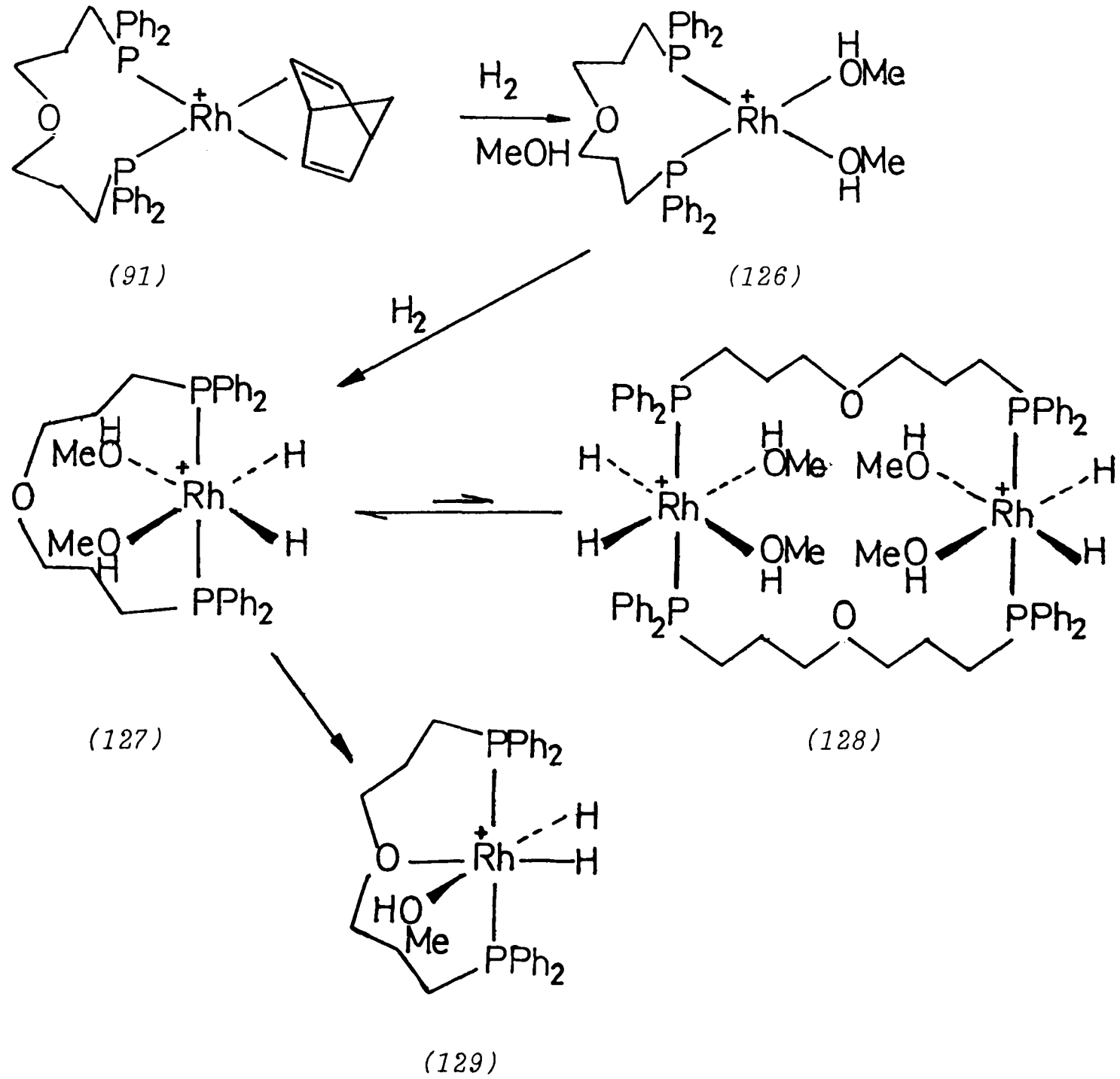
(127). The relative proportions of complexes *(127)* and *(128)* varied between experiments depending on concentration of the starting material *(91)* and reaction time. Insertion into C-H of the inter-phosphine chain was deemed not to have taken place since this would render the *trans*-coordinated phosphorus atoms inequivalent, which is not consistent with the observed coupling pattern, *i.e.* only P-Rh coupled doublets were observed. On standing under hydrogen the proportion of species *(126)*, *(127)* and *(128)* decreased relative to complex *(129)* until only the latter was observed. ^{1}H-NMR was employed to obtain more information about the hydridic complexes *(127)*, *(128)* and *(129)*.

Table II.2.4

Spectral data pertaining to complexes *(126)* to *(129)*

	^{31}P-NMR		^{1}H-NMR			
Complex	δ(ppm)	$J_{P,Rh}$ (Hz)	δ(ppm)	$J_{H,P}$	$J_{H,Rh}$	$J_{H,H}$ (Hz)
(126)	47.9	204			-	
(127)	34.3	118	-22.8	18	25	-
(128)	34.7	118	-22.6	15	25	-
(129)	31.7	118	-21.9 and -22.3	14	28	14

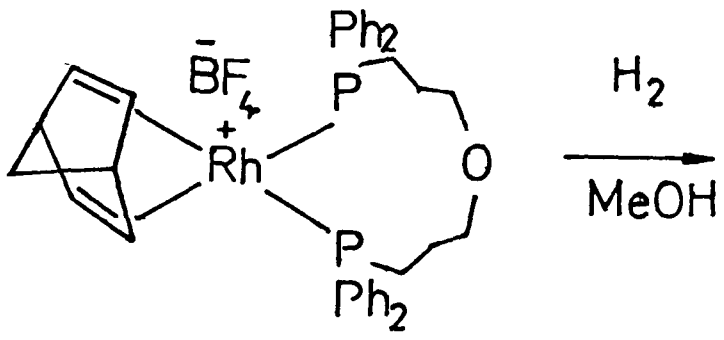
Hydrogenation of complex *(91)* in methanol-d_4 and immediate observation of the ^{1}H-NMR spectra always showed a mixture of the three species *(127)* to *(129)*, although the relative proportions varied in a manner similar to that described earlier. Figure II.2.7 illustrates an experiment where all three hydride species have been established [spectrum 1]; on cooling to 247° K [spectrum 4] the resonance at -22.2 ppm changes from a quintet to a double sextet, whereas the other two species *(127)* and *(128)* show no temperature dependence. On warming, the resonance due to species *(129)* reaches coalescence at *ca.* 267° K [spectrum 2] . Scheme II.2.3 illustrates proposed structures for complexes *(126)* to *(129)*.



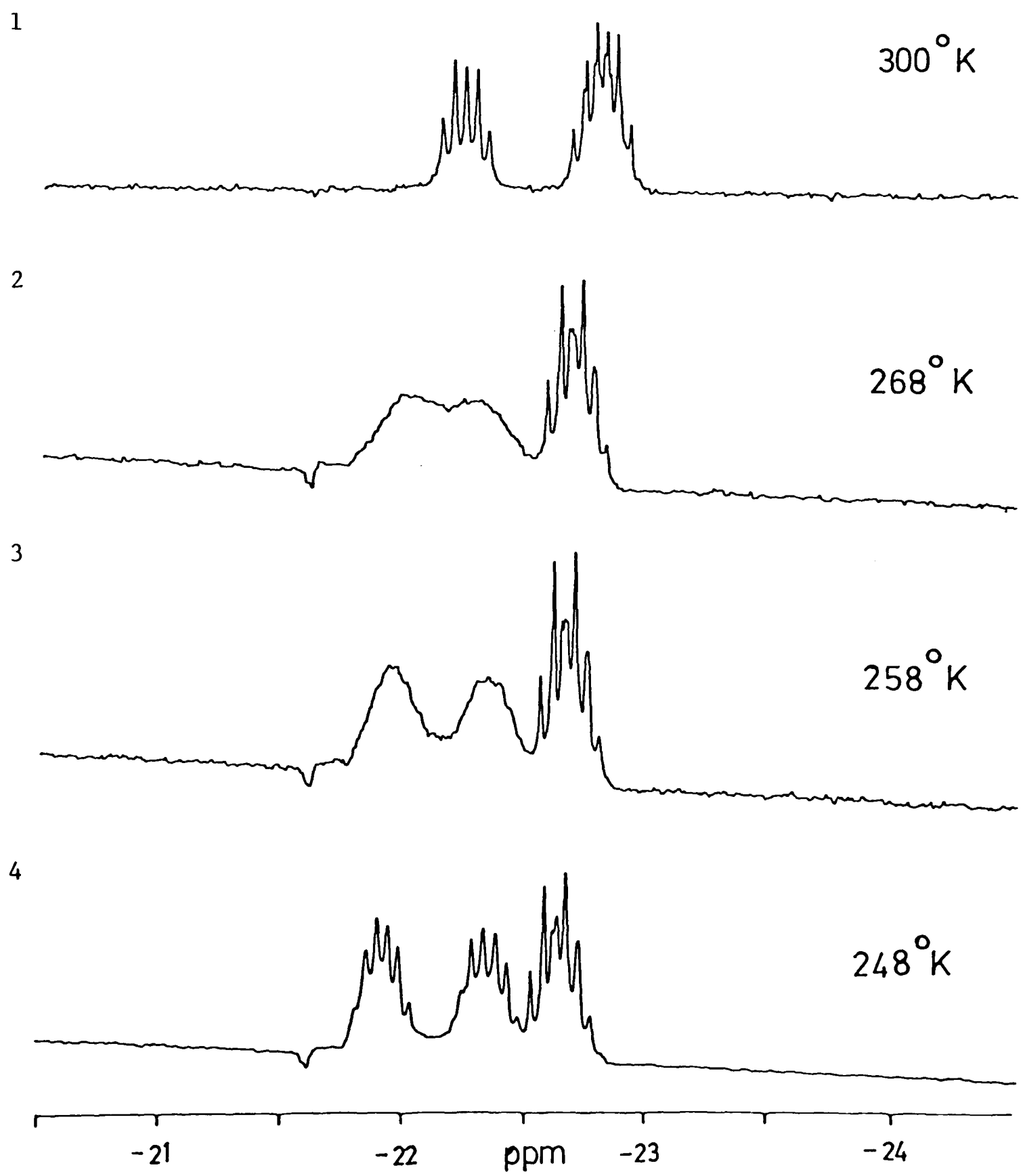
Scheme II.2.3.

Figure II.2.7

Reduction of rhodium diolefin complex *(91)* in methanol, monitored by ^{1}H-NMR spectroscopy



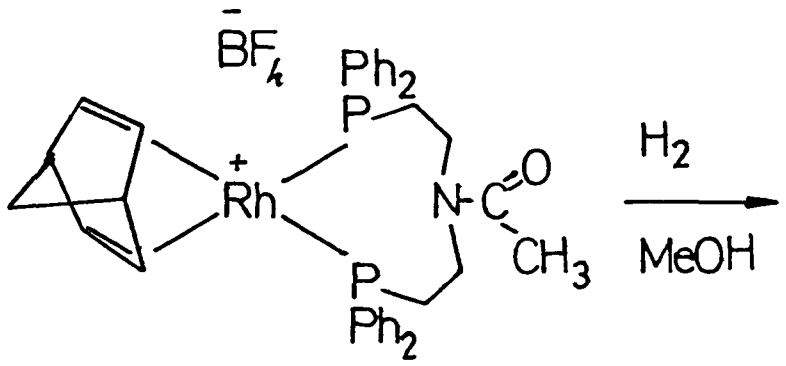
(91)



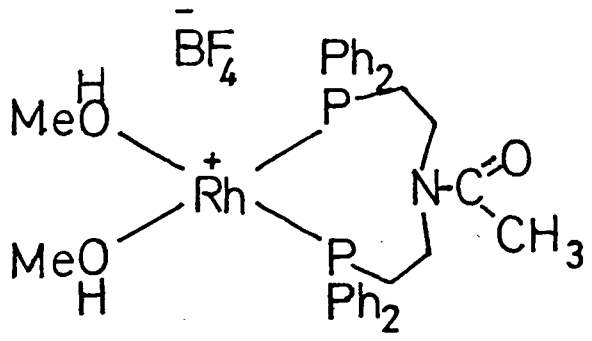
The course of the reaction may be rationalized. Unlike the 3-oxapentane derived complex *(90)* the 1,7-*bis*(diphenylphosphino-4-oxaheptane rhodium complex *(91)* forms a *cis*-chelate solvate adduct *(126)* on hydrogenation. This is due to the phosphine backbone of the latter complex being less rigid. Oxidative addition of hydrogen to the coordinatively unsaturated compound *(126)* produces two dihydrides *(127)* and *(128)*. Weak electrostatic bonding of oxygen to rhodium, or more likely, through H-bonding to coordinated methanol molecules (for which there is precedent [111]) stabilizes complex *(127)* (the major isomer), dimerization of which gives complex *(128)*. The third dihydride complex *(129)* is formed by decoordination of solvent with consecutive coordination of the interphosphine chain oxygen atom. This latter species *(129)* is analogous to complexes *(122)* and *(123)*. The rate of oxygen decoordination/recoordination of complex *(129)* must be faster than the similar process for complex *(122)* since coalescence of hydride signals in the former occurs at *ca.* 268°K whereas the latter requires a temperature greater than 300°K. Presumably this is accounted for by the relative stability of five and six-ring rhodium chelates.

The remaining phosphine with an interphosphine chain substituent is *N*-acetyl-1,5-*bis*(diphenylphosphino)-3-azapentane *(66)*. Reduction of its diolefin complex *(93)* gave only a solvate complex *(130)* but no dihydride even on prolonged hydrogenation. The ^{31}P-NMR spectrum of the solvate complex *(130)* consists of a rhodium coupled AB quartet because restricted rotation of the amide group results in inequivalent phosphorus nuclei.

The rigid biphosphine complex *(94)* was hydrogenated in a similar manner to complexes *(88)* to *(93)*, and formed a dihydride *(131)* identified by ^{31}P- and ^{1}H-NMR spectroscopy. This latter complex decomposed over

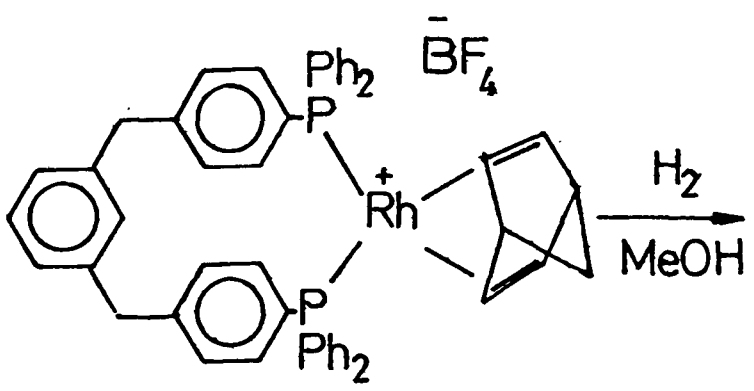


(93)

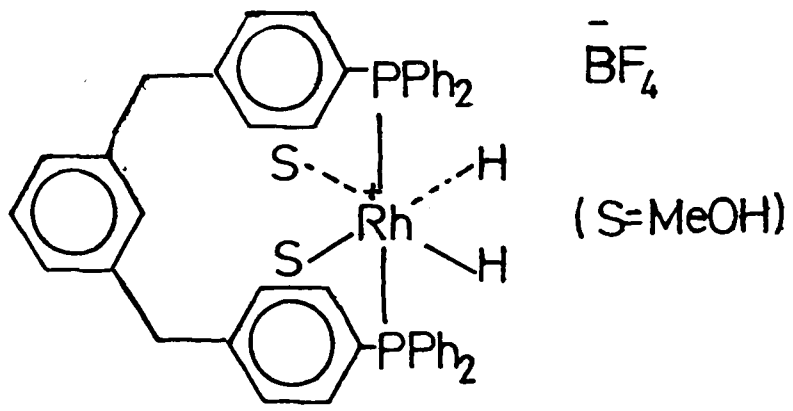


(130)

a period of *ca.* 2 hours with deposition of rhodium metal; possibly solvent coordination in the interligand space is sterically hindered resulting in destabilization of the complex.



(94)



(131)

2.2. *Reaction of diolefin rhodium tetrafluoroborates with hydrogen and carbon monoxide in dichloromethane.*

Reactions of diolefin rhodium phosphine complexes with a 1:1 mixture of hydrogen and carbon monoxide were carried out in dichloromethane so that solvent would not compete with CO for rhodium coordination sites. In each case the reaction was monitored by ^{31}P-NMR and I.R. spectroscopy. Tables II.2.5 and II.2.6 record the spectral information obtained from the experiments described below.

The ~~non~~-~~chelated~~ species *bis*(triphenylphosphine)cycloocta-1,5-diene rhodium(I) tetrafluoroborate *(86)* was first studied and reacted with a 1:1 mixture of hydrogen and carbon monoxide in dichloromethane to form a straw yellow solution. Its ^{31}P-NMR spectrum shows only one species *(132)* undergoing rapid site-exchange at 298^{o}K, but is a clearly resolved doublet at 278^{o}K with a rhodium-phosphorus coupling of 72 Hz; ^{1}H-NMR shows no hydridic signals. This species is stable in solution under an atmosphere of hydrogen and carbon monoxide for periods longer than a week. Addition of an equimolar amount of triethylamine caused the formation of two new species with a concurrent decrease in the amount of the initial complex; the first *(133)* is also a doublet ($J_{P,Rh}$ 113 Hz) the proportion of which decreased as the second species *(134)* slowly increased. The latter compound has a more complex ^{31}P-NMR spectrum and is assigned to a dimeric complex (see Chapter II, section 3 for supportive evidence). Figure II.2.8 shows these changes recorded by NMR spectroscopy.

Addition of equimolar amounts of triethylamine and triphenylphosphine to the species *(132)* resulted in the formation of a third new species hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) (by comparison of the ^{31}P-NMR spectrum with that of an authentic sample). A similar series of spectra were obtained from bicyclo[2.2.1]hepta-2,5-diene*bis*

Table II.2.5

^{31}P NMR spectra of phosphine-rhodium (I) complexes in dichloromethane

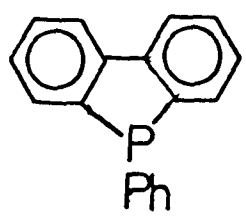
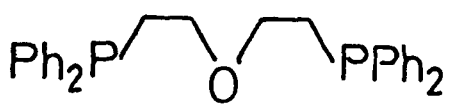
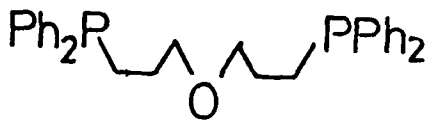
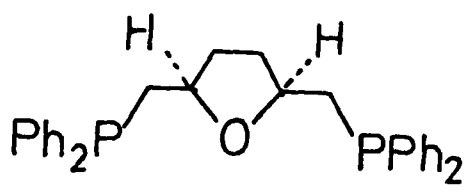
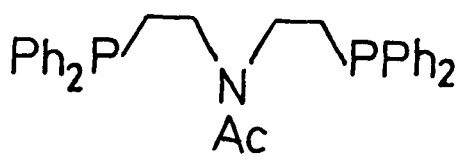
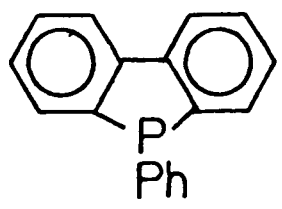
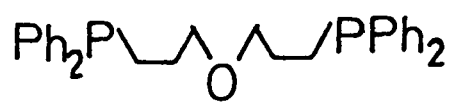
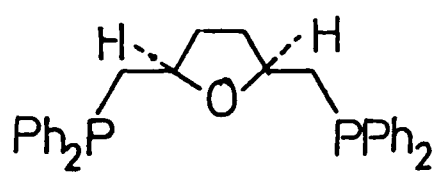
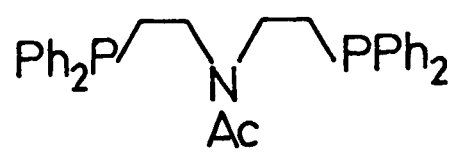
Diolefin Complex	Phosphine	Product with H_2/CO		further product with triethylamine	
		δ(ppm)	$J_{P,Rh}$(Hz)	δ(ppm)	$J_{P,Rh}$(Hz)
(85)	PPh_3	35.2	72	25.0	113
(86)					
(88)		22.0	115	13.0	156
(90)		46.5	129	No reaction	
(91)		20.5	119	16.1	109
(92)		50.5	129	No reaction	
(93)		23.2 and 24.9	125,123.5 ($J_{P,P}$ 313 Hz)	Product not characterized	
		22.3 and 28.1	125,122.9 ($J_{P,P}$ 313.5 Hz)		

Table II.2.6

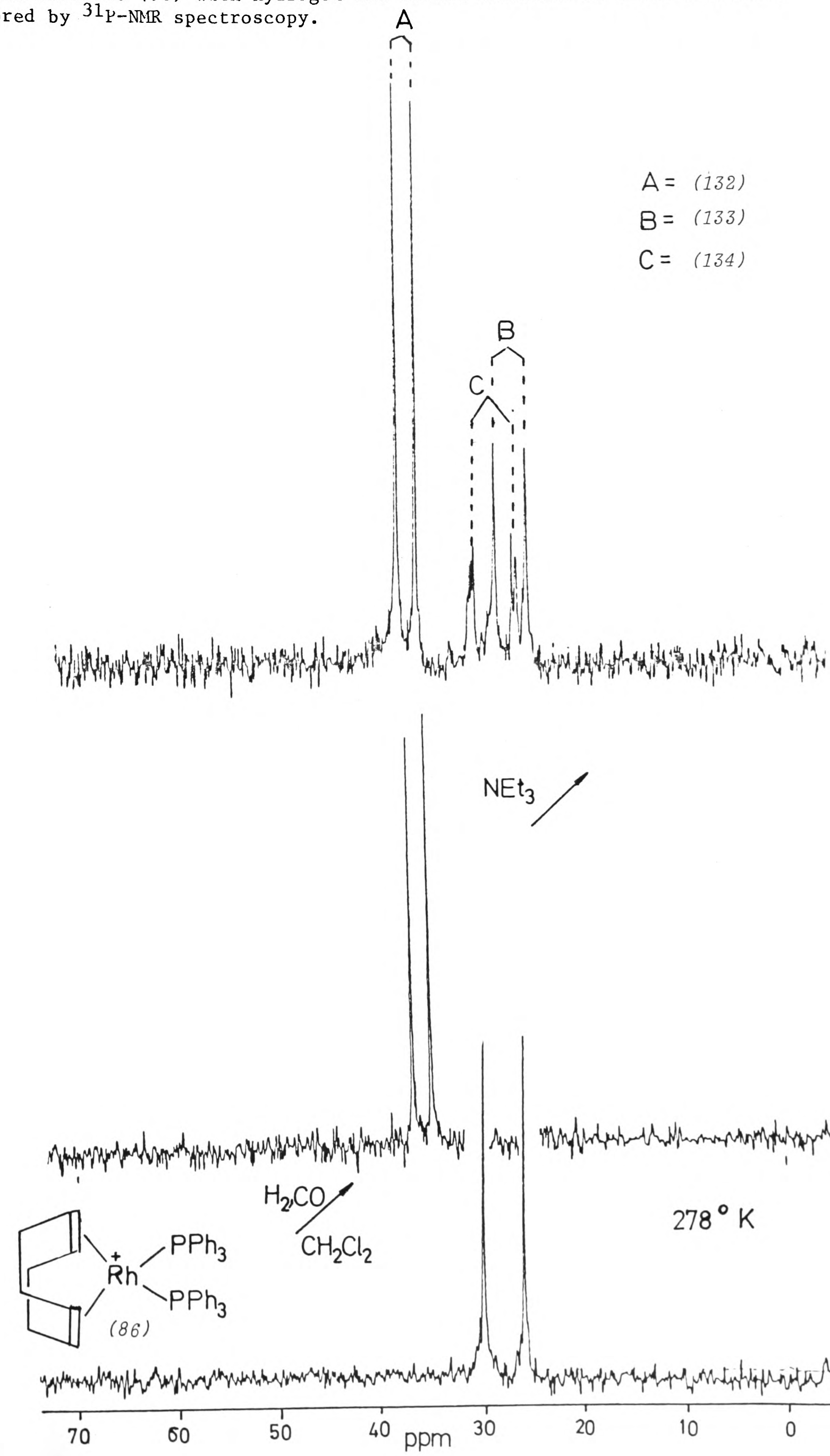
Infra-red spectra of phosphine-rhodium (I) complexes in dichloromethane

Diolefin Complex	Phosphine	Product with H_2/CO $\nu_{CO}(cm^{-1})$ (CH_2Cl_2)	Further products with triethylamine $\nu_{CO}(cm^{-1})$ (CH_2Cl_2)
(85)	PPh_3	2030 and	1980 and
(86)		2020	1745
(88)		2022 and 1987	1760
(90)		1991	no reaction
(91)		1996	1986
(92)		1993	no reaction
(93)[+]		2030, 1980 and 1640	not characterized

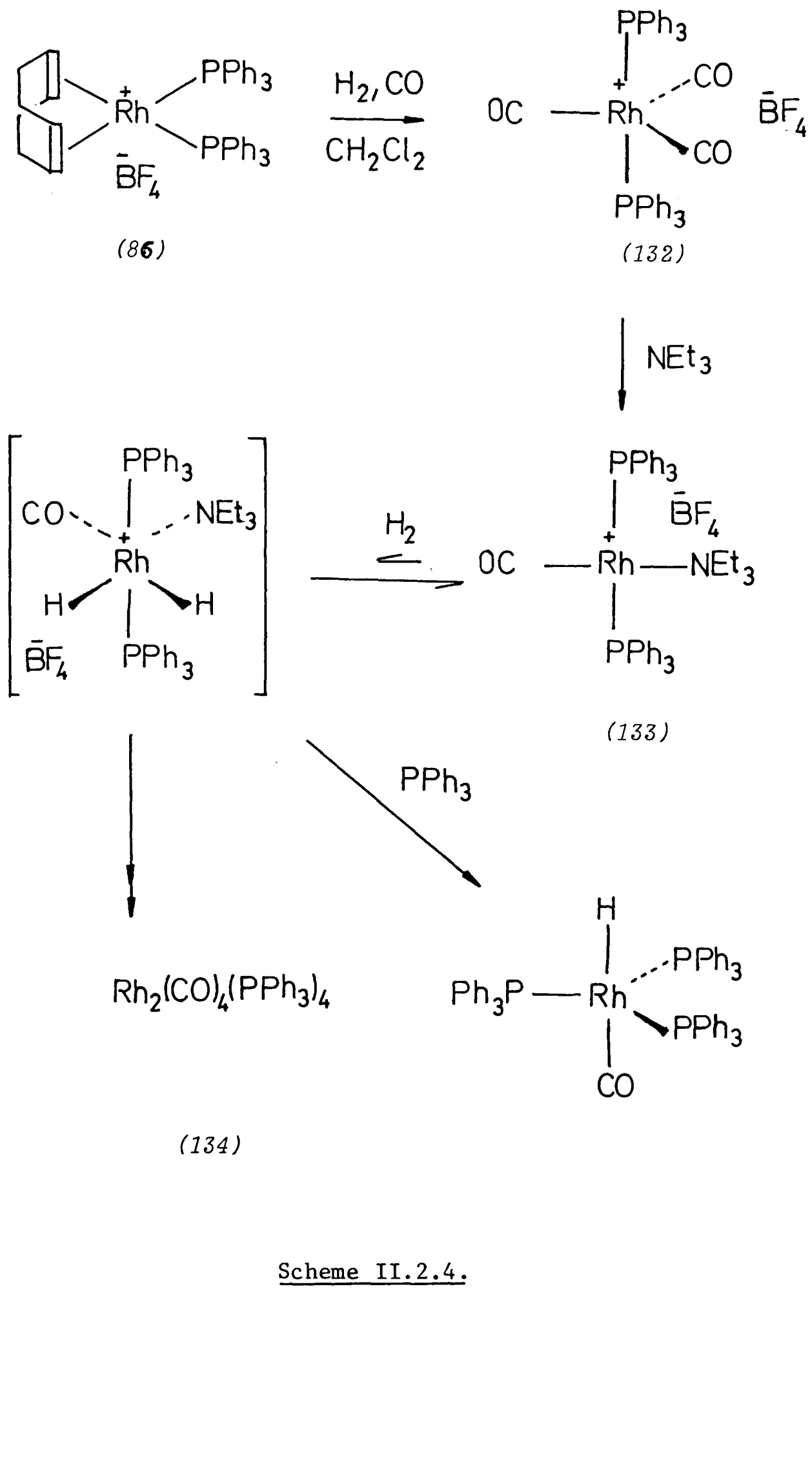
[+] ν_{CO} olefin complex 1645 cm^{-1} (broad)

Figure II.2.8

Reaction of cycloocta-1,5-diene*bis*(triphenylphosphine)rhodium(I) tetrafluoroborate *(85)* with hydrogen and carbon monoxide in dichloromethane monitored by ^{31}P-NMR spectroscopy.

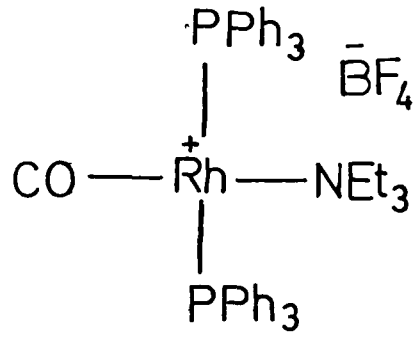


(triphenylphosphine)rhodium (I) tetrafluoroborate *(85)* under these conditions. Proposed structures for complexes *(132)* to *(134)* consistent with the obtained ^{31}P-NMR spectra are shown in Scheme II.2.4.



Scheme II.2.4.

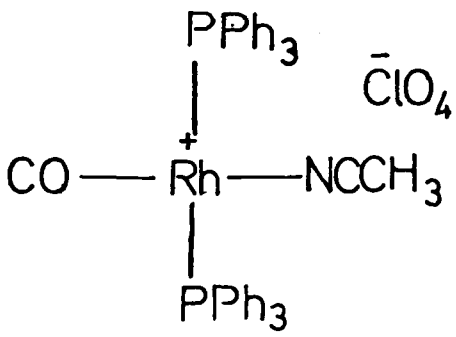
A complex analogous to the cationic tricarbonyl*bis*(triphenylphosphine)-rhodium complex *(132)* differing only in the counterion has previously been prepared by Schrock and Osborn[117] ; the ^{31}P-NMR spectra was not recorded but infra-red spectroscopy confirms the assignment. The low P-Rh coupling constant value (72 Hz) of compound *(132)* is consistent with π-acidic carbonyl ligands withdrawing electron density from the metal centre, thus weakening the phosphorus-rhodium bond. Reaction of the tricarbonyl complex *(132)* with triethylamine displaces carbon monoxide to form the square planar complex *(133)*; previous work[117] has shown that cationic monocarbonyl complexes of this type can be isolated when a strongly coordinating reagent is employed in place of triethylamine. For example the complex *(135)a* has been fully characterized.



(133)

^{31}P-NMR δ 25.0 $J_{P,Rh}$ 113 Hz

ν_{CO} 1980 cm^{-1}



(135)a

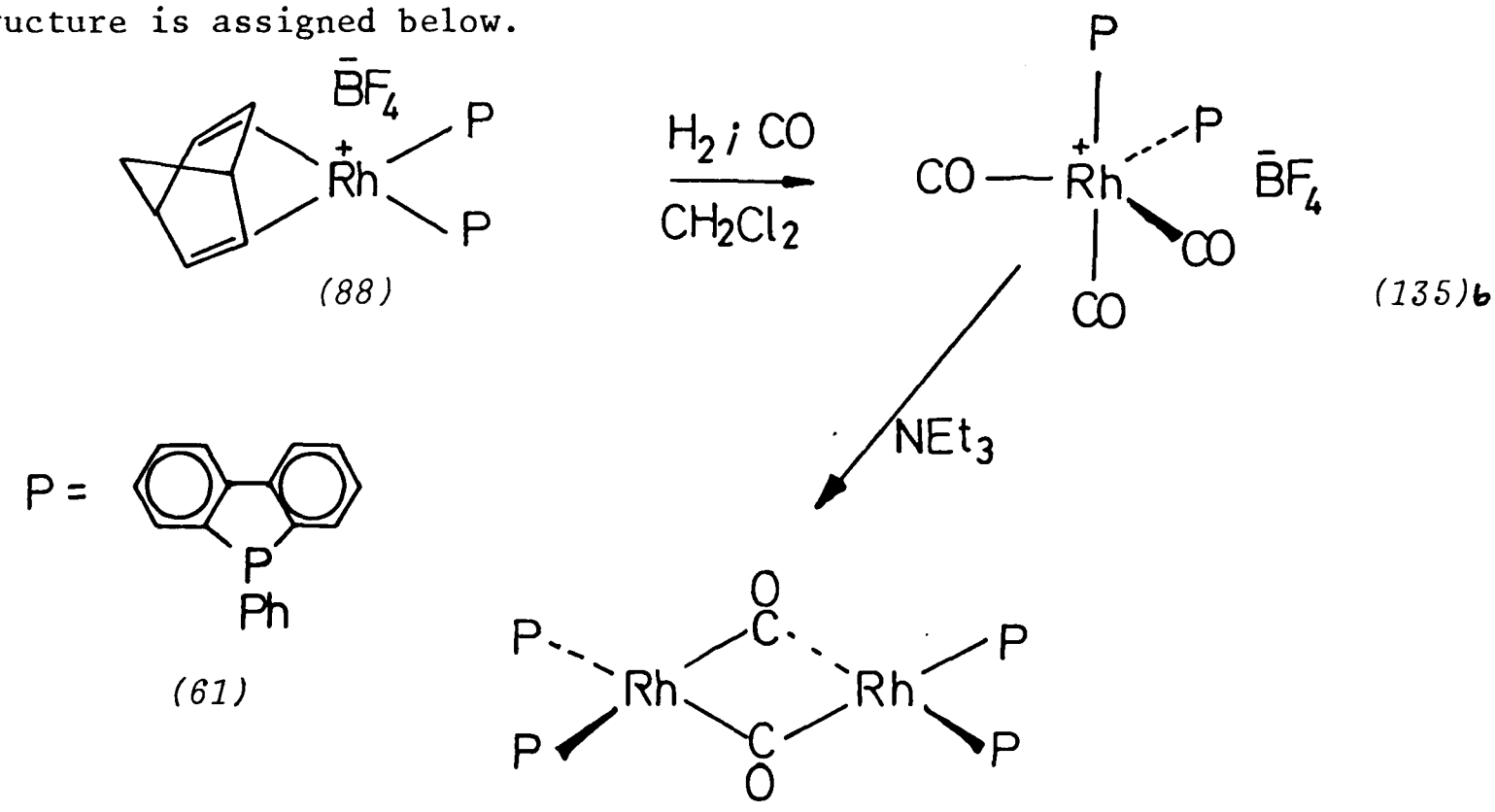
δ 29.4 $J_{P,Rh}$ 119 Hz

2016 cm^{-1}

Slow oxidative addition of hydrogen to complex *(133)* followed by rapid elimination of NEt_3HBF_4 and dimerization gives complex *(134)*. In the presence of triphenylphosphine the alternate pathway to hydrido-carbonyl*tris*(triphenylphosphine)rhodium (I) is preferred. In a separate experiment (see Chapter II, section 3) prolonged reaction of a solution of the latter complex with hydrogen and carbon monoxide produced the dimer *(134)*.

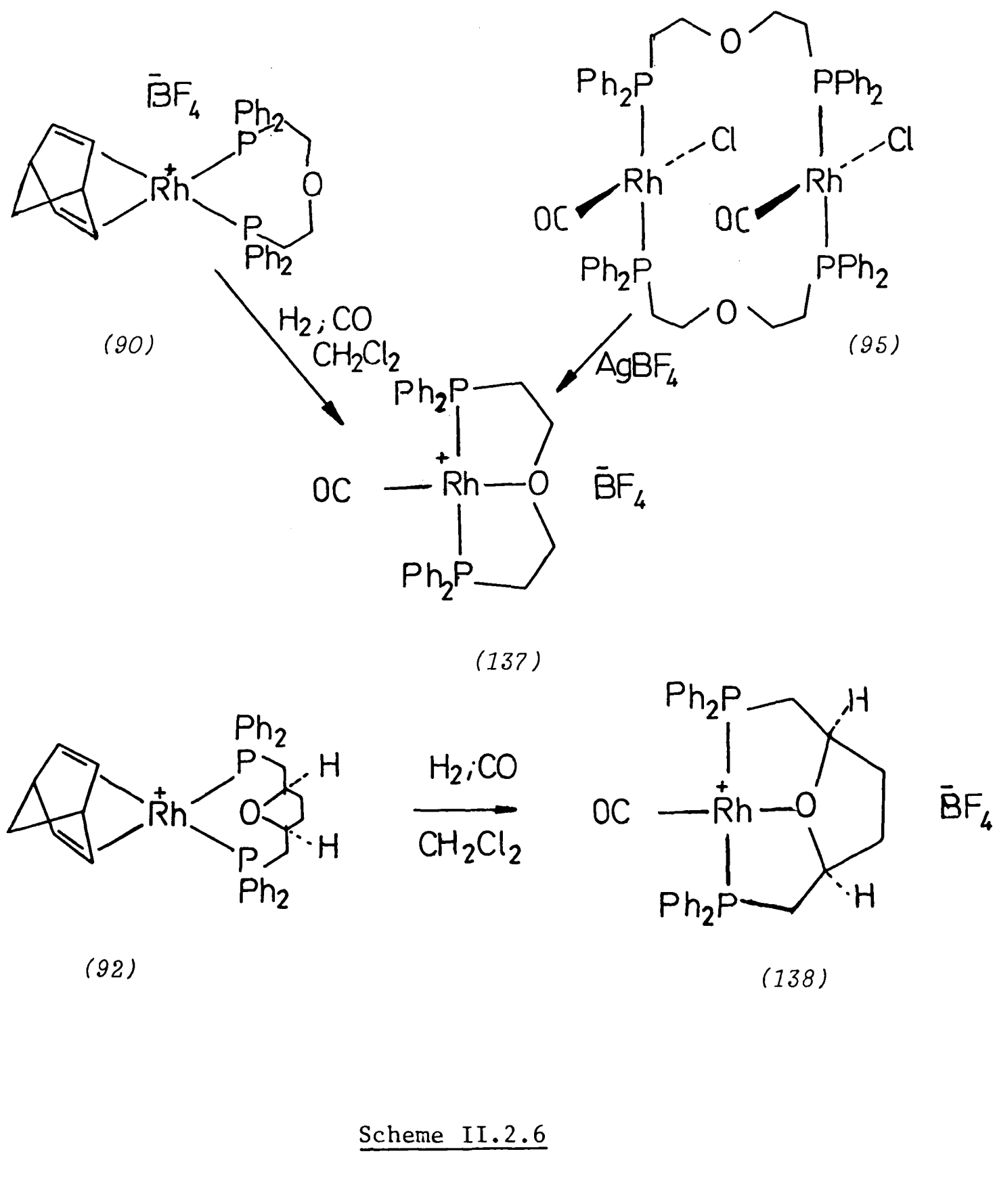
These studies suggest that the diolefin complex *(85)* and $HRh(CO)(PPh_3)_3$ lead to the same neutral rhodium phosphine species which is catalytic under hydroformylation conditions. The role of triethylamine in the former case is critical since complex *(132)* is non-catalytic.

Monitoring of the reaction of the diolefin phosphole complex *(88)* with hydrogen and carbon monoxide in dichloromethane by ^{31}P-NMR shows only one resonance signal, a doublet $J_{P,Rh}$ 115 Hz, with no significant temperature dependence, due to species *(135)b*. ^{1}H-NMR showed no hydridic species. The preference for phosphole ligands to form *cis*-complexes was discussed in Chapter II, section 2.1; therefore a structure containing *cis*-coordinated phosphines as proposed in Scheme II.2.5 might explain the *ca.* 40 Hz difference in coupling constant compared with complex *(132)*. Either rapid dissociation-recoordination of carbonyl ligands or pseudorotation could account for the equivalence of the phosphorus nuclei. The addition of triethylamine slowly produced only one new species *(136)* ($J_{P,Rh}$ 156 Hz). This latter complex was isolated and showed a molecular ion of 1302 (field desorption mass spectrometry); infra-red spectroscopy identified bridging but no terminal carbonyl groups (ν_{CO} 1760 cm^{-1}). On the basis of this evidence the structure is assigned below.



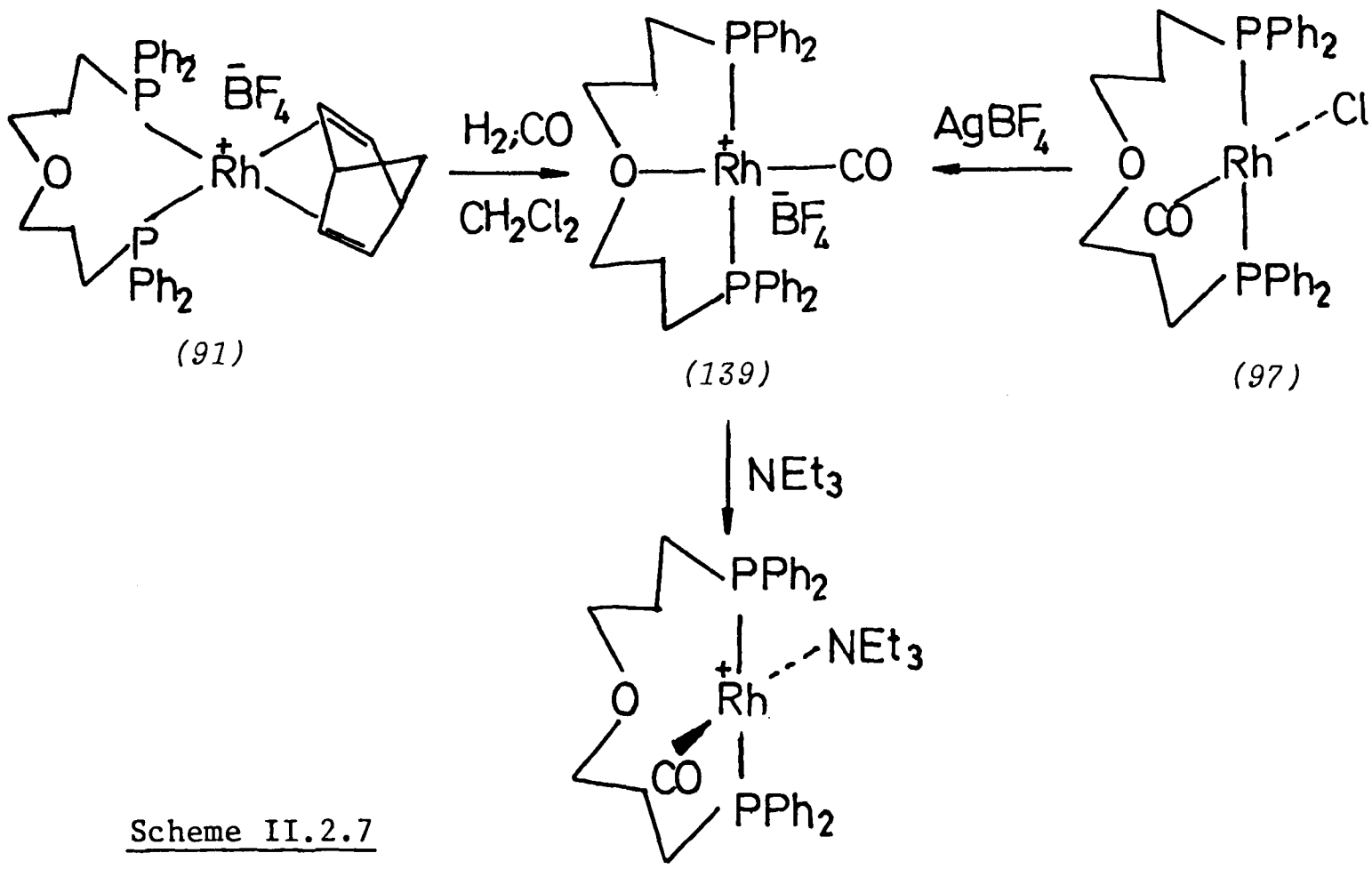
Scheme II.2.5

The behaviour of complexes *(90)* to *(93)* containing chelating biphosphines *(63)*, *(64)*, *(65)* and *(66)* respectively is somewhat different. ^{31}P-NMR analysis shows that complexes *(90)* and *(92)* each form a single species *(137)* and *(138)* on reaction with hydrogen and carbon monoxide in dichloromethane; no change is revealed on addition of triethylamine. The identical species was produced by *in situ* reaction of the chloro-carbonylbiphosphine complex *(95)* with silver tetrafluoroborate, suggesting that complexes *(137)* and *(138)* are cationic carbonyl rhodium complexes with intrachain ether-metal bonding (Scheme II.2.6). Precedent for phosphine-ether bonding to a cationic rhodium metal centre has been reported by Alcock and Brown.[102] The 1,7-*bis*(diphenylphosphino)-4-



Scheme II.2.6

oxaheptane diolefin complex *(91)* reacts similarly, forming the species *(139)*, which likewise is formed by *in situ* addition of excess silver tetrafluoroborate to a solution of the carbonylchlororhodium complex *(97)* (Scheme II.2.7). Rhodium-phosphorus coupling constants, obtained from ^{31}P-NMR spectroscopy, are useful in establishing the stereochemistry at rhodium; thus a large number of square planar carbonyl rhodium(I) complexes with *trans*-phosphine geometry have been shown to have Rh-P coupling constant values of *ca.* 125 Hz.[118] The cationic monocarbonyl complex *(139)* reacts with triethylamine to give a new species *(140)* whose ^{31}P-NMR spectrum shows a $J_{P,Rh}$ value of 109 Hz. This complex is tentatively assigned the structure below, in which triethylamine has replaced the phosphinoether-oxygen as the ligand which occupies the fourth coordination site at rhodium. In view of the lability of the inter-chain-oxygen atom compared with that of the homologous complex *(137)* this particular assignment seems reasonable, and similar conclusions were reached regarding the reduction products of complexes *(90)* and *(91)* in methanol.



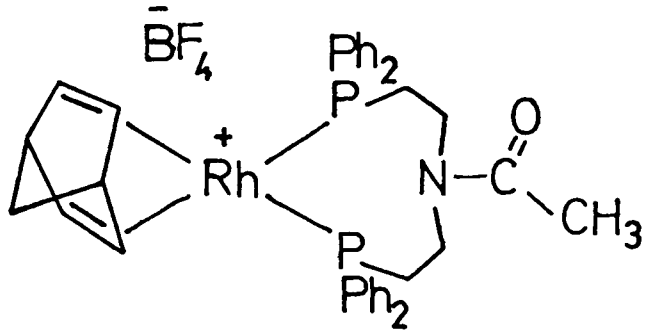
(91) *(139)* *(97)*

(140)

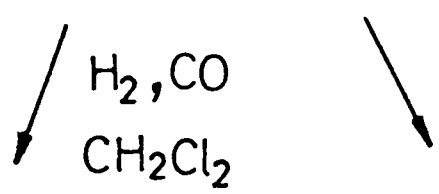
Scheme II.2.7

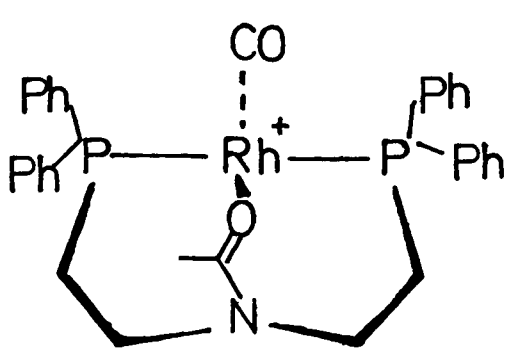
N-Acetyl-1,5-*bis*(diphenylphosphino)-3-azapentanebicyclo [2.2.1] hepta-2,5-diene rhodium(I) tetrafluoroborate *(93)* was reacted with hydrogen and carbon monoxide in dichloromethane and the solution observed by ^{31}P-NMR spectroscopy. Figure II.2.9 shows that two species *(141)* and *(142)* are formed, whose Rh-P and P-P coupling constants are informative. The spectrum of each arises from the AB part of an ABX system; two iterative simulations were carried out(A and B Figure II.2.9) using a Bruker WH 300 computer and *PANIC* spin simulation program. $J_{P,P}$ Values are ca. 300 Hz typical of *trans*-rhodium coordinated phosphorus atoms,[118] with $J_{P,Rh}$ values very similar to those of the cationic rhodium carbonyl complexes *(137)*, *(138)* and *(139)* described earlier. ^{1}H-NMR spectroscopy of the same solution prepared above showed a lack of hydridic resonances.

The ^{31}P chemical shifts and phosphorus-rhodium coupling constants are consistent with a complex containing coordinated amide. (Carboxamides are known to bind strongly to cationic rhodium.[93]) Infra-red spectroscopy shows a small shift to lower wavenumber (*ca.* 10 cm^{-1}) of the amide carbonyl band on reaction of the parent diolefin complex *(93)* with hydrogen and carbon monoxide; a more significant change would be expected if strong bonding of amide-carbonyl to rhodium were significant. It was previously shown that ligand *(66)* showed no tendency to form *trans*-chelating complexes in the presence of a donor solvent (methanol) and in this case complexation is enforced by the absence of alternatives, even though the chelate ring appears to be rather strained. The reason why two similar complexes are formed is not obvious but may be due to disastereoisomerism in the rather rigid chelate ring as indicated by structures *(141)* and *(142)* overleaf.



(93)





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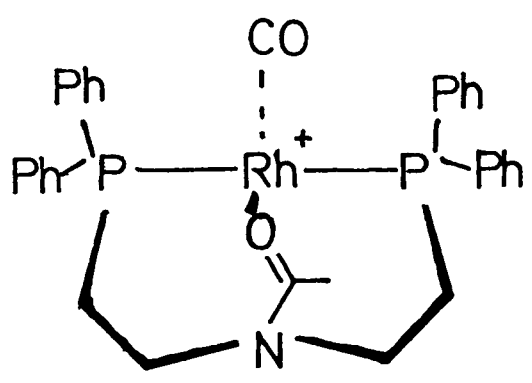
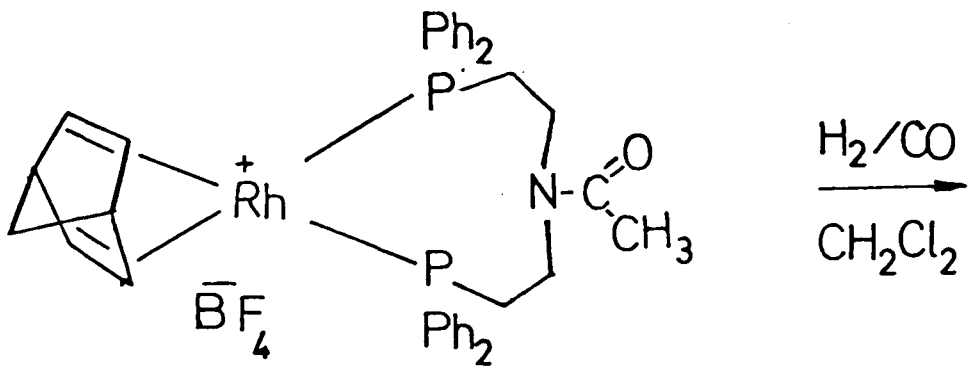


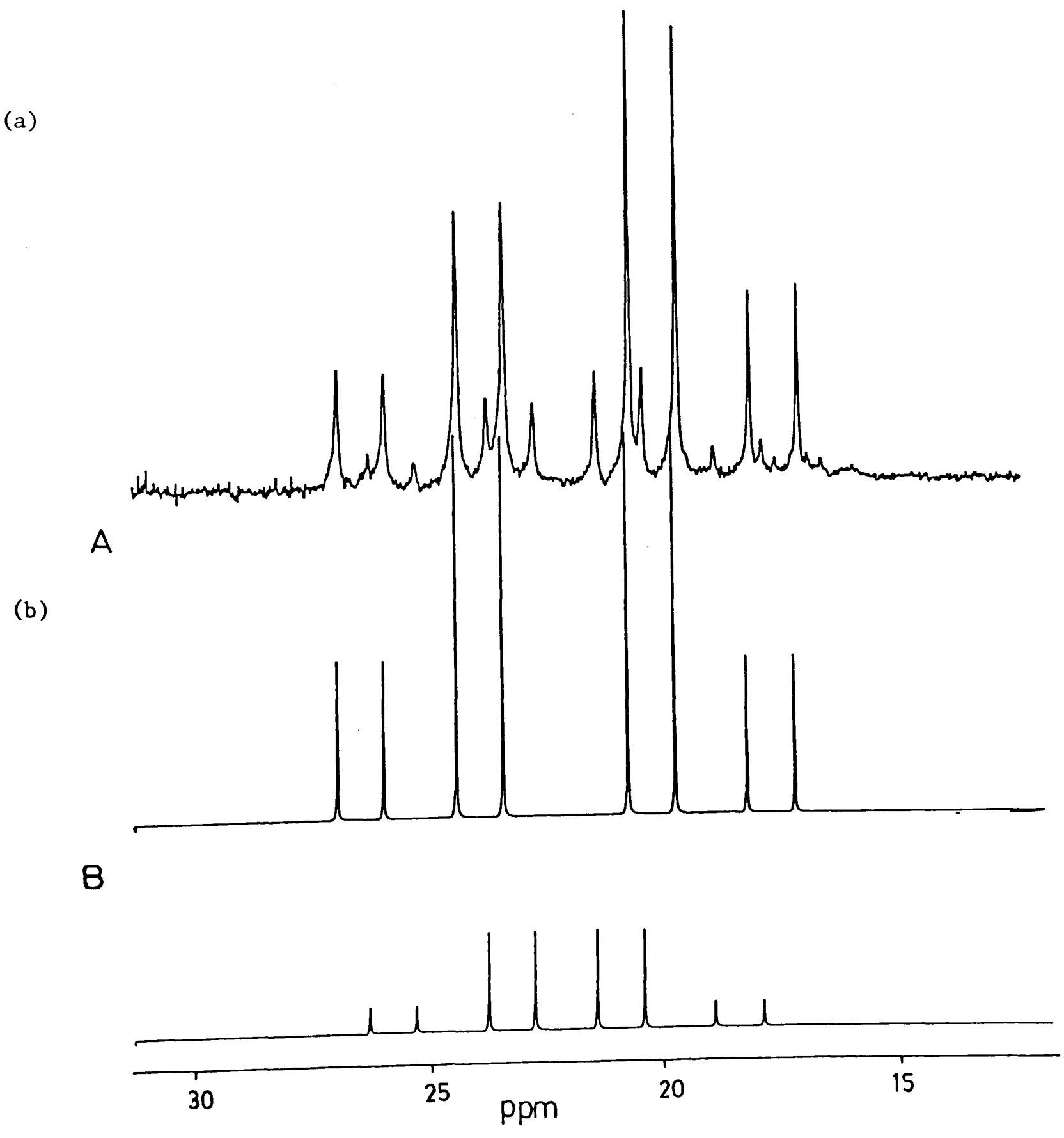
(142)

Figure II.2.9

Reaction of rhodium-diolefin complex *(93)* with hydrogen/ carbon monoxide in dichloromethane (a) experimental spectrum (b) simulated (^{31}P-NMR)



(93)



II.3. A Study of the Mechanism of Olefin Hydroformylation

The mechanism of rhodium catalysed hydroformylation proposed by Wilkinson, as a result of studies carried out between 1966 and 1971,[15-18,81,119] is illustrated in Chapter I, Section 3. For reference, the principal steps and intermediate species are summarized here. Initial attack of olefin on a hydrido-carbonyl-phosphine rhodium complex produces a metal-alkyl species, possibly *via* a hydrido-olefin complex. The next stage is alkyl transfer to coordinated carbon monoxide forming a rhodium-acyl complex. Oxidative addition of hydrogen to this gives the aldehyde product on elimination and regenerates the catalytic species.

The studies by Wilkinson and co-workers,[16] mentioned above, attempted to investigate the interaction of carbon monoxide with hydridocarbonyl*tris*-(triphenylphosphine)rhodium(I) *(143)* and later, to isolate or characterize hydroformylation intermediates by infra-red and NMR spectroscopy. The following discussion relates to these investigations. The reaction of $HRh(CO)(PPh_3)_3$ *(143)* with carbon monoxide in benzene or dichloromethane was interpreted in terms of three primary species, namely $HRh(CO)(PPh_3)_2$ *(144)*, $HRh(CO)_2(PPh_3)_2$ *(145)* and a dimeric complex $Rh_2(CO)_4(PPh_3)_4$ *(146)* with bridging and terminal carbonyl groups. Several changes were recorded on addition of carbon monoxide to a dichloromethane solution of $HRh(CO)(PPh_3)_3$ by infra-red spectroscopy. Firstly, absorptions at 2000 (ν_{RhH}) and 1920 (ν_{CO}) cm^{-1} due to complex *(143)* disappeared and bands at 2038, 1980 and 1939 cm^{-1} due to dicarbonyl complex *(145)* appeared within a few seconds. These latter bands weakened commensurate with the observation of peaks at 2005, 1985, 1790 and 1765 cm^{-1} due to the dimer *(146)*; no further changes were observed. This second slower step was accompanied by evolution of molecular hydrogen (according to

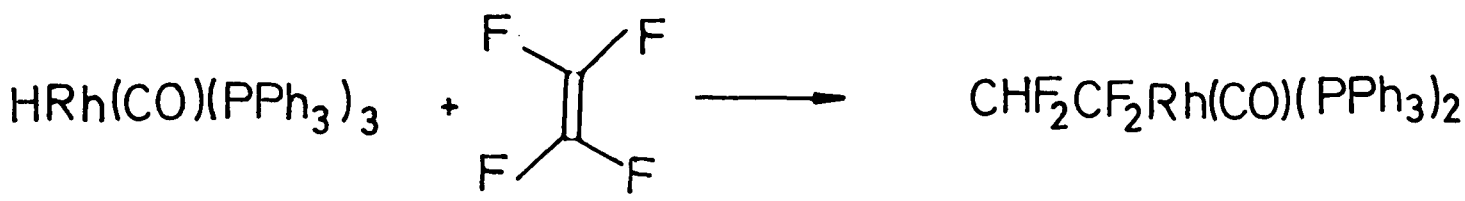
mass spectrometry). NMR spectroscopy of the hydride region of complex *(143)* showed a broad line (δ-9.2 ppm) at 25°; it was suggested that the chemical shift of complex *(143)* was almost coincident with that of the dissociated species *(144)* with which it was undergoing exchange as shown below.

$$HRh(CO)(PPh_3)_3 \rightleftharpoons HRh(CO)(PPh_3)_2 + PPh_3$$

(143) *(144)*

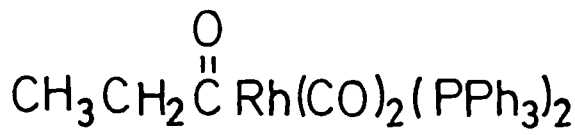
Reaction of such a solution with a mixture of hydrogen and carbon monoxide showed a new hydride resonance 0.17 ppm to lower field, attributed to complex *(146)*. This latter complex was line-broadened even at 243°K in toluene.

Studies were also conducted in the presence of olefinic substrates. No evidence was obtained for the formation of rhodium-alkyl complexes from $HRh(CO)(PPh_3)_3$ *(143)* and ethylene (*ca.* 50 atmospheres) in the absence or presence of hydrogen or carbon monoxide. Reaction of tetrafluoroethylene, however produced the rhodium-alkyl complex *(147)*.



(147)

Reaction of *(147)* with CO produced only a dicarbonyl species (ν_{CO} 2075 and 2020 cm^{-1}) and not an acyl-rhodium complex. Alkyl-rhodium complexes were not observed for ethylene, but the reaction of hydridocarbonyl*tris*-(triphenylphosphine)rhodium(I) and carbon monoxide in the presence of excess ethylene showed new infra-red carbonyl bands at 1975, 1923 and 1634 cm^{-1} assigned to acyl-complex *(148)*. The NMR spectrum obtained

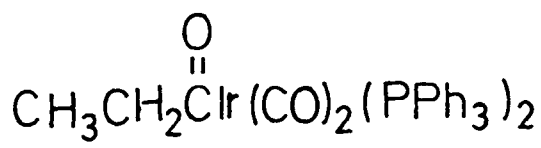


(148)

under similar conditions showed a triplet and quartet at δ 0.74 and 2.93 ppm respectively, characteristic of a propionyl group. The complex *(148)* was stable in solution under carbon monoxide and ethylene but decomposed to ethylene under a nitrogen atmosphere. Addition of hydrogen to the acyl complex *(148)* formed propanal quantitatively.

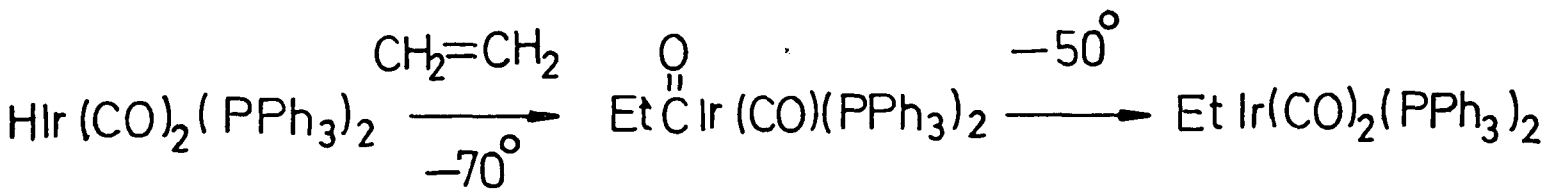
Analogous iridium complexes appear to be more stable and less labile, and therefore easier to characterize. Hydridocarbonyl*bis*(triphenylphosphine)iridium(I) *(149)*, an isolable complex,[120] reacted with carbon monoxide and ethylene (30 atm., 1:1 mixture) to form the stable crystalline acyl species *(150)*, whose infra-red and NMR spectra are very similar to those of complex *(148)*.

The acyl species *(150)* reacted slowly with hydrogen to form propanal and the initial complex *(149)*. The reaction of complex *(149)* with ethylene in the absence of carbon monoxide, monitored by infra-red



(150)

spectroscopy was also informative. In toluene at -70° a solid assigned to species *(151)* was isolated (ν_{CO} 1955 cm^{-1}; on warming to -50° a second complex (ν_{CO} 1959 and 1910 cm^{-1}), probably the alkyl complex *(152)* was obtained (Scheme II.3.1). Decomposition of either



(149) *(151)* *(152)*

Scheme II.3.1

complex *(151)* or *(152)* to species *(149)* and ethylene occurred readily. Thus characterization of rhodium or iridium complexes, corresponding closely to the rhodium complexes invoked as hydroformylation reactive intermediates, was possible in certain circumstances.

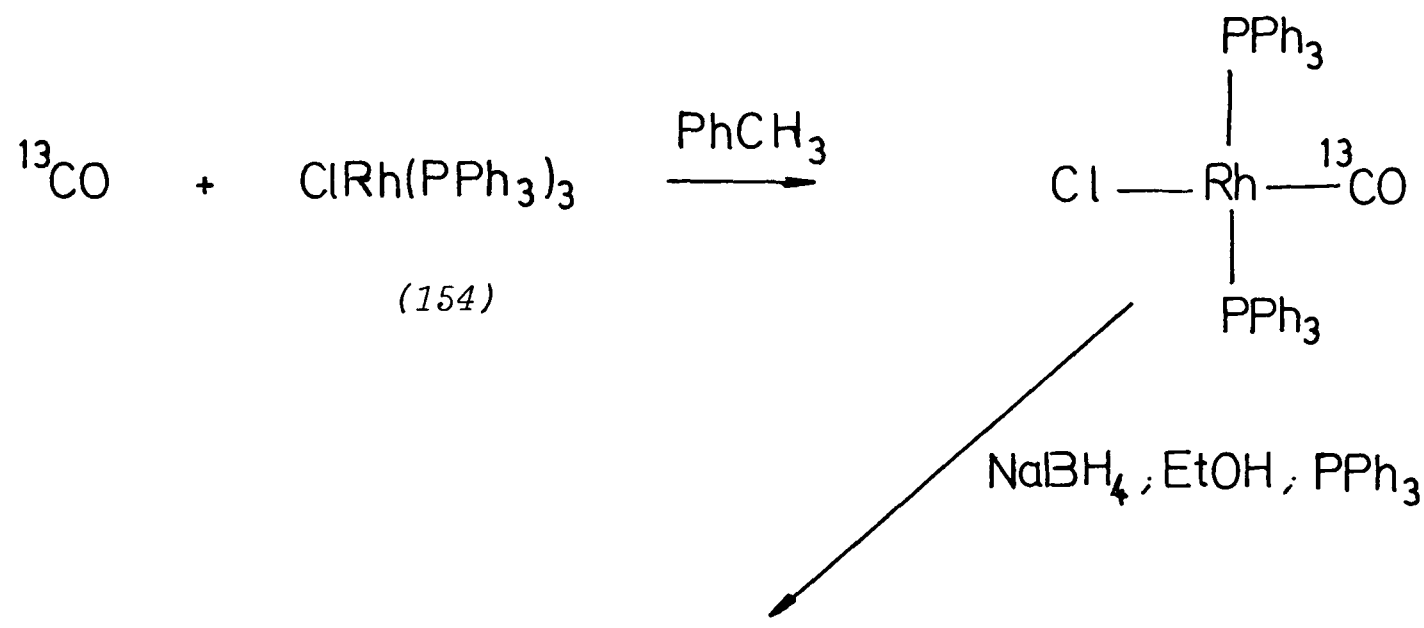
During the course of this project an investigation of the mechanism of rhodium catalysed olefin hydroformylation was approached in two new ways, both employing NMR techniques - particularly heteronuclear studies. Firstly, the nature of rhodium-phosphine species present under hydroformylation conditions was examined and those reactive towards olefins identified. Secondly specifically and stereospecifically labelled

olefins were used to identify reactive intermediates, which are potentially part of the hydroformylation catalytic cycle.

II.3.1. *Syntheses*

3.1.1. *Synthesis of rhodium-phosphine complexes*

Hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)*, was prepared according to a published procedure.[121] The analogous complex *(153)*, 92% enriched with ^{13}C in the carbonyl group, was made from ^{13}C-carbon monoxide according to Scheme II.3.2. below.



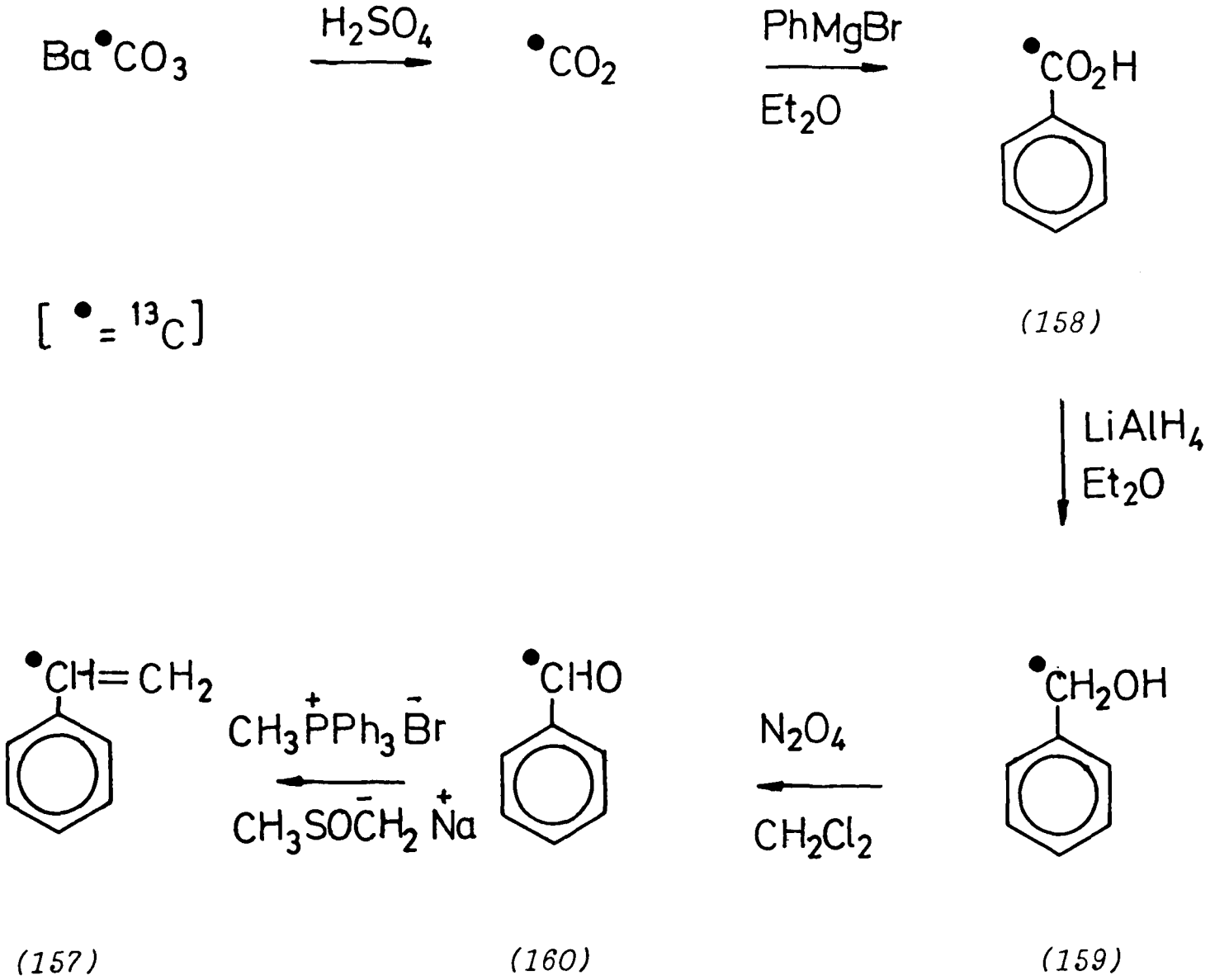
Scheme II.3.2.

Chloro*tris*(triphenylphosphine)rhodium(I) *(154)* was prepared by the method of Wilkinson.[122] Hydrido*tetrakis*(triphenylphosphine)rhodium(I) *(155)*[123a] and hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole) *(156)*[123b] were obtained using standard literature methods.

3.1.2. *Synthesis of olefinic substrates*

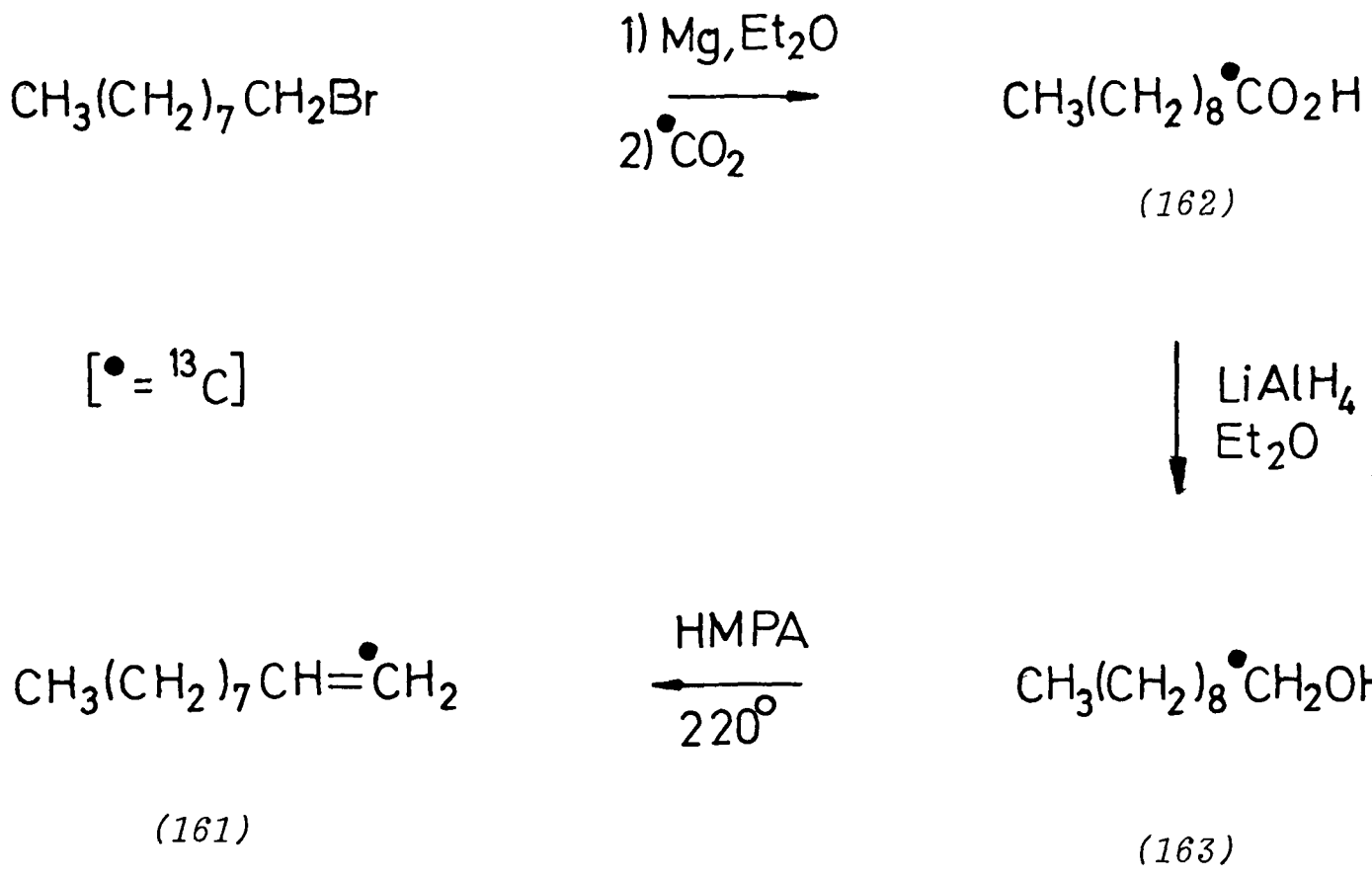
A synthesis of α-^{13}C-styrene *(157)* from ^{13}C-barium carbonate (92% enrichment) was conveniently achieved in five steps (Scheme II.3.3).

^{13}C-Carbon dioxide, generated from ^{13}C-barium carbonate and sulphuric acid[124] was readily handled in a sealed system; reaction of the gas with phenylmagnesium bromide produced ^{13}C-benzoic acid *(158)*[124]. Reduction to α-^{13}C-benzyl alcohol *(159)* was effected by lithium aluminium hydride using a standard published method for ^{12}C-material.[125] Other workers[126,127] have had considerable success using dinitrogen tetroxide as a high-yield selective alcohol to aldehyde oxidizing agent and this was the method of choice for making α-^{13}C-benzaldehyde *(160)* in 63% yield. The final step was reaction of this latter compound with methylenetriphenylphosphorane (generated *in situ* by Corey's method[128]) to give the labelled styrene *(157)*.



Scheme II.3.3.

The synthesis of α-^{13}C-1-decene *(161)* is shown in Scheme II.3.4. and was similarly derived from ^{13}C-carbon dioxide. α-^{13}C-Decanoic acid *(162)*, made by an analogous procedure to that described for benzoic acid *(158)* was reduced to α-^{13}C-decyl alcohol *(163)* with lithium aluminium hydride. The final step, dehydration by hexamethylphosphorus triamide, was based on Monson's method for unlabelled decene,[129] and gave the required olefin *(161)*.



Scheme II.3.4.

Schrock and Osborn[130] reported that alkynes were stereospecifically reduced by one equivalent of hydrogen, catalysed by bicyclo[2.2.1]hepta-2,5-diene*bis*(diphenylmethylphosphine)rhodium(I) tetrafluoroborate *(164)*, to give *cis*-olefins. *Cis*-1,2-Dideuteriostyrene *(165)*, shown to be chemically and stereochemically pure by NMR, was conveniently obtained by a modification of this procedure which involved deuterium in place

of hydrogen. This method may be generally applicable for the production of other stereospecifically *cis*-d_2-labelled olefins.

Methylenecyclopropane *(166)* was made by the reaction of 3-Chloro-2-methylprop-1-ene with potassium amide in tetrohydrofuran,[131] and stored as a sealed solution in toluene.

II.3.2 *Rhodium-Phosphine species present under Hydroformylation Conditions in the absence of Substrate.*

3.2.1. *Rhodium-Dibenzophosphole complexes*

The reaction of hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium (I) *(156)* with carbon monoxide was examined first since it was observed that NMR spectra of the reaction products were not dynamic at ambient temperature. Figure II.3.1 shows the changes observed throughout the course of the reaction monitored by ^{31}P-NMR spectroscopy. The initial species *(156)* was replaced by a new species *(167)*, a rhodium coupled doublet (δ 31.2 ppm, $J_{P,Rh}$ 149 Hz) and 5-phenyl-5*H*-dibenzophosphole *(61)*. On standing the reaction solution under carbon monoxide a second new species *(136)* appeared (δ 14.0 ppm, $J_{P,Rh}$ 156 Hz) and became the sole rhodium complex after *ca.* 48 hours. Yellow-orange crystals were deposited from the solution at this stage, the infra-red spectrum of which showed a carbonyl band at 1760 cm^{-1} and, by field-desorption mass spectrometry, a molecular ion of 1302. Monitoring the rhodium-hydride region of the ^{1}H-NMR spectrum during carbonylation showed that an additional species *(168)* was formed at low concentration (Figure II.3.2). The initial tetraphosphine complex *(156)* has a hydride proton with double quintet fine structure (δ -10.1 ppm, $J_{H,Rh}$ 7 Hz, $J_{H,P}$ 19 Hz); on reaction of the complex with carbon monoxide the new hydridic species *(167)* and *(168)*, with double quartet (δ -9.2 ppm, $J_{H,Rh}$ 3 Hz, $J_{H,P}$ 13 Hz) and double triplet (δ -8.3 ppm, $J_{H,Rh}$ 7 Hz, $J_{H,P}$ 19 Hz) fine structure respectively, were formed. Only (transient) minor amounts of the second species *(168)* were formed irrespective of the concentration of the initial complex *(156)* or length of exposure of this to carbon monoxide.

Similar changes were monitored by ^{13}C-NMR on reaction of hydrido-*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium(I) *(156)* with ^{13}C-carbon

Figure II.3.1

Reaction of hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium (I) *(156)* with carbon monoxide in toluene monitored by ^{31}P-NMR

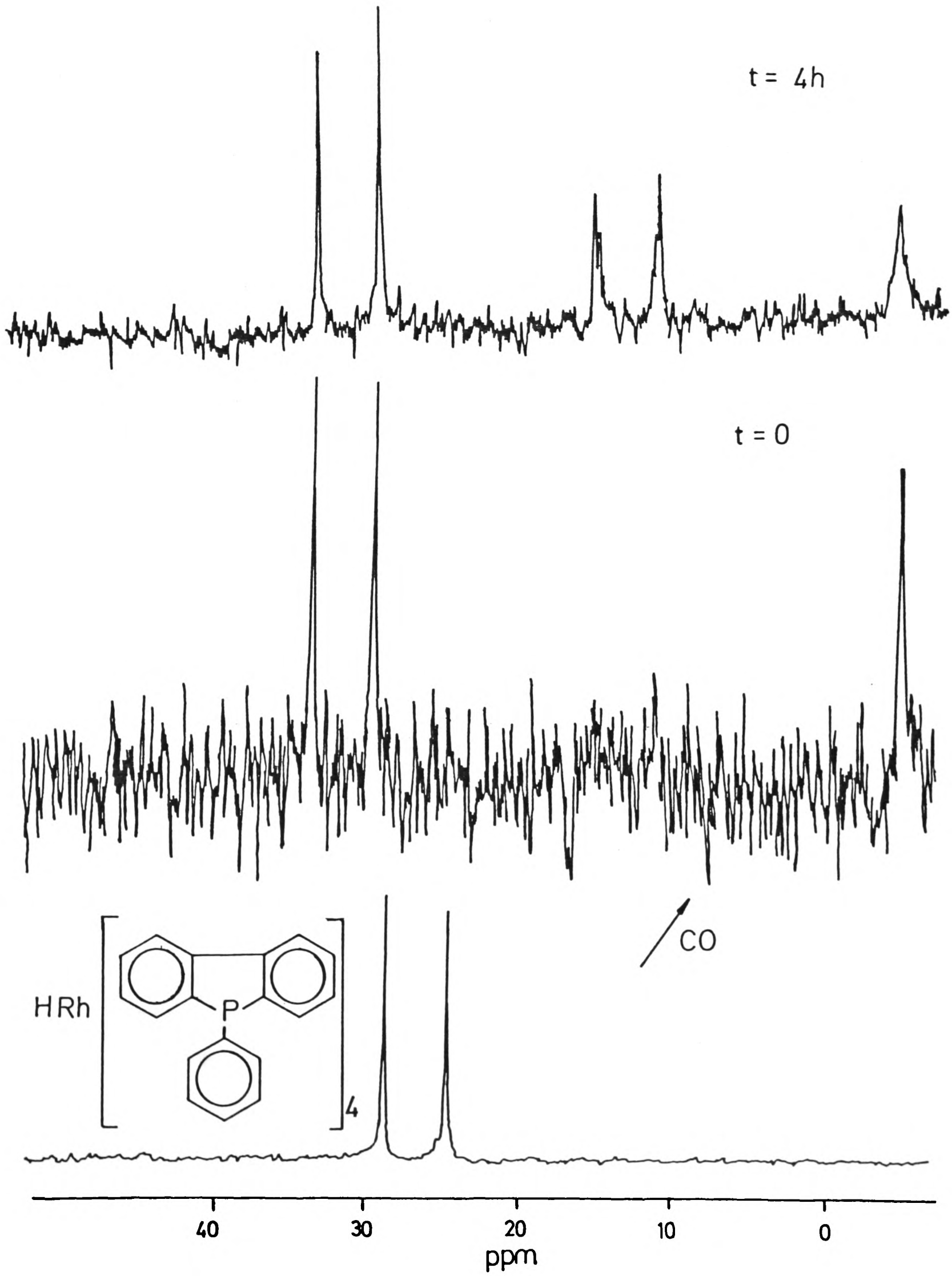
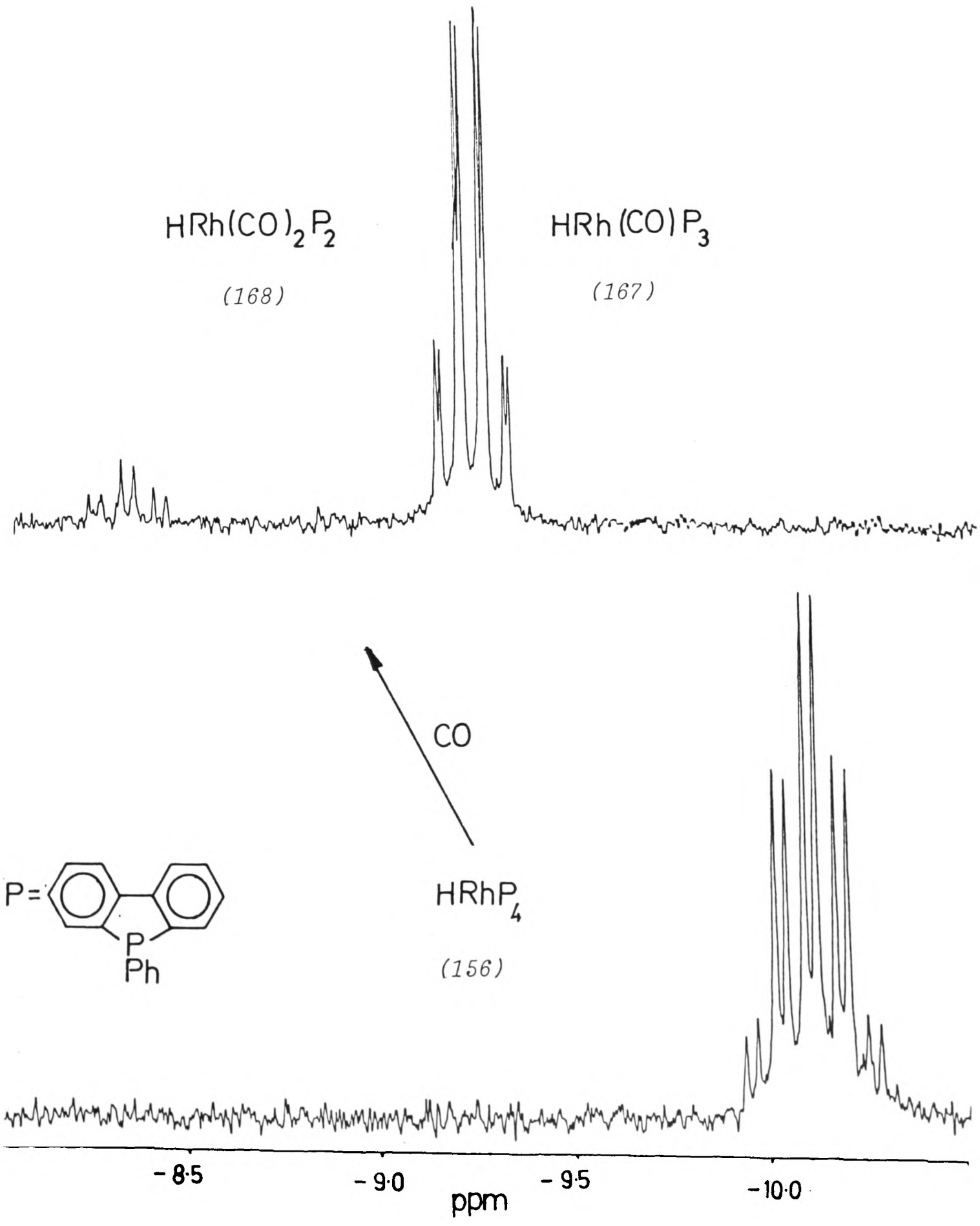
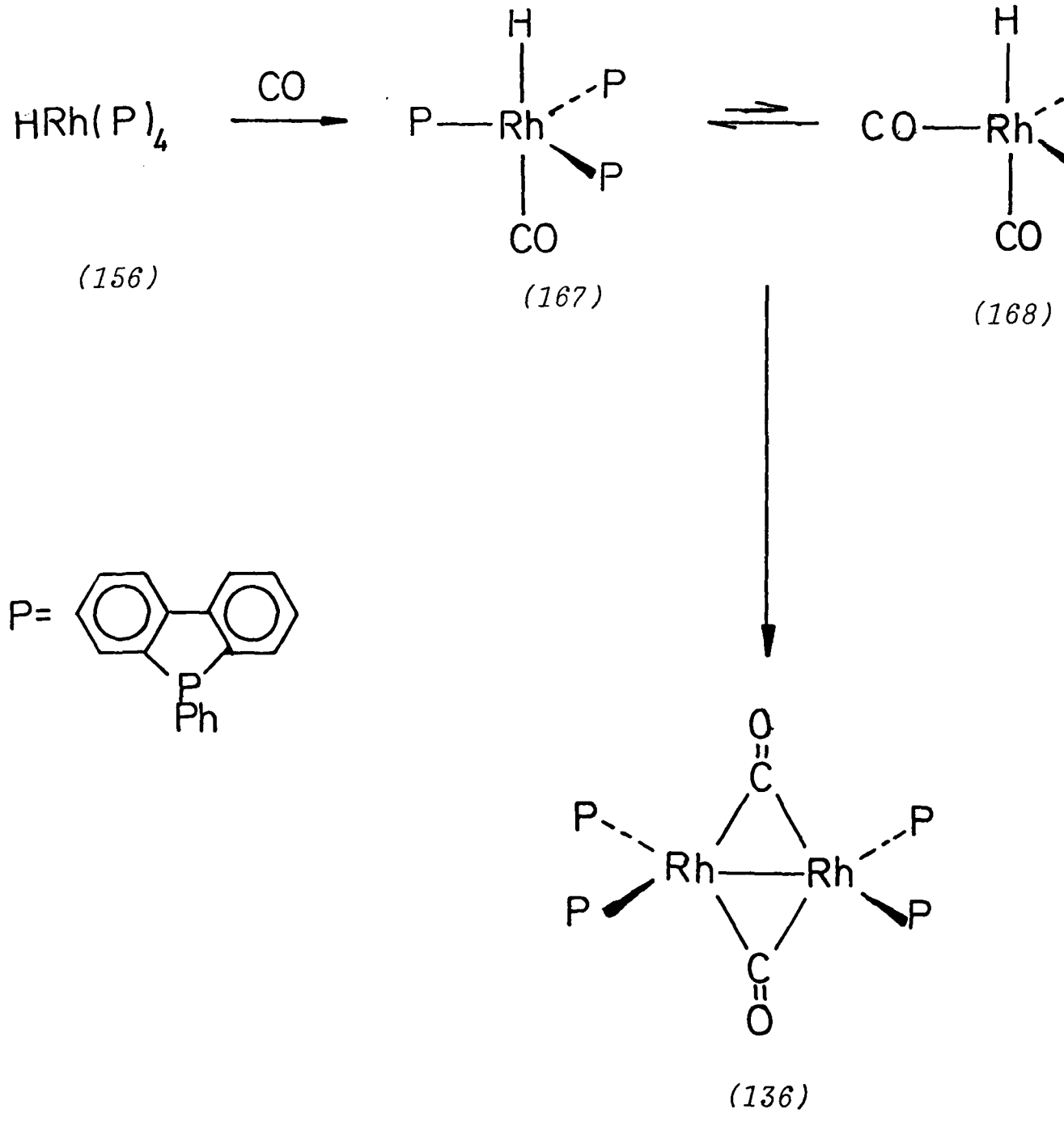


Figure II.3.2.

Reaction of hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium (I) *(156)* with carbon monoxide in toluene monitored by ^{1}H-NMR



monoxide (Figure II.3.3), the exception being that complex *(168)* was not now observed, presumably due to its low concentration. The resonance of the carbonyl-carbon atom of complex *(167)* appeared as a double rhodium-coupled quartet (δ 205.1 ppm) and decreased as the second species *(136)* with a ^{13}C-CO resonance of more complex structure was formed at lower field (δ 221 ppm). A similar series of spectra were obtained when the reaction was performed with a 1:1 mixture of hydrogen and carbon monoxide. Scheme II.3.5 shows the proposed structures for complexes *(167)*, *(168)* and *(136)* and Table II.3.1 contains spectral data pertaining to these complexes.



(156) *(167)* *(168)* *(136)*

Scheme II.3.5.

Figure II.3.3.

Reaction of hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium (I) *(156)* with ^{13}C-carbon monoxide in toluene monitored by ^{13}C-NMR

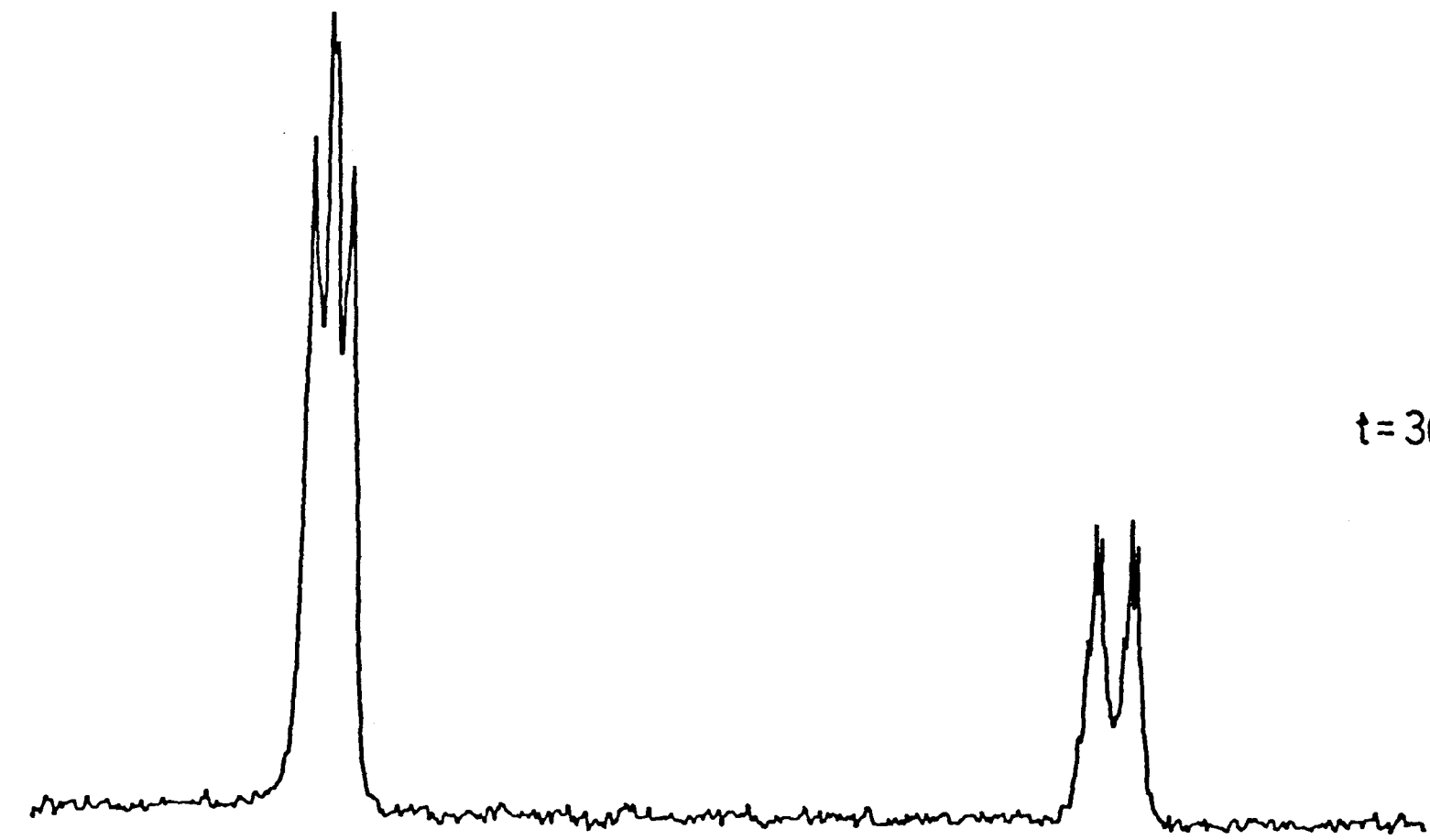


Table II.3.1

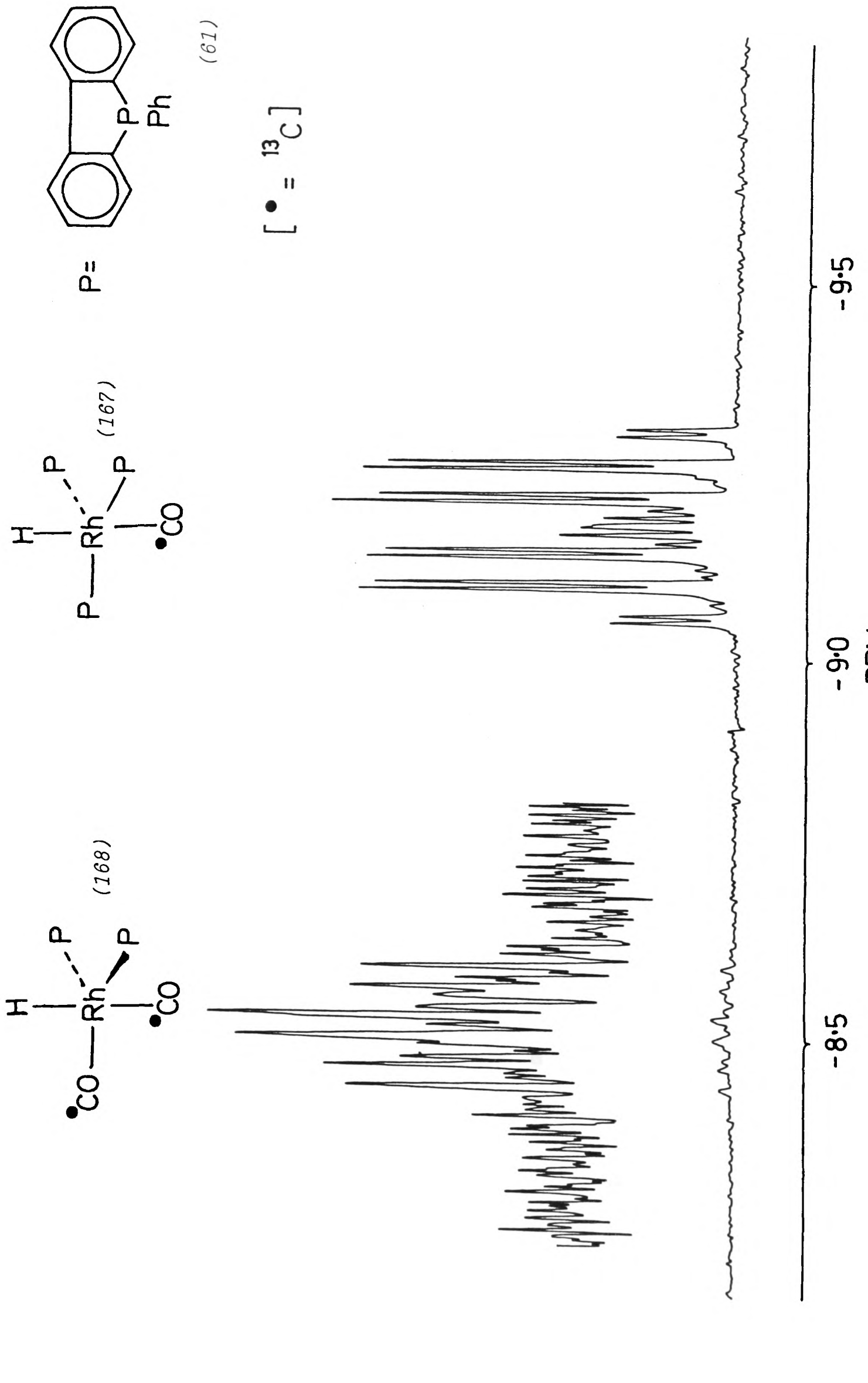
NMR Data of Rhodium-5-phenyl-5*H*-dibenzophosphole complexes

Complex	$HRh(DBP)_4$ *(156)*	$HRh(CO)(DBP)_3$ *(167)*	$HRh(CO)_2(DBP)_2$ *(168)*	$Rh_2(CO)_2(DBP)_4$ *(136)*
^{1}H-NMR				
Rh-*H* δ(ppm) (d_8-toluene)	-10.1	-9.2	-8.3	-
$J_{H,Rh}$(Hz)	7	3	7	-
$J_{H,P}$(Hz)	19	13	19	-
$J_{H,C}$(Hz)	-	34	*ca.* 20	-
^{31}P-NMR				
Rh-*P* δ(ppm) (toluene)	27.6	31.2	not observed	14.0
$J_{P,Rh}$(Hz)	146	149		156
$J_{P,C}$(Hz)	-	10		-
^{13}C-NMR				
Rh-*CO* δ(ppm) (toluene)	-	205.1	not observed	221
$J_{C,Rh}$(Hz)	-	54		30
$J_{C,P}$(Hz)	-	10		-

The *tris*(phosphine)monocarbonyl complex *(167)* had been prepared independently by Holah and co-workers[123c] and the reported ^{1}H-NMR spectrum agrees with that of complex *(167)*; the complexes *(168)* and *(136)* are new. The fine structure of the ^{1}H-NMR hydridic resonance of species *(168)* requires coupling of the proton to rhodium and two equivalent phosphorus atoms; carbonylation with ^{13}C-carbon monoxide (Figure II.3.4) allowed further coupling to two carbon atoms to be discerned. The stoichiometry attributed to the 5-coordinate complex *(168)* (Scheme II.3.5) is therefore

Figure II.3.4.

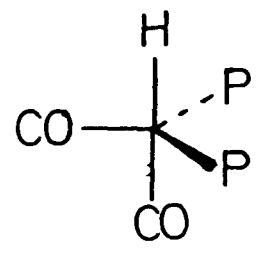
Reaction of hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium (I) *(156)* with ^{13}C-carbon monoxide in toluene monitored by ^{1}H-NMR



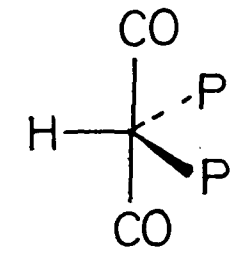
reasonable; its geometry is not immediately clear however. Yagupsky and Wilkinson[120] and later Muetterties and co-workers[132] have examined the ^{1}H-NMR temperature dependence of the stable analogue hydridodicarbonyl-*bis*(triphenylphosphine)iridium(I) *(149)* and the spectra obtained were interpreted in terms of an equilibrium between two isomers *A* and *B*. In principle five trigonal bipyramidal structures are possible for a complex of composition $HIr(CO)_2(PPh_3)_2$; these are depicted below:

$HIr(CO)_2(PPh_3)_2$

(149)



1



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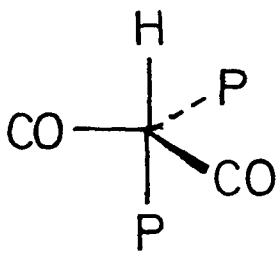

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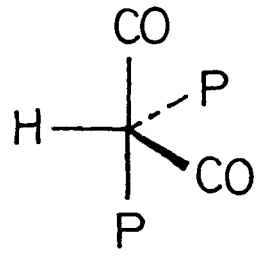

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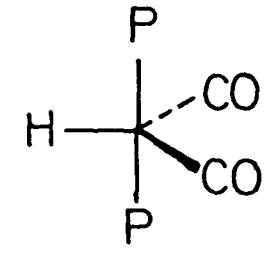
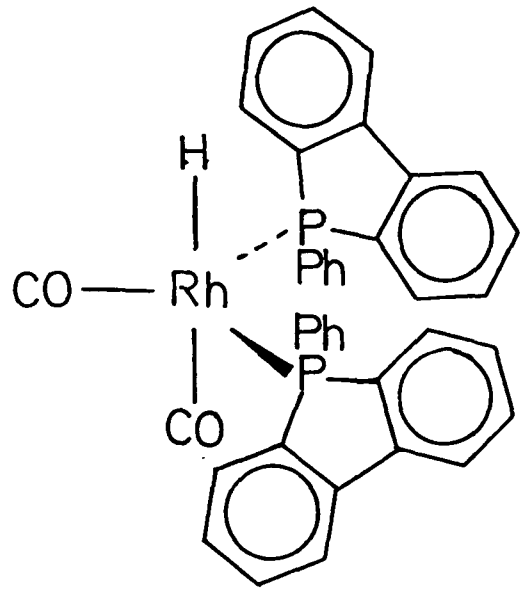


5

On the basis of coupling constant values (*A* $J_{H,P}$ 20 Hz and *B* $J_{H,P}$ 92 and 24 Hz) isomer *A* was assigned structure 1 and isomer *B* assigned structure 3. A crystal structure study of the complex *(149)* showed isomer 3 to be the only species present in the solid state.[133] An investigation of the temperature dependence of the ^{1}H-NMR spectrum of complex *(168)* was not carried out, but one experiment recorded at 273^{o}K showed essentially no change from the spectrum shown in Figure II.3.2.

The magnetic equivalence of the phosphorus atoms and preference for *cis*-geometry, together with a $J_{H,P}$ value of 19 Hz are consistent with the structure proposed below; an averaged $J_{H,P}$ value of about 60 Hz would be expected for *trans*- H-Rh-P coordination.



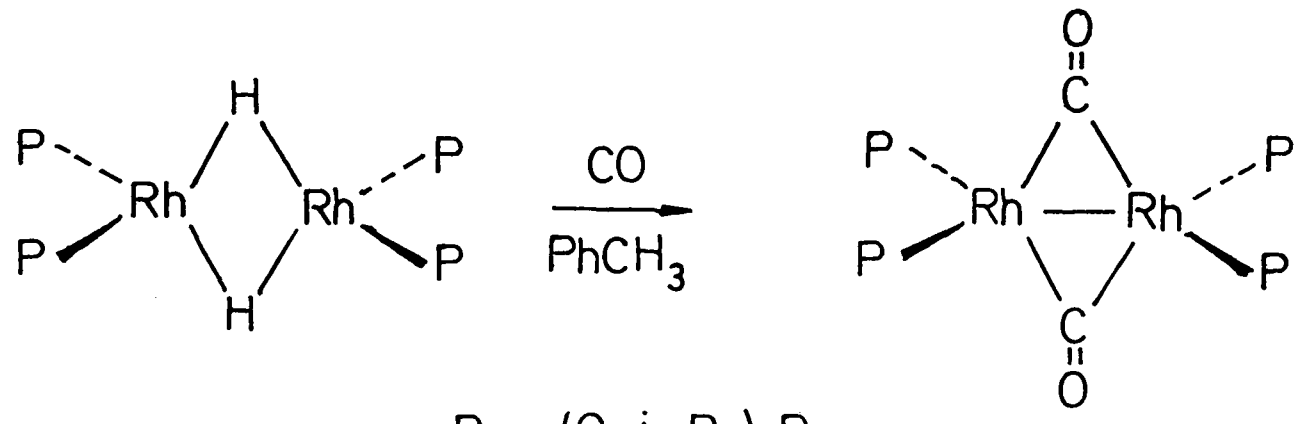
(168)

The fact that the carbon-hydrogen coupling constant in complex *(168)* is 20 Hz and in complex *(167)* it is 34 Hz supports this assignment since a fluxional structure for *(168)* having one *cis* carbonyl ($J_{C,H}$ ~ 10 Hz) and one *trans*-carbonyl ($J_{C,H}$ ~ 30 Hz) with respect to the hydride would exhibit the observed splitting.

The addition of a reactive olefin, methylenecyclopropane *(166)*, to a solution containing both mono- and di-carbonyl complexes *(167)* and *(168)* caused immediate disappearance of the ^{1}H-NMR hydride resonance attributed to complex *(168)*. Complex changes were observed in region 0 to 10δ, and 1,3-butadiene a rearrangement product of methylenecyclopropane, was the major organic compound after 2 hours.

Precedent exists for dimeric species analogous to complex *(136)*. Muetterties and co-workers[134] have recently shown that the fully characterized carbonyl bridged complex *(169)* may be prepared by carbonylation of a solution of di-μ-hydrido*tetrakis*tri(*iso*-propyloxy)phosphine *(170)* in

toluene (Scheme II.3.6). ^{31}P-NMR of complex *(169)* showed an AA'BB'XX'



(170) *(169)*

Scheme II.3.6.

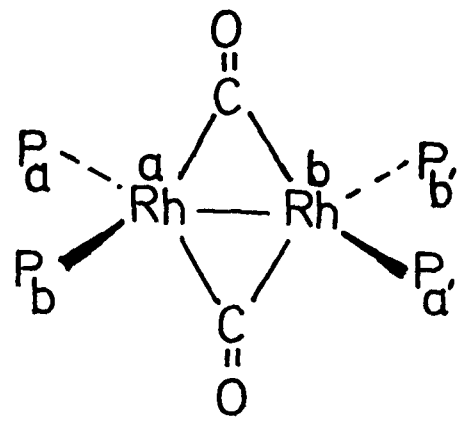
type system which is consistent with the ^{31}P-NMR spectrum of complex *(136)* obtained here (Figure II.3.5). An imperfect ^{31}P-NMR spectral simulation of the latter complex indicated a $J_{H,P}$ value of *ca.* 150 Hz; a J_{Rh-Rh} value of 12 Hz also obtained is consistent with other dimeric rhodium carbonylphosphine complexes.[135] A similar, less well defined complex of composition $Rh_2(CO)_2(PPh_3)_4$ is claimed to have been observed by Wilkinson[81] by decarbonylation of a solution of tetracarbonyltetra(triphenylphosphine)dirhodium *(146)*; the complex exhibits an infra-red carbonyl absorption at 1765 cm^{-1}. Under hydroformylation conditions this red complex is in equilibrium with a yellow hydride-containing dimer.

3.2.2. *Rhodium-triphenylphosphine complexes*

The next reaction considered was that of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* with carbon monoxide; this is of particular relevance to rhodium-catalysed hydroformylation. The changes that were observed by ^{31}P-NMR spectroscopy are shown in Figure II.3.6; the initial complex *(143)* showed line broadening at 293^{o}K but was a

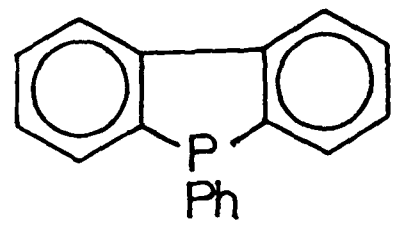
Figure II.3.5.

^{31}P-NMR spectrum of the dimeric rhodium-phosphole complex *(136)* in benzene (a) experimental, (b) simulated (see text)



(136)

P=



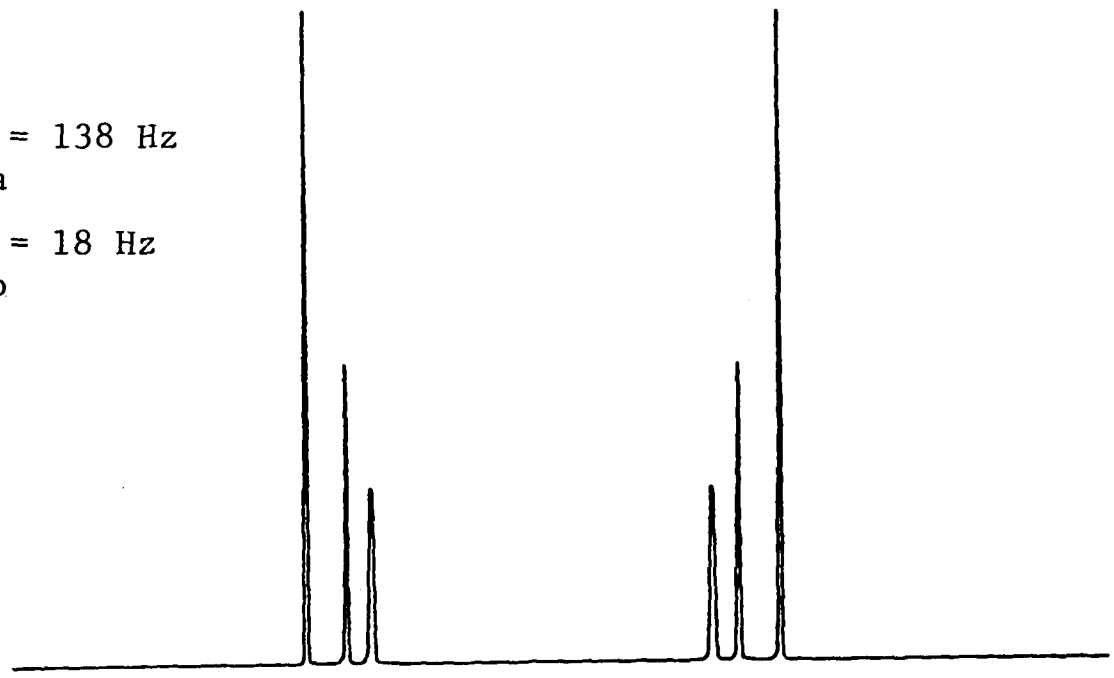
(b)

J_{P_a,P_b} = 150 Hz

J_{P_a,Rh_a} = J_{P_b,Rh_a} = 138 Hz

J_{P_a,Rh_b} = J_{P_b,Rh_b} = 18 Hz

J_{Rh_a,Rh_b} = 8 Hz



(a)

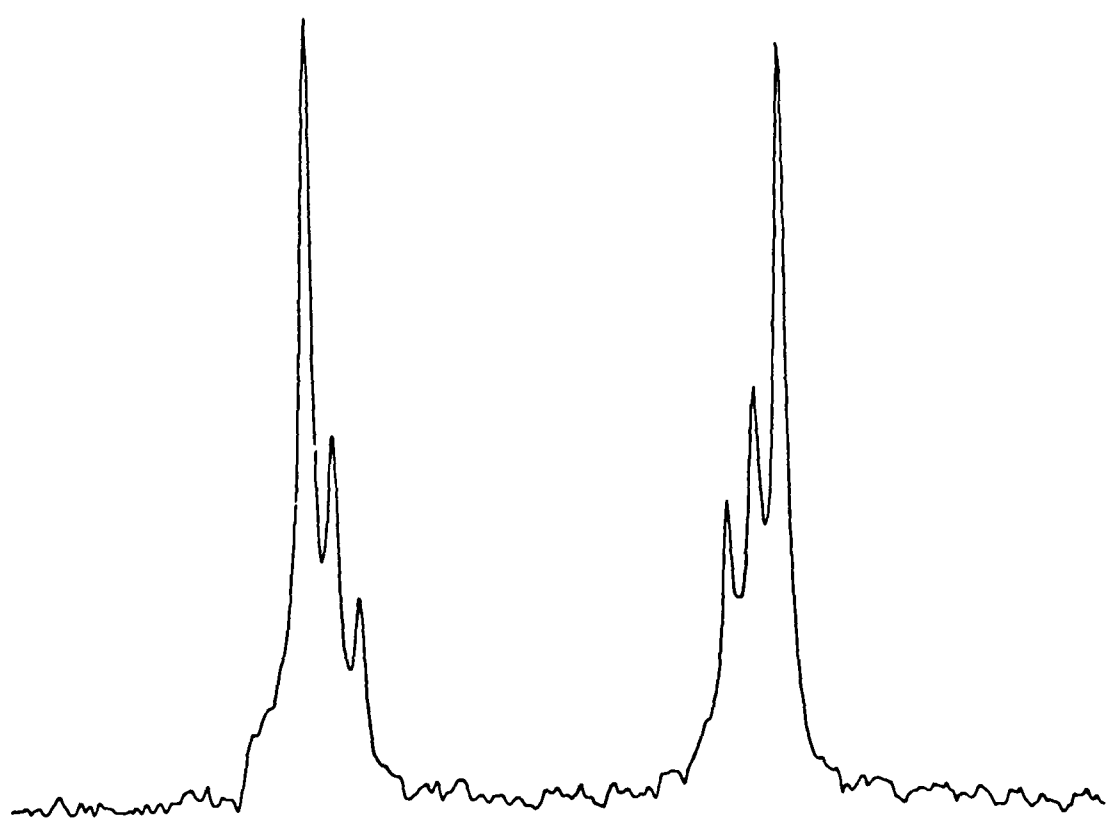
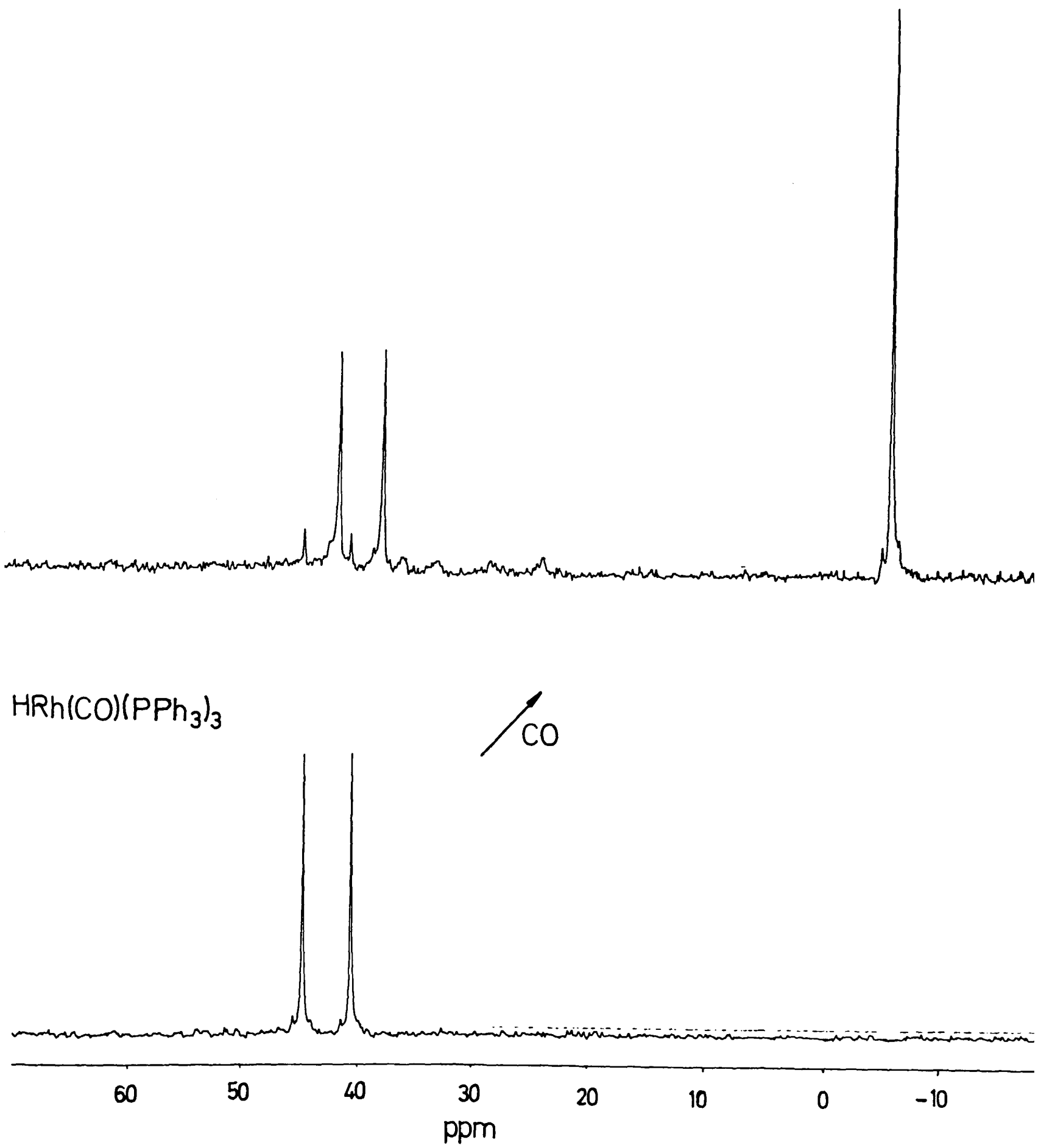


Figure II.3.6.

Reaction of hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) *(143)* with carbon monoxide in toluene, monitored by ^{31}P-NMR

$$HRh(CO)(PPh_3)_3 \overset{CO}{\rightleftharpoons} HRh(CO)_2(PPh_3)_2 + PPh_3$$

(143) *(145)*



clearly resolved doublet at 273°K (δ 42.5 ppm) with a phosphorus-rhodium coupling of 155 Hz. On reaction with carbon monoxide in toluene solution the proportion of the original species *(143)* decreased as two new species were formed, namely triphenylphosphine and a new complex *(145)* to higher field (δ 39.9) with a $J_{P,Rh}$ value of 138 Hz. Similar changes were observed when ^{13}C-carbon monoxide (92% enrichment) was employed, when ^{13}C-^{31}P coupling was apparent. Thus the original species *(143)* appeared as a double doublet ($J_{P,C}$ 10 Hz) (with a residuum of the complex containing ^{12}CO), together with the new species *(145)* which showed further coupling due to two ^{13}C-carbon atoms (double triplet, $J_{P,C}$ 11 Hz). On standing the solution (prepared from ^{12}C- or ^{13}C-carbon monoxide) a third new species *(146)* (δ 26.0, $J_{P,Rh}$ *ca.* 160 Hz) was obtained whose ^{31}P-NMR spectrum was more complex than either that of species *(143)* or *(145)*. This third rhodium complex *(146)* was deposited from its solutions as an air-sensitive yellow solid and infra-red spectroscopy of this material showed carbonyl bands at 1990, 1805 and 1780 cm^{-1} (KBr disc). It was not possible to detect a molecular ion greater than *ca.* 300 for the complex using field desorption mass spectrometry presumably due to facile dissociation under these conditions, or decomposition.

Monitoring the hydride region of the ^{1}H-NMR spectrum throughout the course of the reaction was also informative and Figure II.3.7 illustrates spectra observed at a probe temperature of 248°K (d_8-toluene solvent). Hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* showed a hydridic resonance at δ -9.3 as a broadened quartet; the H-Rh coupling constant, therefore, being less than or equal to the linewidth (*ca.* 1 Hz). On agitation of the solution with ^{12}C-carbon monoxide an immediate colour change from deep yellow to light yellow was observed and the ^{1}H-NMR showed the formation of the new species *(145)* (δ -8.9 ppm). The fine structure

Figure II.3.7.

Reaction of $HRh(CO)(PPh_3)_4$ *(143)* with (a) ^{12}C- and (b) ^{13}C-carbon monoxide in toluene monitored by ^{1}H-NMR

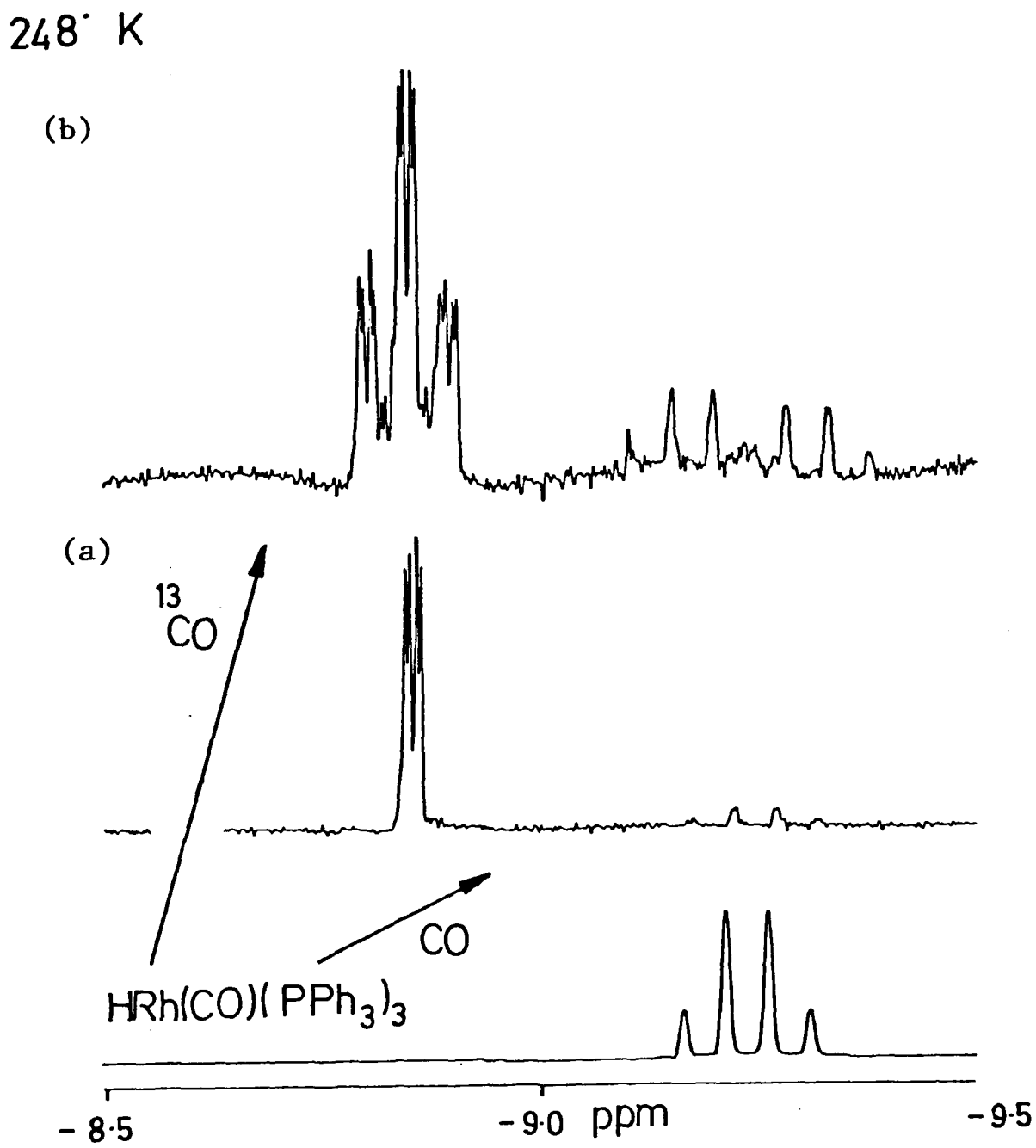
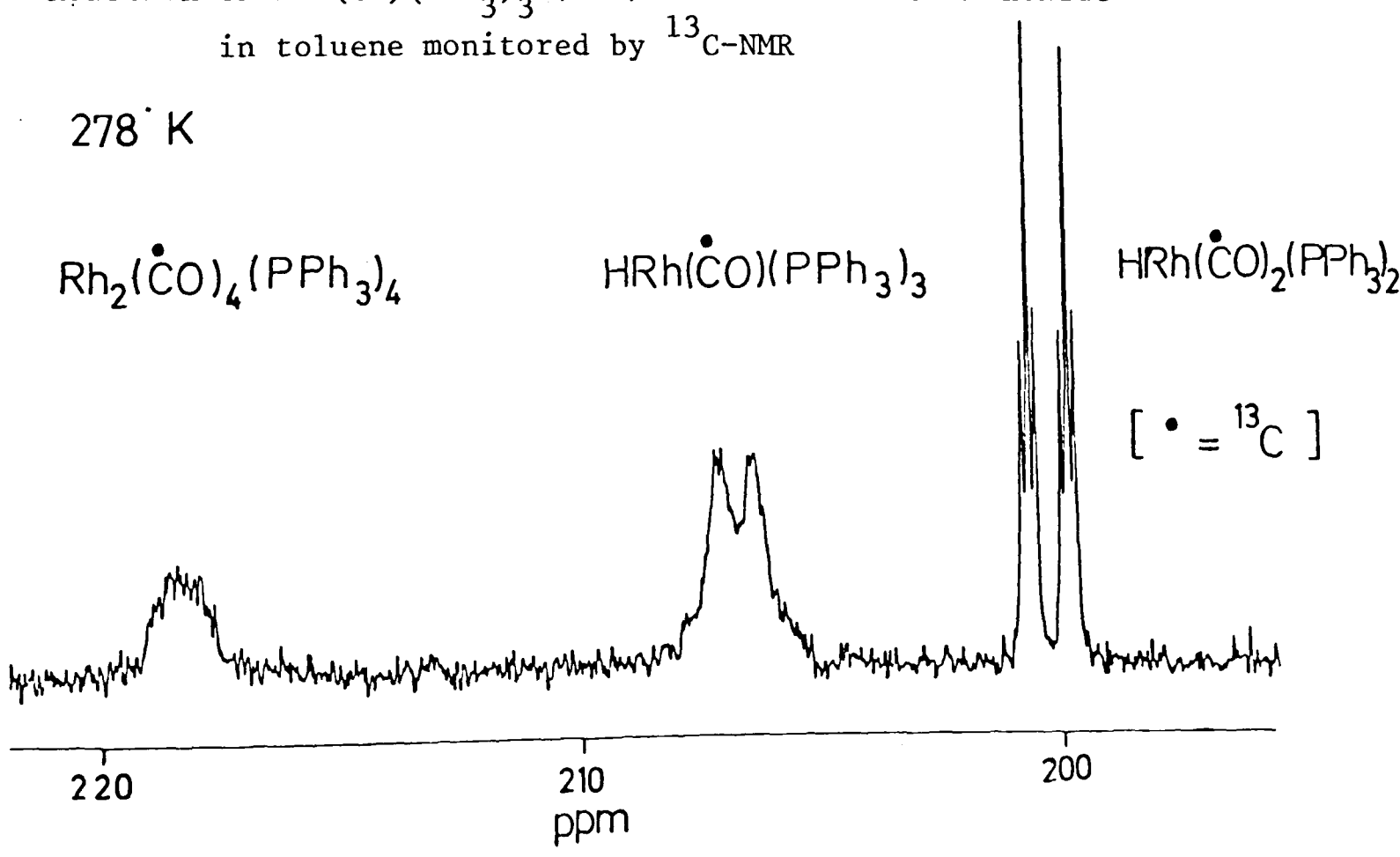


Figure II.3.8.

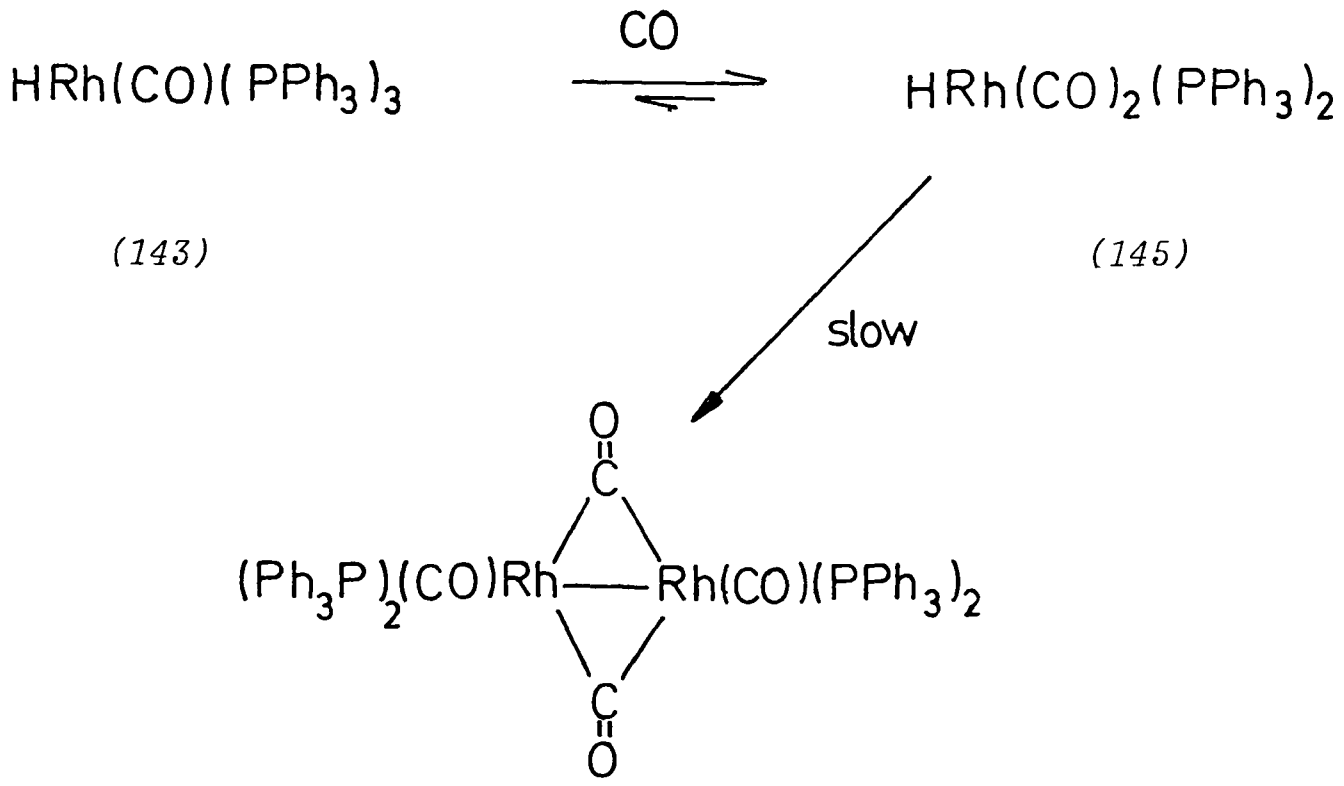
Reaction of $HRh(CO)(PPh_3)_3$ *(143)* with ^{13}C-carbon monoxide in toluene monitored by ^{13}C-NMR



of this latter complex (double doublet) suggests coupling to two inequivalent heteroatoms, which may be either two phosphorus nuclei or one rhodium and one phosphorus nucleus. Reaction of ^{13}C-carbon monoxide (in place of the ^{12}C-labelled gas) with ^{13}C-labelled complex *(153)* caused a triplet of double doublets to be observed; therefore the presence of two rhodium coordinated ^{13}C-carbonyl groups is confirmed. Standing the reaction solutions under carbon monoxide or prolonged agitation with the gas produced no new species in the region δ=0 to -15 ppm, implying that the complex *(146)* is not a rhodium-hydride. The ^{13}C-NMR spectrum of a solution containing all three rhodium complexes *(143)*, *(145)* and *(146)* produced by reaction of complex *(143)* with ^{13}C-carbon monoxide, confirmed the presence of coordinated ^{13}CO groups in all three species (Figure II.3.8). The spectrum of complex *(146)* was broad over a range of temperatures (243-278^{o}K) and no coupling constants could be obtained; the ^{13}C-carbonyl resonance of complex *(145)*, however, was clearly defined as a double triplet, due to coupling to a single rhodium and two magnetically equivalent phosphorus atoms. All NMR spectra were considerably broadened at ambient temperatures. Similar results were obtained when hydrogen and carbon monoxide (1:1 mixture) were used in place of carbon monoxide, or when the reaction was performed in dichloromethane. It was shown, however, that prolonged standing (*ca.* 1 week) of the dichloromethane reaction solution deposited crystals of the rhodium Vaska complex *trans-bis*(triphenylphosphine)chlorocarbonyl-rhodium(I) *(100)* (by comparison with an authentic sample).

The structures attributed to complex *(145)* and *(146)* are shown in Scheme II.3.7 and the subsequent Table (II.3.2) contains NMR data obtained from the experiments described above.

The majority of studies on the reaction of hydridocarbonyl*tris*(tri-



Scheme II.3.7.

Table II.3.2

NMR-Data of Rhodium-triphenylphosphine complexes

Complex	$HRh(CO)(PPh_3)_3$ *(143)*	$HRh(CO)_2(PPh_3)_2$ *(145)*	$Rh_2(CO)_4(PPh_3)_4$ *(146)*
^{1}H-NMR			
Rh-H δ(ppm)(d_8-(toluene)	-9.3	-8.9	-
$J_{H,Rh}$(Hz)	⩽1	(see text)	-
$J_{H,P}$(Hz)	14		-
$J_{H,C}$(Hz)	38	15	-
^{31}P-NMR			
Rh-P δ(ppm)(toluene)	42.5	39.9	26
$J_{P,Rh}$(Hz)	155	138	*ca.*160
$J_{P,C}$(Hz)	10	11	-
^{13}C-NMR			
Rh-*CO* δ(ppm)(d_8-toluene)	206.8	200.3	218.5
$J_{C,Rh}$(Hz)	50	63	-
$J_{C,P}$ (Hz)	10	11	-

phenylphosphine)rhodium(I) reported in the literature were carried out by Wilkinson and co-workers (see page 86 for more detailed discussion); many authors refer to these studies when discussing rhodium catalysed hydroformylation. It had, however, not been conclusively established that hydridodicarbonyl*bis*(triphenylphosphine)rhodium(I) *(145)* is the initial carbonylation product of $HRh(CO)(PPh_3)_3$ since previous conclusions were based primarily on infra-red evidence. Using ^{13}C-carbon monoxide and by observation of ^{1}H- and ^{31}P-NMR it has been possible to show that the initial carbonylation product has two rhodium-coordinated carbonyl groups. The CO group equivalence may be due to their being in identical chemical environments in a structure static on the NMR timescale, or more likely, to their interconversion by a process which is fast on the NMR timescale. The mechanism for this latter process may be intermolecular or rapid dissociation - reassociation of ligands. Interpretation of the hydride region due to $HRh(CO)_2(PPh_3)_2$ *(145)* (Figure II.3.7) was more difficult since H-P and H-Rh couplings could not be distinguished. The spectra obtained, however, were temperature dependent, possibly due to an equilibrium between two or more isomers as was proposed for hydridodicarbonyl*bis*(triphenylphosphine)-iridium(I) *(149)* described earlier.[120] The complex *(170)* prepared by Muetterties and co-workers,[134] hydridodicarbonyl*tris* tri(O-*iso*-propyloxy)-phosphine rhodium, may be isostructural since ^{1}H-NMR showed the major species at low temperature ($208^{o}K$) consisted of a doublet of doublets analogous with that reported here. The spectrum of the former complex *(170)* was temperature dependent so that at ambient temperature a resonance at δ -10.0 ppm with $J_{H,Rh}$ 9 Hz and $J_{H,P}$ 63 Hz was observed.

The complex *(146)*, slowly formed under the reaction conditions appears to be the carbonyl bridged dimeric complex tetracarbonyltetra(triphenyl-

$$HRh(CO)_2[P(O\text{-}\underline{i}\text{-}C_3H_7)_3]_2$$

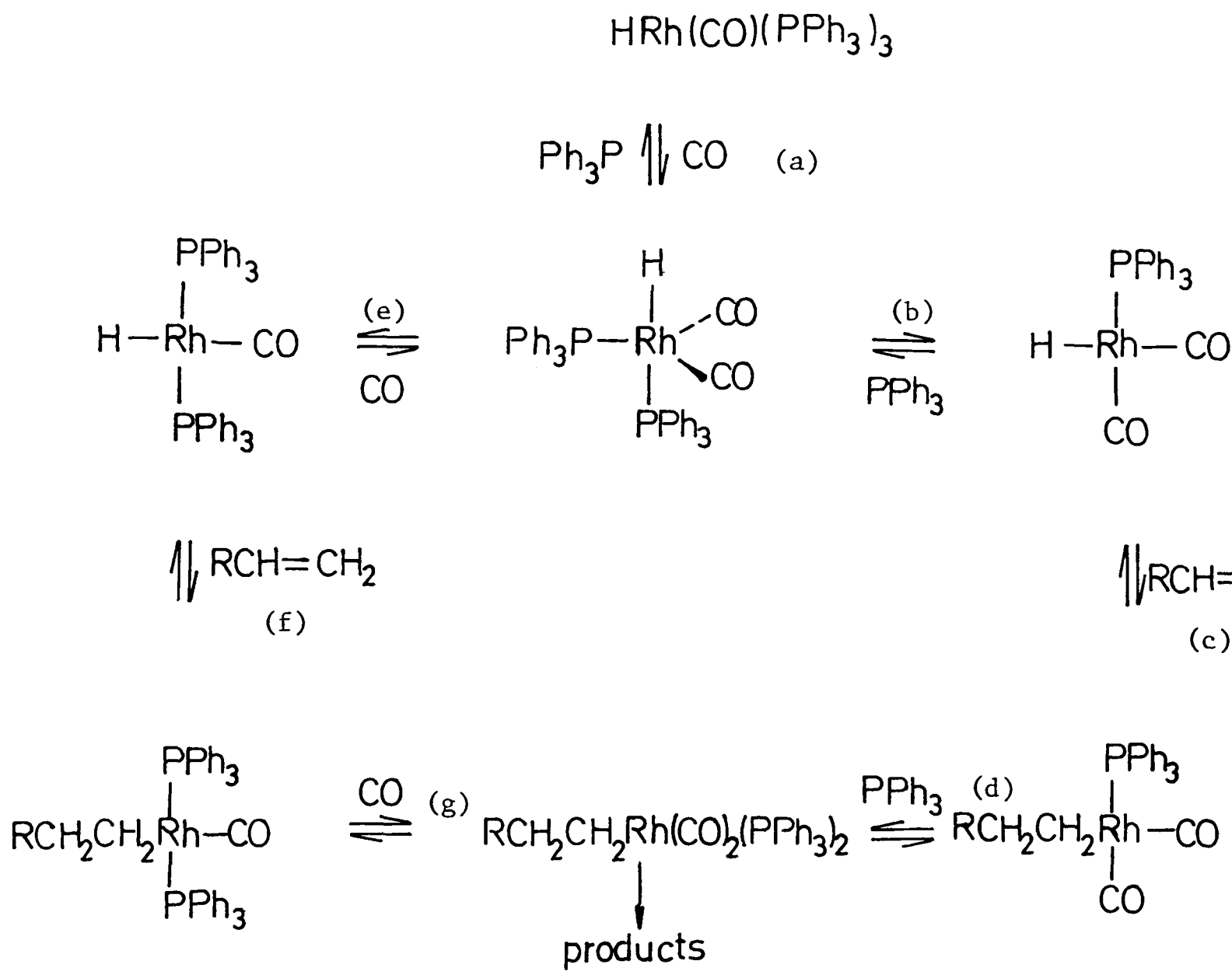
(170)

phosphine)dirhodium which had previously been identified by Wilkinson.[81] The presence of bridging and terminal carbonyl groups was confirmed by infra-red spectroscopy (ν_{CO} 1990, 1805 and 1780 cm^{-1}).

In a similar manner to that described for 5-phenyl-5*H*-dibenzophosphole complexes, methylenecyclopropane *(166)* was added to a toluene solution containing both monocarbonyl *(143)* and dicarbonyl *(145)* complexes at 278°K. This caused immediate disappearance of the ^{1}H-NMR hydride resonance attributed to $HRh(CO)_2(PPh_3)_2$ and so it seems likely that the complex *(145)* is responsible for the initiation of the hydroformylation catalytic cycle. In a further experiment complexes *(143)* and *(145)* were also formed on reaction of hydrido*tetrakis*(triphenylphosphine)rhodium(I) *(155)* with carbon monoxide, and similarly gave rise to the dimeric complex *(146)* on standing.

The rhodium-phosphine species described above are present under hydroformylation conditions and therefore must be of critical importance to the understanding of the reaction mechanism. Very little information is available regarding rates or equilibria of ligand exchange processes occurring in the carbonyl-phosphine complexes *(143)* and *(145)*. Indeed Wilkinson claims[81] that hydridocarbonyl*bis*(triphenylphosphine)rhodium(I) *(144)* is present in finite quantity; this has never been refuted.

On present knowledge the pathways (b) to (d) or (e) to (g) (Scheme II.3.8) are equally probable.



Scheme II.3.8.

The rate constants of rapid intermolecular reactions may be measured by NMR techniques and spin saturation has been widely used in this context.[136] The original method of Forsen and Hoffmann[137] applied a coherent radiofrequency source to a single site frequency in the spectrum and observed changes which occurred in the time period after irradiation

ceased. This may be applied to Fourier Transform NMR spectroscopy provided that a single frequency homonuclear decoupler is available. When it is not, the pulse sequence *DANTE*, introduced by Freeman and co-workers, may be employed.[138] This involved a rapid series of weak radiofrequency pulses at a single site and monitoring the changes in the spectrum through the pulse sequence shown below.

(1) Wait for equilibrium (D1)

(2) *DANTE* pulse sequence with 180^{o} flip angle on resonance

(3) Variable exchange delay t

(4) Acquire free-induction decay and add to store

(5) Improve signal-to-noise by repeating (1) to (4)

The site of irradiation may be inverted and recovers by spin-lattice relaxation transfer. By varying t, the rate constants for all the relaxations may be obtained. Thus a solution containing hydridocarbonyl-triphenylphosphine (0.100 M) was first examined and the ^{31}P-NMR spectrum obtained at $280^{o}K^{*}$. Then the resonance due to triphenylphosphine was irradiated as described earlier and a series of spectra were obtained for different values of t, starting shortly after the irradiation (Figure II.3.9). Plots of signal intensity for triphenylphosphine and complex *(143)* versus t are illustrated in Figure II.3.10. It is evident from these time dependences that exchange between free and rhodium-coordinated triphenylphosphine was taking place because part of the saturation is transferred to the rhodium complex by the mechanism shown below.

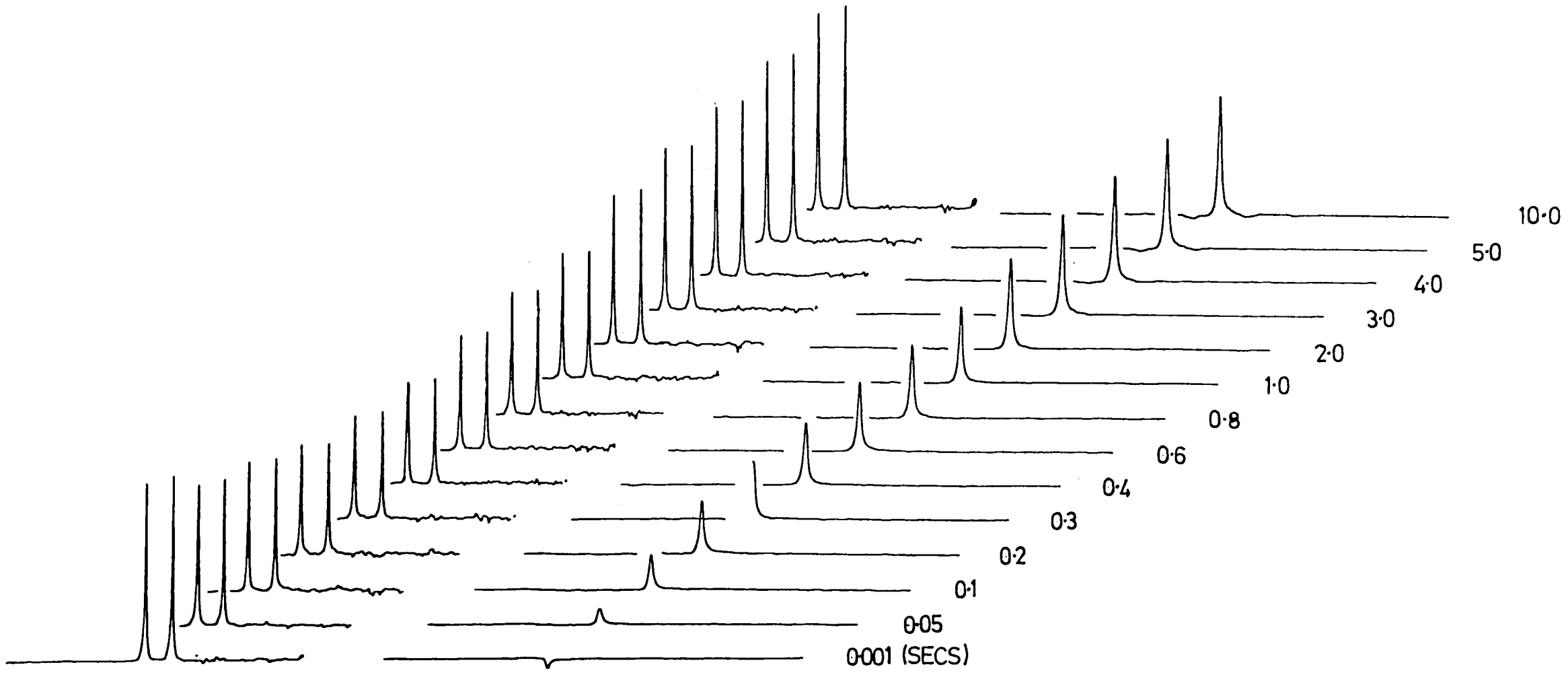
$$^{\bullet}PPh_3 + HRh(CO)(PPh_3)_3 \rightleftharpoons PPh_3 + HRh(CO)(PPh_3)_2(^{\bullet}PPh_3)$$

$^{\bullet}P$ is the excited nucleus

* At this temperature the pure complex shows only a doublet at δ 42.5 ppm so that there is no significant dissociation at equilibrium.

Figure II.3.9.

Study of rates of phosphine exchange between $HRh(CO)(PPh_3)_3$ and free PPh_3 by ^{31}P-NMR using a *DANTE* pulse sequence of seventy pulses of flip angle $\pi/70$ radians, lasting 70 μ sec. The time axis represents the delay t after selective inversion of the triphenylphosphine resonance.



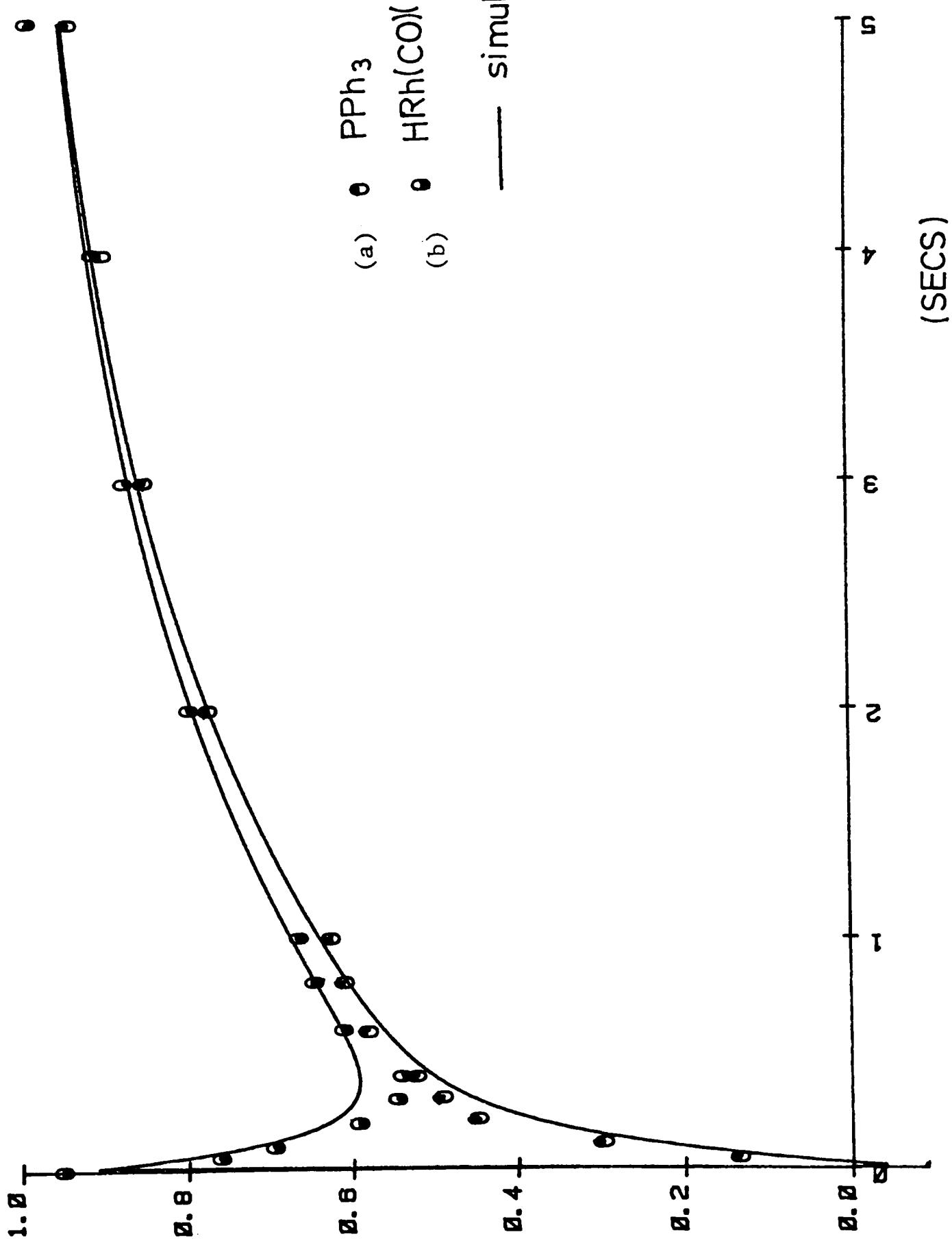


Figure II.3.10

Plots of signal intensities of (a) PPh_3 and (b) $HRh(CO)(PPh_3)_3$ versus t (from *DANTE* ^{31}P-NMR experiment)

Simulation of the experimental data (Figure II.3.10) using programs described in Appendix A gave values for the rate constant k_1 of 4 s^{-1} and spin-lattice relaxation times for triphenylphosphine and complex *(143)* of 16.7 s^{-1} and 1.2 s^{-1} respectively. Assuming that exchange in the 18-electron complex occurs entirely by a single mechanism the rate constant k_1 is the rate constant for dissociation of one triphenylphosphine in *(143)*. This analysis does not include a statistical correction which would be necessary to account for the three PPh_3 residues in *(143)* at higher levels of excitation transfer. At room temperature this implies a dissociation rate constant for the catalyst of *ca.* 10 s^{-1}, much faster than catalytic turnover under ambient conditions.

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) *(143)* and hydridodicarbonyl*bis*(triphenylphosphine)rhodium (I) *(145)* [prepared by carbonylation of the former complex (0.050 $\underline{M}$)] was examined in a similar manner. Thus the resonance due to triphenylphosphine was irradiated and the effect on complexes *(143)* and *(145)* observed with respect to t (Figure II.3.11). The plots of signal intensity versus t are shown in Figure II.3.12. Since there are now six interdependent variables (*i.e.* the three spin-lattice relaxation times and the three rate constants) the accuracy of the analysis is lower. Three of the parameters may be derived from the earlier experiment since conditions of observation are identical. Attempts to fit the data ignoring one or other of the new relaxation processes corresponding to k_2 and k_3(Figure II.3.13) make it clear that *both* are necessary to explain the time dependence of the spectra. Inspection of these (Figure II.3.11) suggested that some saturation was transferred to complexes *(143)* and *(145)*; in addition there is another transfer process which must correspond to an interaction between complexes *(143)* and *(145)*. This is summarized in Figure II.3.13.

Figure II.3.11

Study of rates of phosphine exchange between $HRh(CO)(PPh_3)_3$, $HRh(CO)_2(PPh_3)_2$ and free PPh_3 by ^{31}P-NMR using a *DANTE* pulse sequence of eighteen pulses of flip angle $\pi/18$ radians, lasting 72 μ sec. The time axis represents the delay t after selective excitation of the triphenylphosphine resonance.

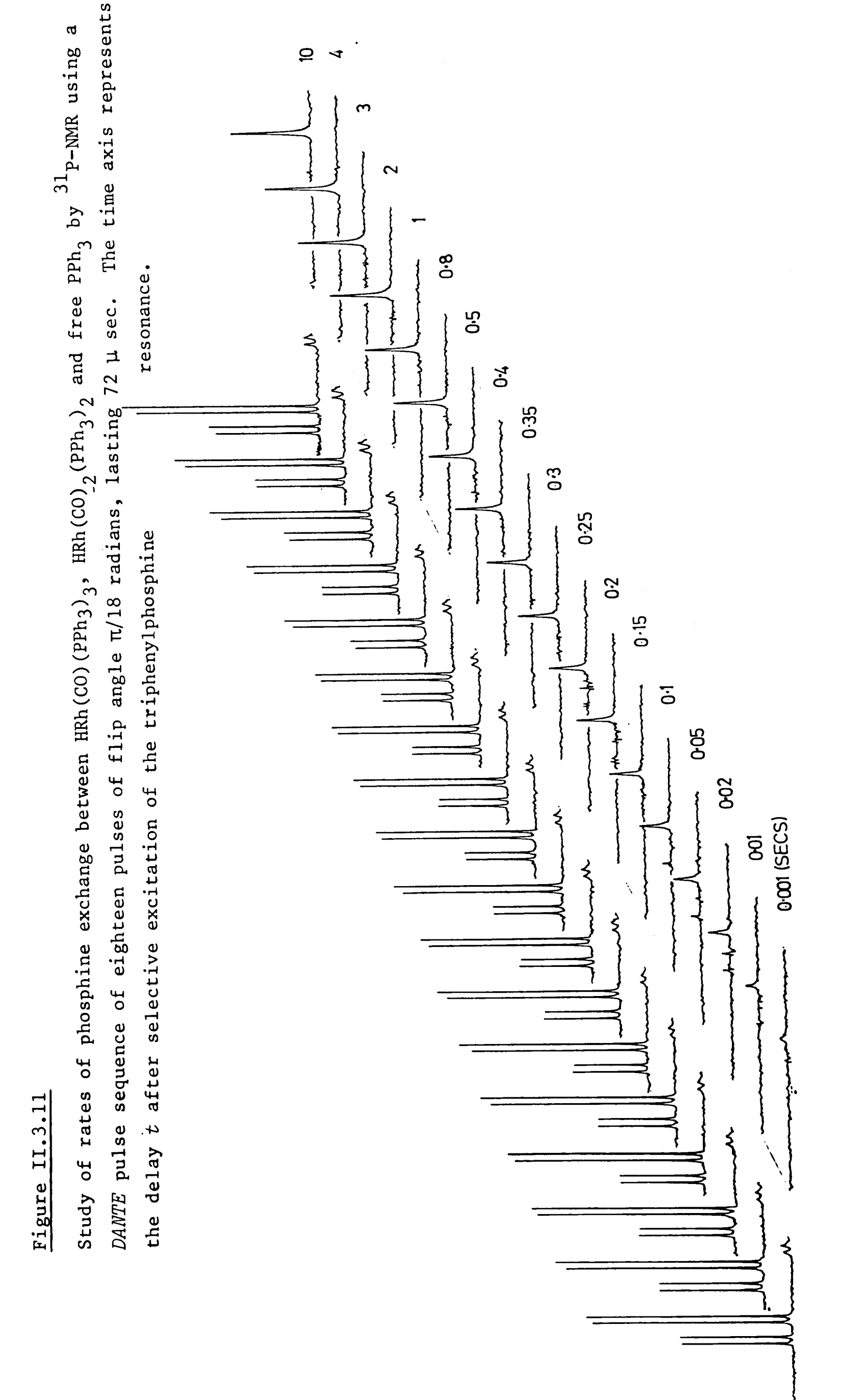
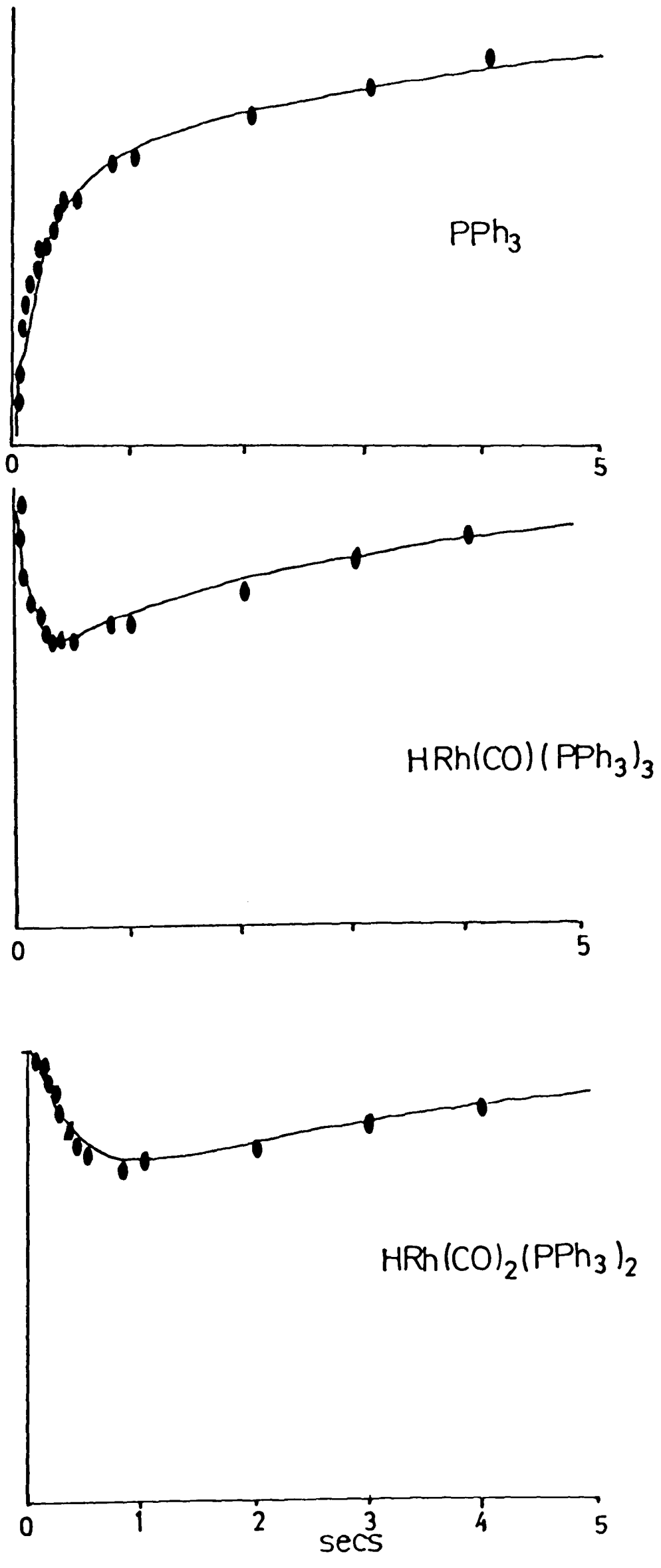


Figure II.3.12

Plots of signal intensities of (a) PPh_3, (b) $HRh(CO)(PPh_3)_3$ and (c) $HRh(CO)_2(PPh_3)_2$ versus t (from *DANTE* ^{31}P-NMR experiment).



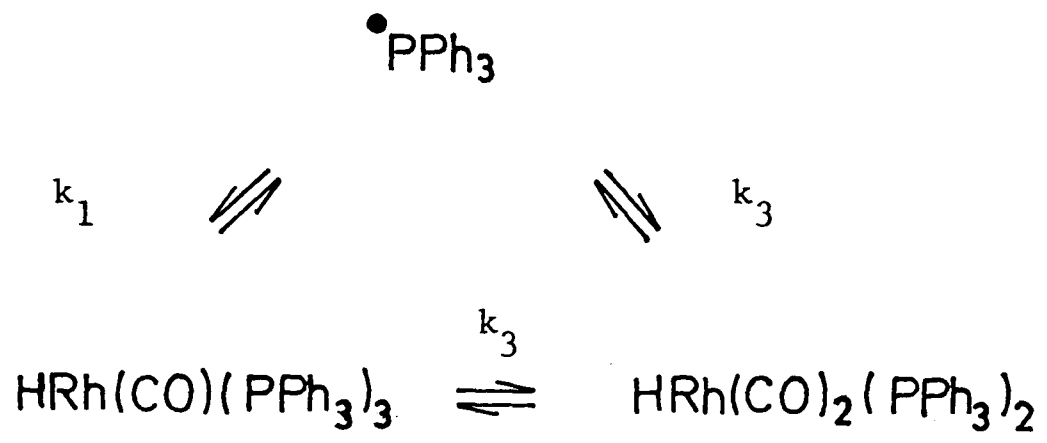


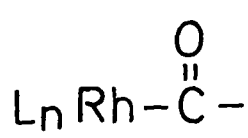
Figure II.3.13

Simulation of the data using the program described in Appendix A as before, the rate constants of the dissociative processes K_1, K_2 and K_3 are 2.5 s^{-1}, 1.75 s^{-1} and 0.5 s^{-1} respectively at 280°K. (Spin-lattice relaxation times of PPh_3, $HRh(CO)(PPh_3)_3$ and $HRh(CO)_2(PPh_3)_2$ are 20 s^{-1}, 2.5 s^{-1}, and 3.0 s^{-1} respectively).

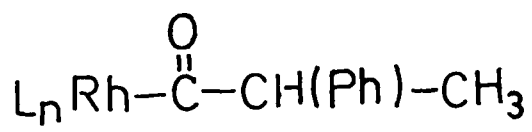
These experiments demonstrate that all the kinetic processes shown in Figure II.3.12 are rapid under hydroformylation conditions. Dissociation of triphenylphosphine from the monocarbonyl complex *(143)* is more rapid than its dissociation from the dicarbonyl complex *(145)* but both square planar intermediates derived from the latter complex (Scheme II.3.8) may contribute to the catalytic cycle. The interconversion of hydridocarbonyl-*tris*(triphenylphosphine)rhodium (I) *(143)* and hydridodicarbonyl*bis*(triphenylphosphine)rhodium (I) *(145)*, presumed to occur *via* the unsaturated complex hydridocarbonyl*bis*(triphenylphosphine)rhodium (I) *(144)*, is also rapid and reversible. Trapping of this intermediate by carbon monoxide occurs at a similar rate to its trapping by triphenylphosphine.

III.3.3. *Rhodium-phosphine species present under hydroformylation conditions in the presence of substrate.*

The only published NMR study of reactive intermediates formed under hydroformylation conditions at ambient temperature and low pressure was performed by Wilkinson and co-workers.[18,81] It was shown that no apparent reaction occurred between styrene and hydridocarbonyl*tris*-(triphenylphosphine)rhodium(I) under nitrogen, but under carbon monoxide new species were formed which were tentatively suggested to be the rhodium acyl-complexes *(171)* and *(172)*, these structures being considered consistent with the ^{1}H-NMR spectrum. Infra-red spectroscopy showed a band at 1645 cm^{-1} confirming the presence of an acyl group but



(171)



(172)

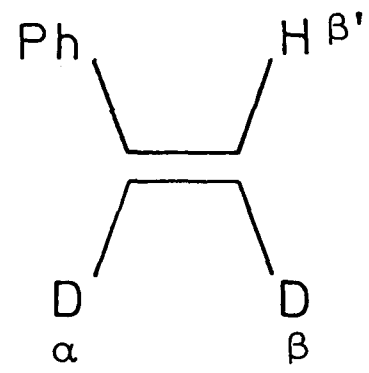
L = PPh_3 , CO

gave no clear information about substitution and stereochemistry at rhodium. In this section it will be shown that acyl complexes of the type *(171)* and *(172)* are indeed formed under the reaction conditions described above, but Wilkinson's NMR observations are incomplete, and incorrect in one instance.

III.3.3.1 *Styrene Isomerization*

Hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) is known to be an efficient olefin isomerization catalyst[17] and the aim of initial experiments was to detect a reaction between the complex and styrene.

The identification of a styrene isomerization process requires the use of a deuterium labelled reactant. Thus the time dependence of a solution of specifically *cis*-labelled dideuterio-styrene *(165)* (0.5 M) and the complex *(143)* (0.02 M) was monitored by ^{1}H-NMR spectroscopy (Figure II.3.14). The results obtained show that β to β' and not α to β' deuterium-hydrogen exchange is the major olefin isomerization pathway. Whereas β and β' sites had been equilibrated



(165)

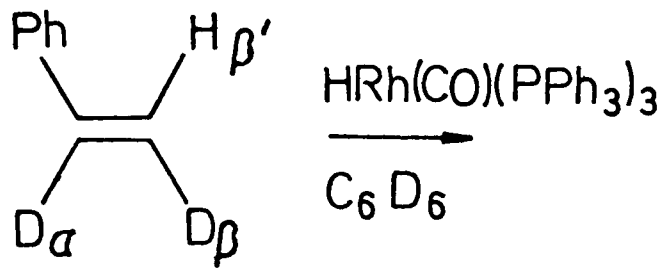
after *ca.* 30 min, even after 120 min. the relative integrals of the α, β and β' sites were 10:35:55. The turnover number for the faster process is quite comparable with the overall rate of hydroformylation under ambient conditions at similar catalyst and reactant concentrations *(vide infra)*.

The effects of triphenylphosphine (0.05 M) and subsequently carbon monoxide on the isomerization of styrene *(165)* were considered next and ^{1}H-NMR spectra and plots of β and β' sites versus time for these experiments are shown in Figures II.3.15 and II.3.16 respectively. In both cases the isomerization was suppressed since only 10% or less of the olefin was isomerized after 30 min; this corresponds to a drop in reaction rate of at least fifty-fold.

It is probable that the catalytic reaction proceeds *via* a 16-electron coordinatively unsaturated complex derived from hydridocarbonyl*tris*-

Figure II.3.14

Reaction of *cis*-1,2-$[^2H]_2$-styrene *(165)* with $HRh(CO)(PPh_3)_3$ in benzene monitored by ^1H-NMR



(165)

Figure II.3.15

Reaction of *cis*-1,2-$[^2H]_2$-styrene (*165*) with $HRh(CO)(PPh_3)_3$ in benzene monitored by ^1H-NMR; (a) in the presence of five equivalents of PPh_3; (b) under CO.

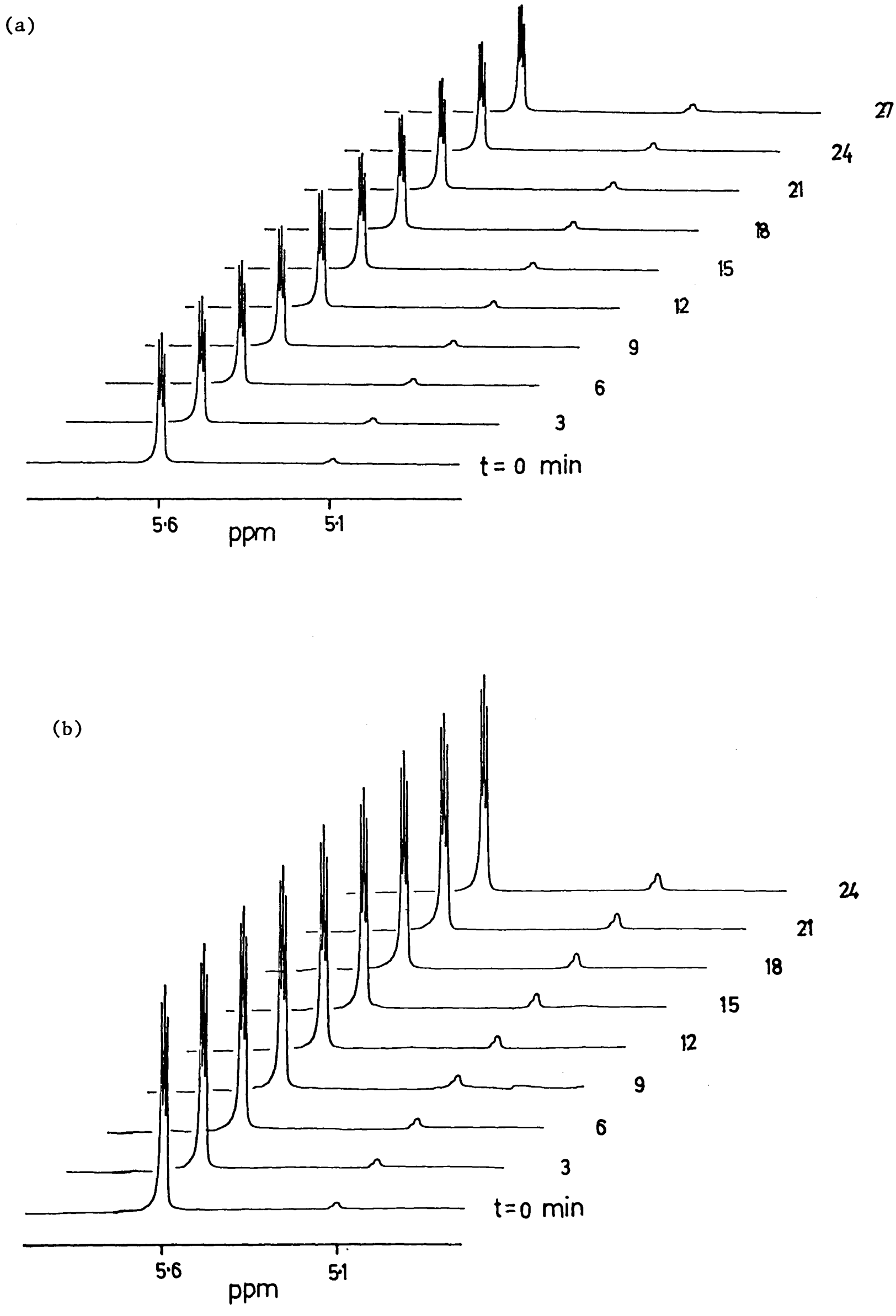
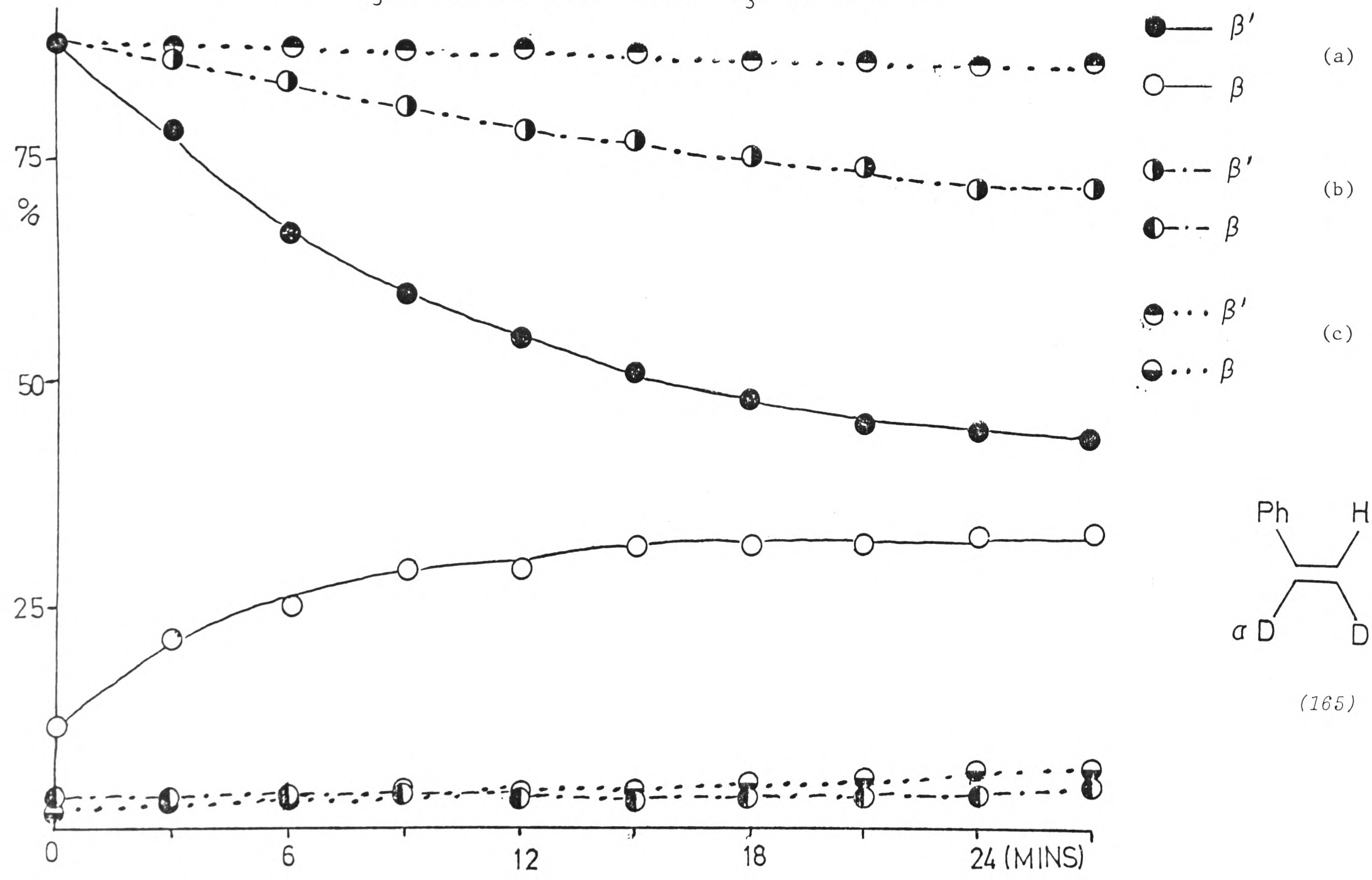


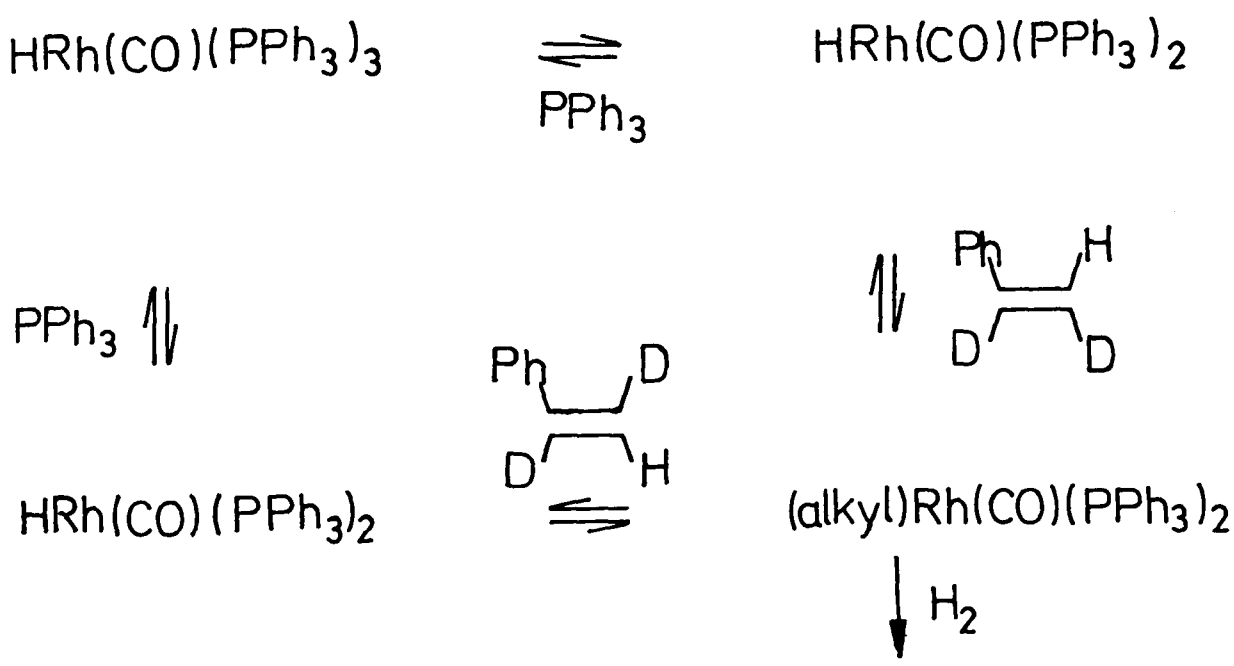
Figure II.3.16

Plots of relative signal intensities of β' and β sites of styrene *(165)* on reaction with $HRh(CO)(PPh_3)_3$ versus time; (a) no PPh_3, no CO; (b) 5 equivalents PPh_3; (c) under CO



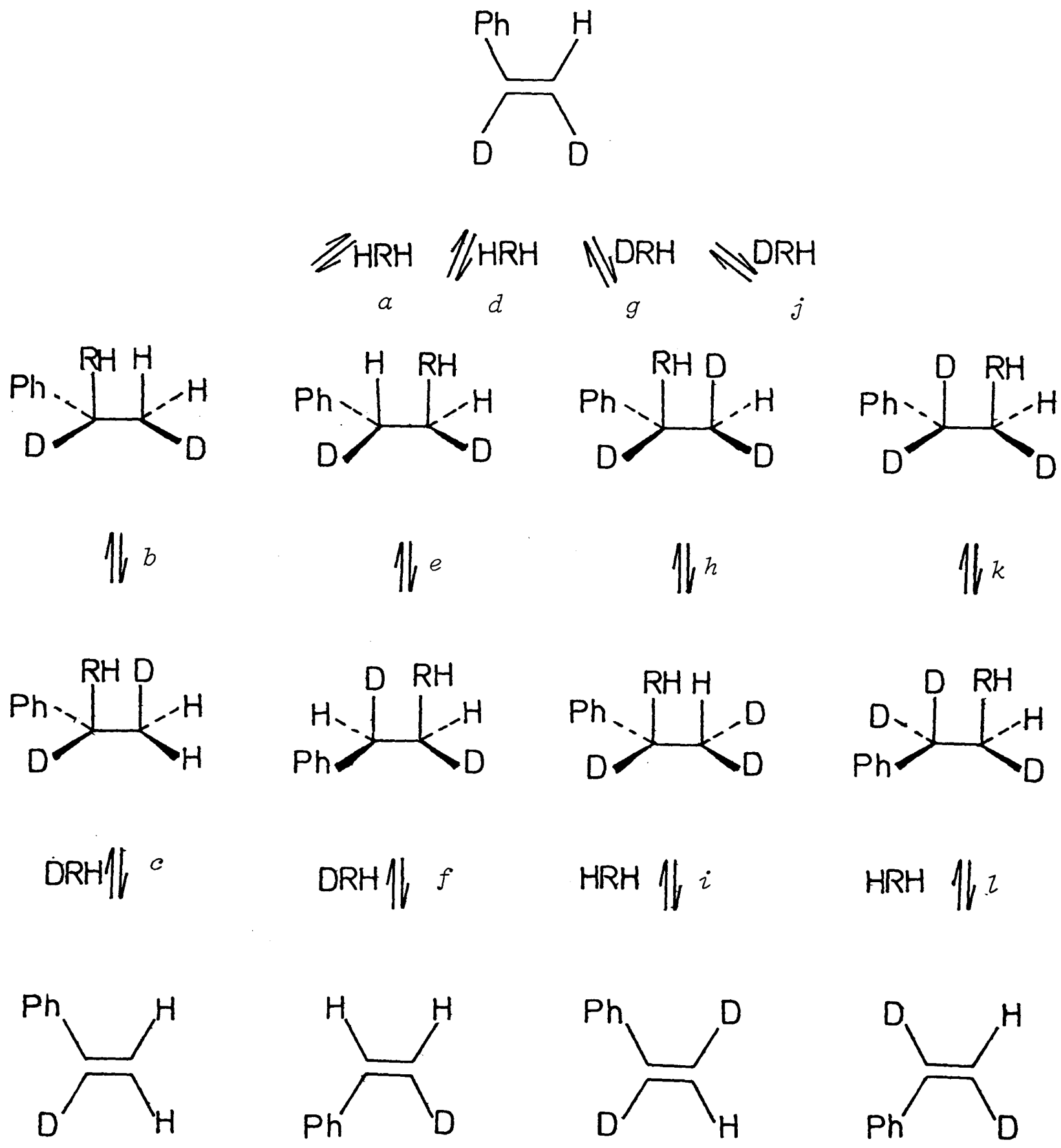
(165)

(triphenylphosphine)rhodium (I) by phosphine dissociation since addition of triphenylphosphine markedly lowers the rate of reaction. Hydridocarbonyl*bis*(triphenylphosphine)rhodium (I) *(144)* is proposed as the true catalytic species for the hydrogenation of olefins with the *tris*(phosphine) complex *(143)*;[139] this suggests that the former coordinatively unsaturated species *(144)* is also an active olefin isomerization catalyst since the initial reaction steps for isomerization and hydrogenation must be the same. Scheme II.3.9. illustrates these steps for deuterated reactant.



Scheme II.3.9.

These experiments demonstrate that reversible addition of rhodium hydride to styrene is rapid, but are not directly informative about the regioselectivity. This is because the catalyst itself undergoes H-D exchange in the initial stages of reaction (Scheme II.3.10 (a)-(c) and (d)-(f)). Stereospecific addition of rhodium deuteride to styrene to form the 2-phenylethylrhodium complex does not lead to β to β' to α



HRH= $HRh(CO)(PPh_3)_2$

DRH= $DRh(CO)(PPh_3)_2$

Scheme II.3.10

hydrogen-deuterium exchange (Scheme II.3.10 (g)-(i)). When the complex does not contain deuterium this addition affords a pathway for introducing hydrogen into the α-position (Scheme II.3.10 (d)-(f)). It is probable, however, that addition of rhodium to the benzylic site is faster since successive additions to the terminal position would lead to equilibration of α, β and β' sites; this process is very much slower than β,β' isomerization as mentioned earlier.

The reversible addition of olefins to hydrido-metal complexes has been observed in a number of cases; in some circumstances both hydrido-metal and alkyl-metal complexes may be identified by NMR methods. For example the ruthenium complex *(173)* reacts with ethylene (35 atmospheres) to form the alkyl ruthenium complex *(174)*.[140] Other examples of olefin insertion into metal-hydride bonds were discussed in Chapter I. Section 2.

$$HRuCl(PPh_3)_3 \quad \underset{}{\overset{H_2C=CH_2\ ,\ 35atm.}{\rightleftharpoons}} \quad CH_3CH_2RuCl(PPh_3)_3$$

(173) *(174)*

Carbon monoxide also suppresses the isomerization of *cis*-1,2-$[^2H]_2$-styrene *(165)* catalysed by hydridocarbonyl*tris*(triphenylphosphine)rhodium (I). In the previous section it was shown that hydridodicarbonyl*bis*(triphenylphosphine)rhodium (I) *(145)* and triphenylphosphine were the initial species formed on carbonylation of the *tris*(phosphine)-monocarbonyl complex *(143)*. Since k_{-1} (Scheme II.3.11) is dependent on the concentration of free triphenylphosphine, the phosphine produced on formation of species *(145)* may account for the suppression of isomerization.

$$HRh(CO)(PPh_3)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRh(CO)(PPh_3)_2 \overset{CO}{\rightleftharpoons} HRh(CO)_2(PPh_3)_2$$

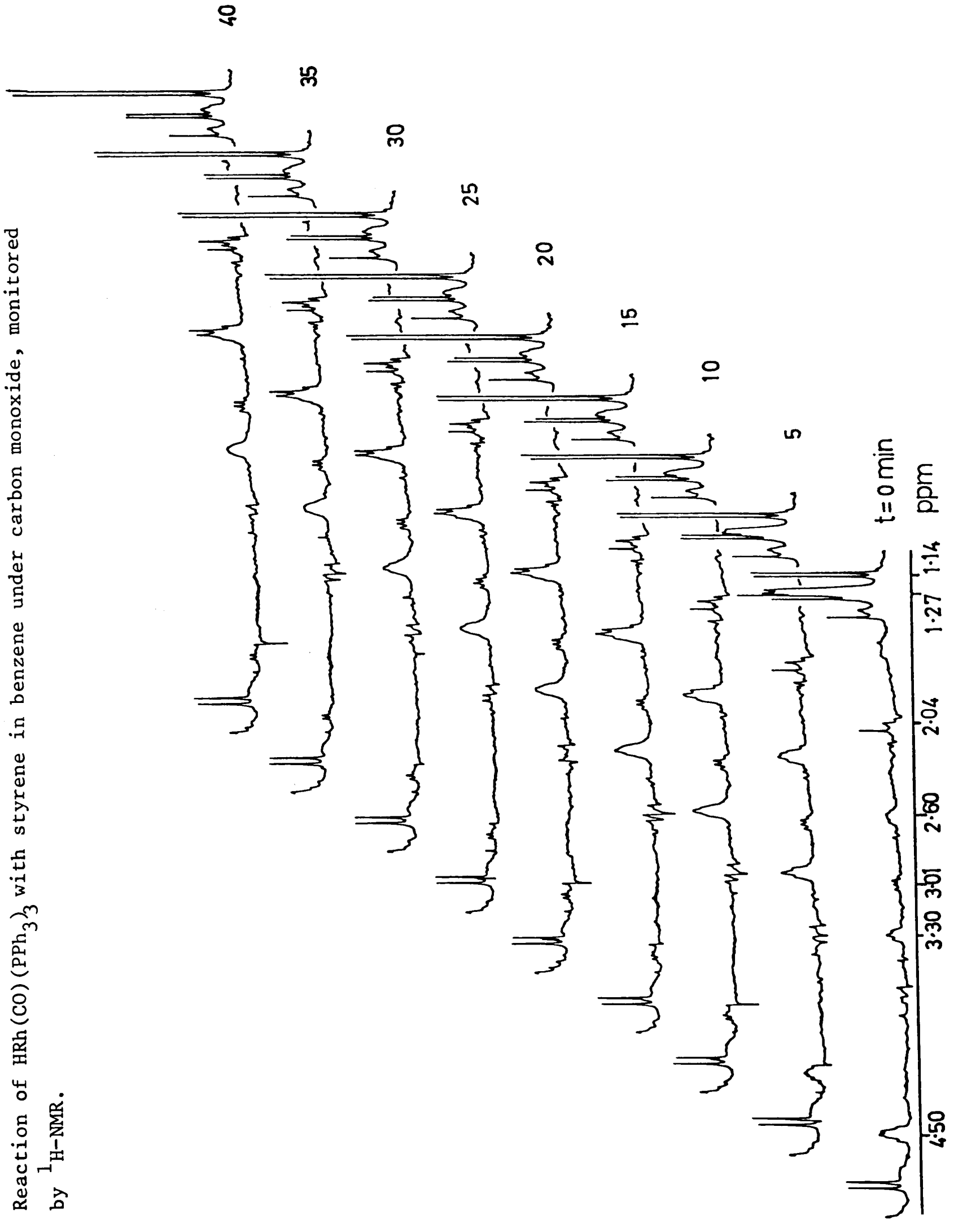
(143) *(144)* *(145)*

III.3.3.2 *The study of rhodium-acyl complexes by* ^{1}*H-NMR*

The next series of experiments involved addition of styrene to a solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) under a carbon monoxide atmosphere and observation of the ^{1}H-NMR spectrum. This was carried out to ascertain the relative concentrations of styrene and complex *(143)* required for optimum formation of acyl complexes *(171)* and *(172)*, so that ^{13}C-labelling studies and heteronuclear techniques could be used to their fullest extent. In these following experiments it was found necessary to employ styrene of high purity, obtained by preparative gas chromatography and used immediately. Thus styrene (0.025 mmol) was added to a solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) *(143)* (0.02 $\underline{\underline{M}}$) in benzene, pre-treated with carbon monoxide and the ^{1}H-NMR spectrum obtained directly after addition. Contrary to expectation[18] the spectrum was time dependent, and changes were recorded for a sequence over the δ=0 to 10 ppm region (Figure II.3.17). These spectra are interpreted in terms of the formation of rhodium-acyl complexes *(171)* and *(172)* together with 3-phenylpropanal *(175)* and 2-phenylpropanal *(176)* (Figure II.3.18). The assignments, differing in the case of the *iso*-acyl complex

Figure II.3.17

Reaction of $HRh(CO)(PPh_3)_3$ with styrene in benzene under carbon monoxide, monitored by ^1H-NMR.



(172) from that proposed by Wilkinson,[18] were made with reference to authentic samples of aldehydes *(175)* and *(176)*, a stable acyl rhodium

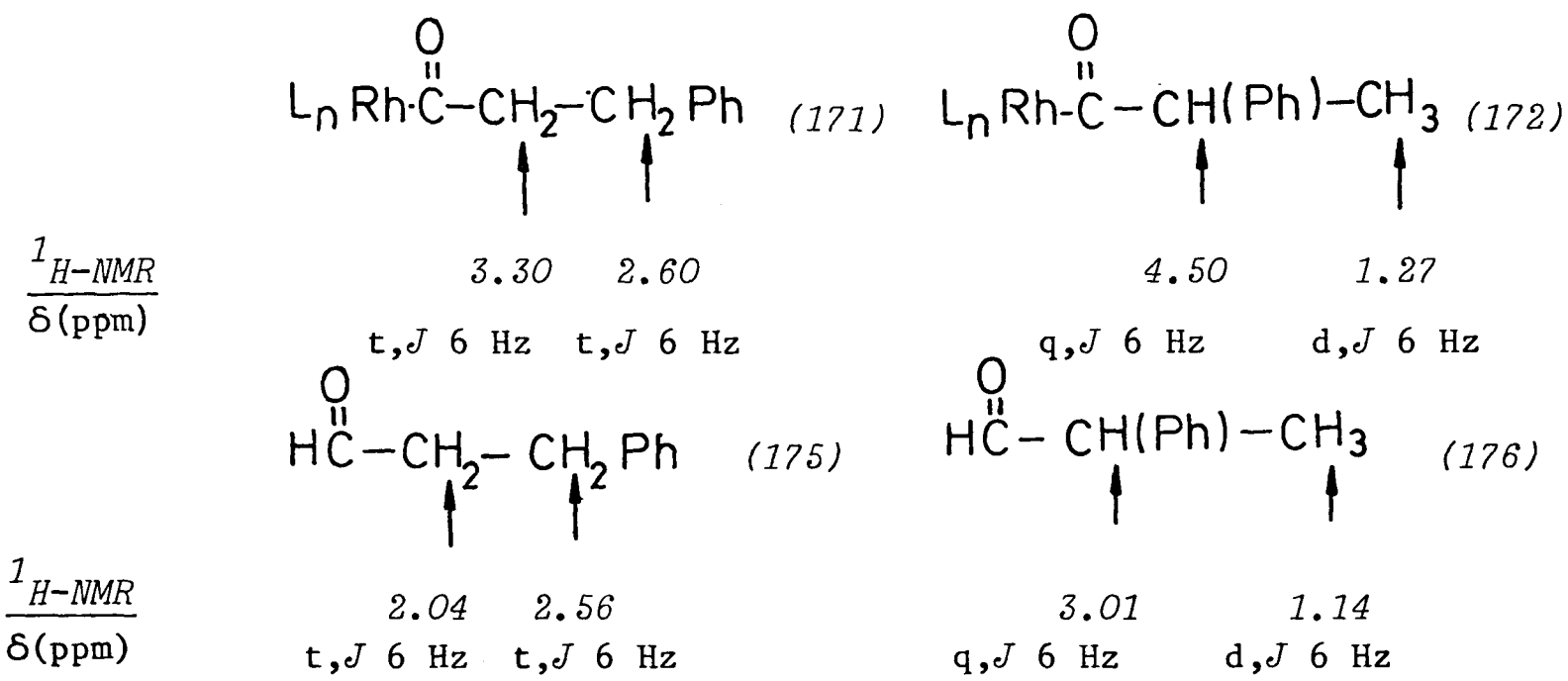


Figure II.3.18

complex (discussed in more detail later) and double resonance experiments. The rhodium acyl-complexes *(171)* and *(172)* comprised *ca.* 30% of the total rhodium in solution after 2 hours, estimated by integration against the ^{13}C-H satellite of the β-*E* proton of styrene at δ 4.8 ppm.

The time dependence of the ^{1}H-NMR spectrum may be interpreted thus. The initial spectrum consists mainly of the *iso*-acyl rhodium complex *(172)* and a small amount of *iso*-aldehyde *(176)*, but only very minor amounts of *n*-acyl complex *(171)* and no 3-phenylpropanal *(175)*. After 5 min. several changes were observed; the proportion of *iso*-acyl complex *(172)* had decreased and the relative amounts of *n*-acyl complex *(171)* and *iso*-aldehyde had increased *(176)*. In the same period a small quantity of 3-phenylpropanal *(175)* was formed. From observations over a further 40 min. it became clear that the decrease in the amount of *iso*-acyl complex *(172)* was simultaneous to the formation of *iso*-product *(176)* and *n*-acyl complex *(171)*. Similarly the amount of *n*-acyl rhodium complex was reduced later in the sequence as 3-phenylpropanal *(175)* was formed.

Plots of relative concentrations of complexes *(171)* and *(172)* and aldehydes *(175)* and *(176)* are illustrated in Figure II.3.19.

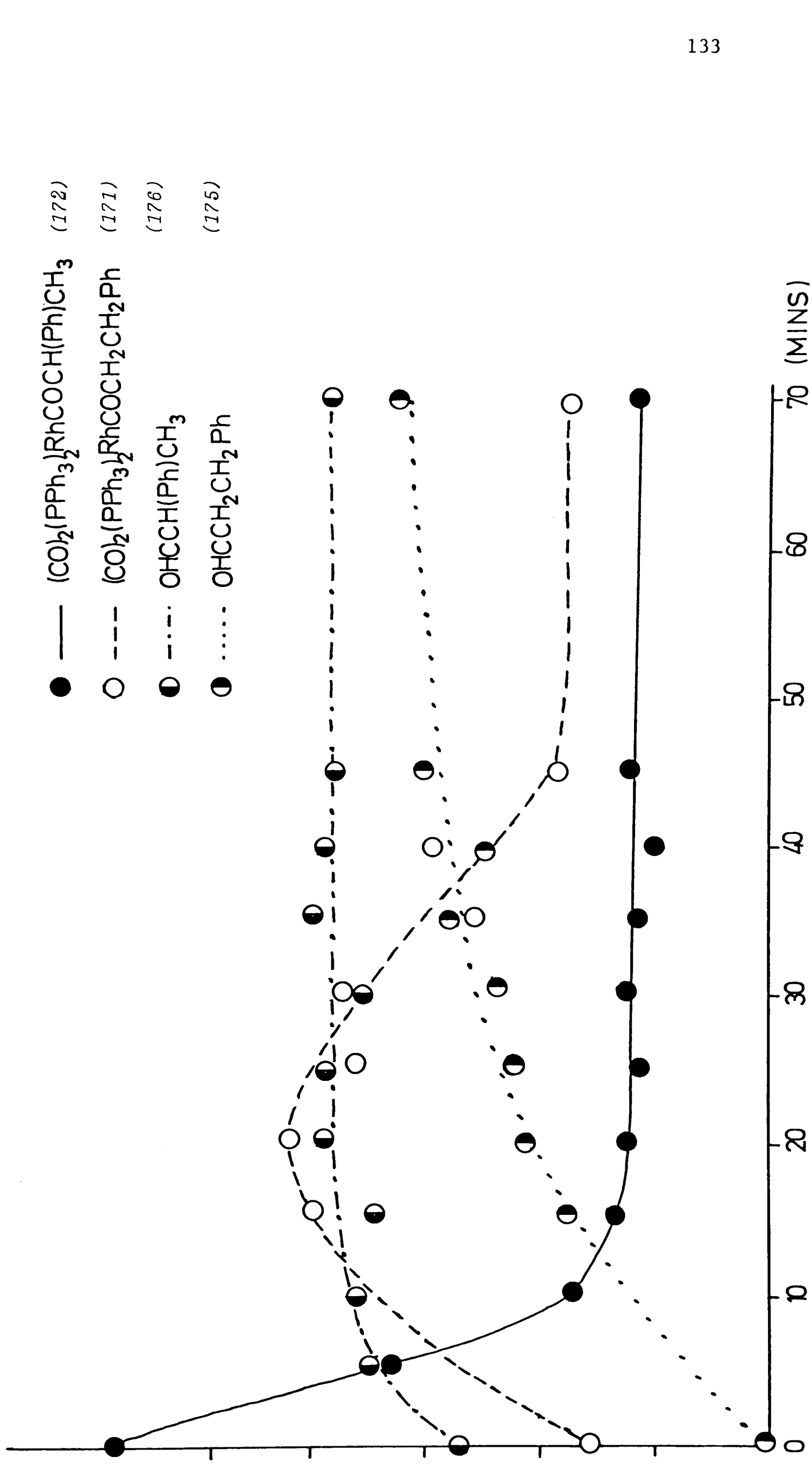
The observations may be accounted for by a self-consistent mechanism. Under hydroformylation conditions, but in the absence of hydrogen, the reaction follows the pathway shown in Scheme II.3.8, producing the *iso*-acyl rhodium complex *(172)* as the major observable intermediate. Once this complex *(172)* has been formed there are two subsequent pathways. The first is isomerization to the more stable *n*-acyl complex *(171)*, probably proceeding *via* metal-alkyl and hydrido-metal-olefin intermediates. The second is formation of 2-phenylpropanal *(176)*. This latter stage is, at first sight, difficult to explain since the reaction was performed in the absence of hydrogen. *In situ* generation of hydrogen may be due to the formation of the dimeric complex *(146)* from hydridocarbonyl-*bis*(triphenylphosphine)rhodium (I) *(145)* which is known to occur under these conditions.[16]

(145) *(146)*

A more likely explanation is that the reductive elimination step required for the formation of aldehyde proceeds *via* the binuclear pathway shown below.

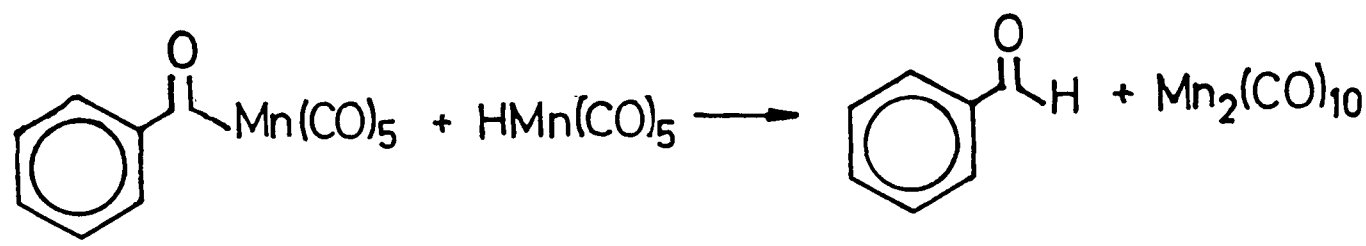
Figure II.3.19

Plots of relative signal intensities of complexes *(171)* and *(172)* and aldehydes *(175)* and *(176)* versus time.



(172) *(176)*

Precedent for this has been reported by Gladyz and co-workers,[66] who showed that the benzoylmanganesepentacarbonyl complex *(177)* reacted with hydridopentacarbonylmanganese *(178)* producing the manganese complex *(179)* and benzaldehyde as the organic product.



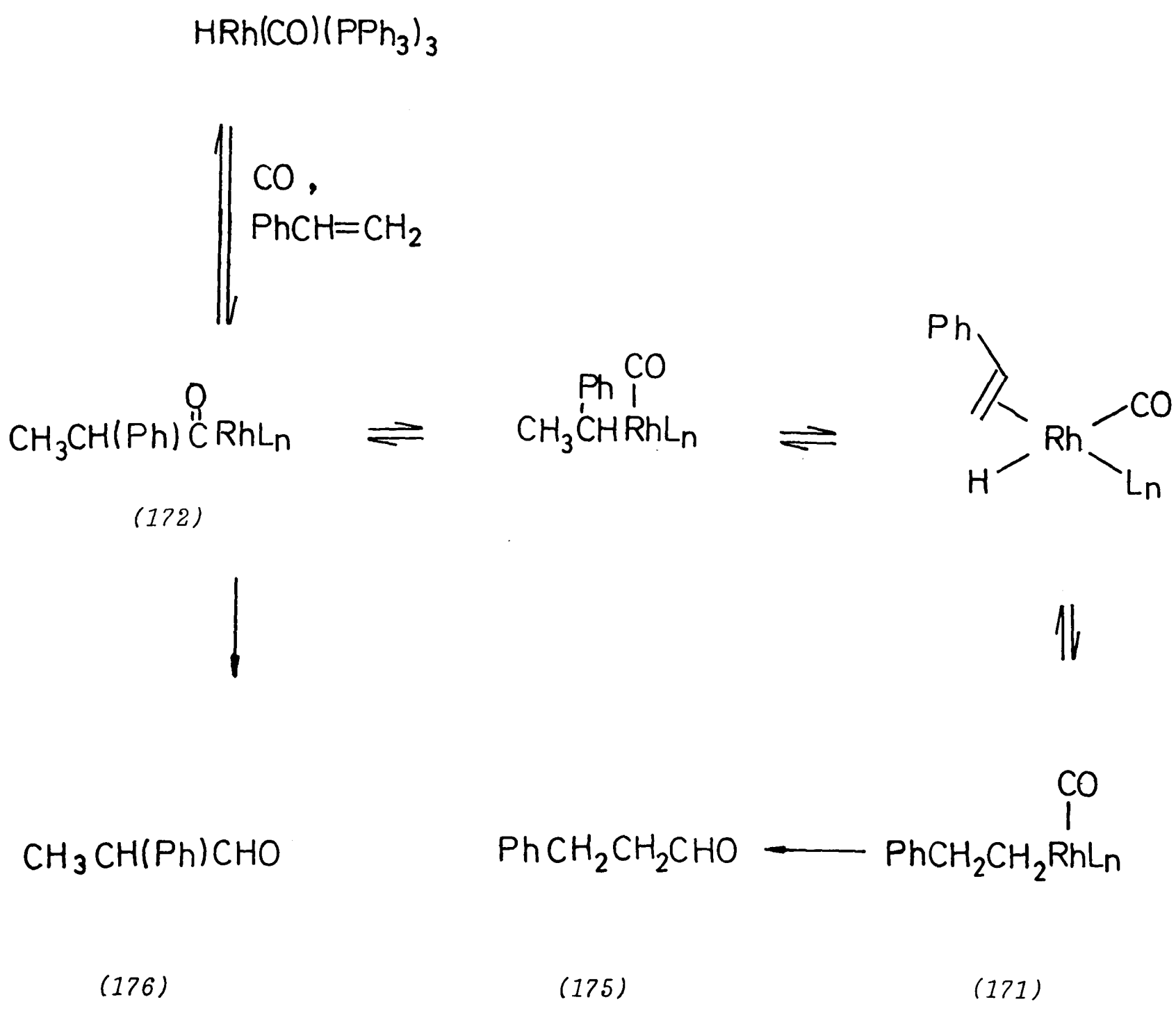
(177) *(178)* *(179)*

A similar explanation has been proposed for cobalt catalysed hydroformylation.[65]

In a similar manner described for the *iso*-acyl complex, the *n*-acyl species *(171)* forms 3-phenylpropanal *(175)*. It appears that acyl complexes *(171)* and *(172)* are the immediate precursors of aldehydes and the concentration dependence shown in Figure II.3.19. makes this clear (since the amount of *n*-aldehyde is very much higher than in hydroformylations where a high pressure of hydrogen competes with isomerization). Unfortunately it is not clear whether this is true of catalytic hydroformylation reactions. In an experiment performed under an atmosphere of hydrogen and carbon monoxide (1:1 mixture) all four species *(171)*, *(172)*, *(175)* and *(176)* were simultaneously observed

although much greater quantities of aldehydes were now formed. The ratio of *iso*- to *n*-aldehyde after 2 hours was *ca.* 9 to 1; a similar result was obtained for a larger scale hydroformylation with $HRh(CO)(PPh_3)_3$ under ambient conditions and is described in Chapter II. Section 4.*

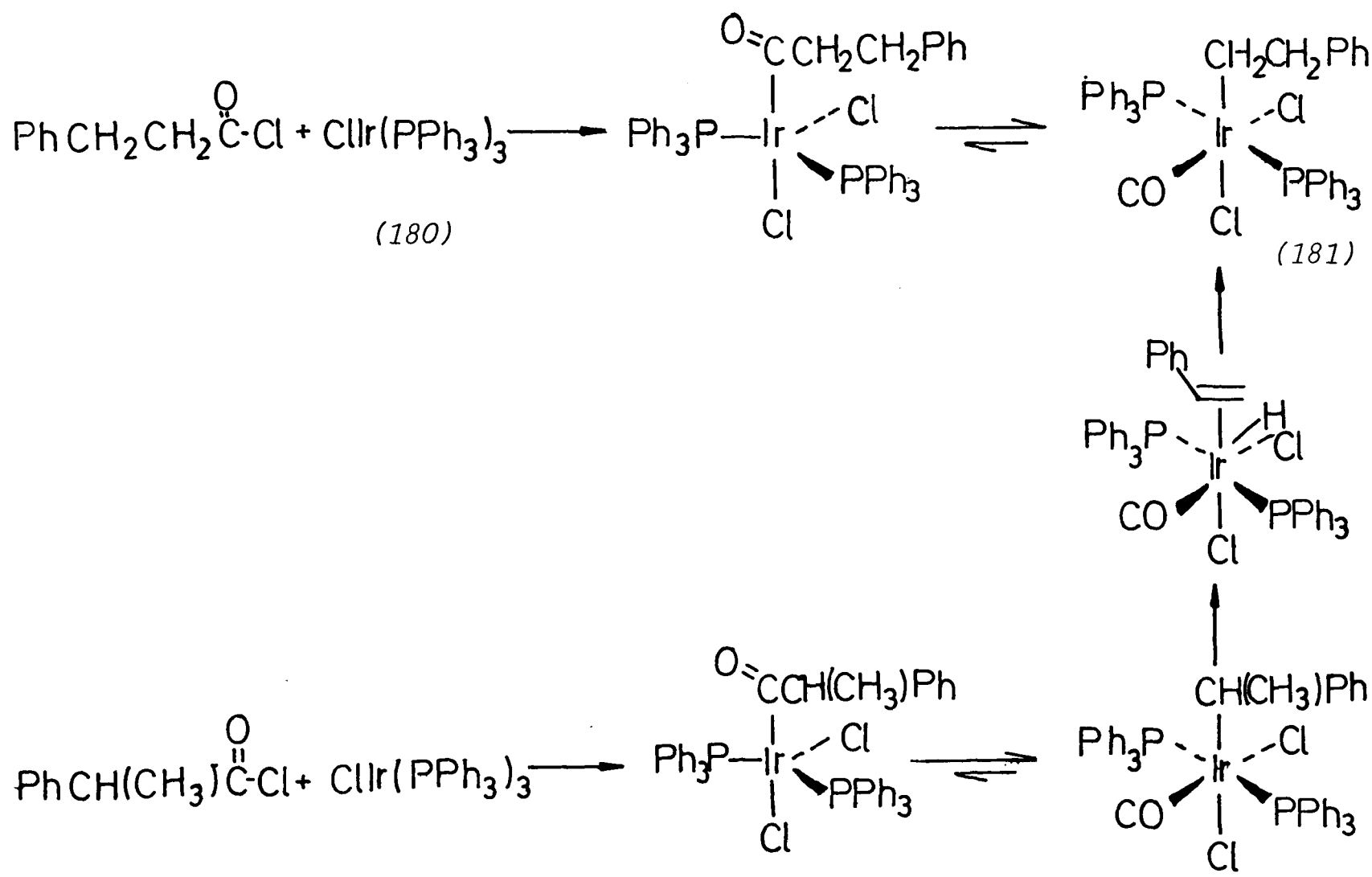
Potential routes for the formation of aldehydes and acyl isomerization are summarized in Scheme II.3.12.



Scheme II.3.12

* Employing a 1:5 H_2/CO atmosphere produces the same result (*n*/*iso* = 0.11).

Acyl-iridium complex isomerization has been reported by Bennett and co-workers.[141] Thus oxidative addition of normal or branched phenyl-propanoyl chloride to chloro*tris*(triphenylphosphine)iridium *(180)* gave the same *n*-alkyl iridium complex *(181)*. This was attributed to the *iso*-alkyl complex *(181)a* undergoing rapid β-hydride migration to form an olefin hydride which reformed the more favourable *n*-alkyl complex *(181)*.



Rupilius and Ordin[142] have shown that the acylcobalt complex *(182)* underwent extensive isomerization and formed *n*- and *i*-C_4 aldehydes irreversibly on standing in solution under nitrogen.

The observations made by Brown and Wilkinson,[18] mentioned earlier indicated that the major acyl complex (assigned to resonances at δ 2.53

$$CH_3CH_2CH_2COCo(CO)_4 \longrightarrow CH_3CH_2CH_2CHO + CH_3CH(CH_3)CHO$$

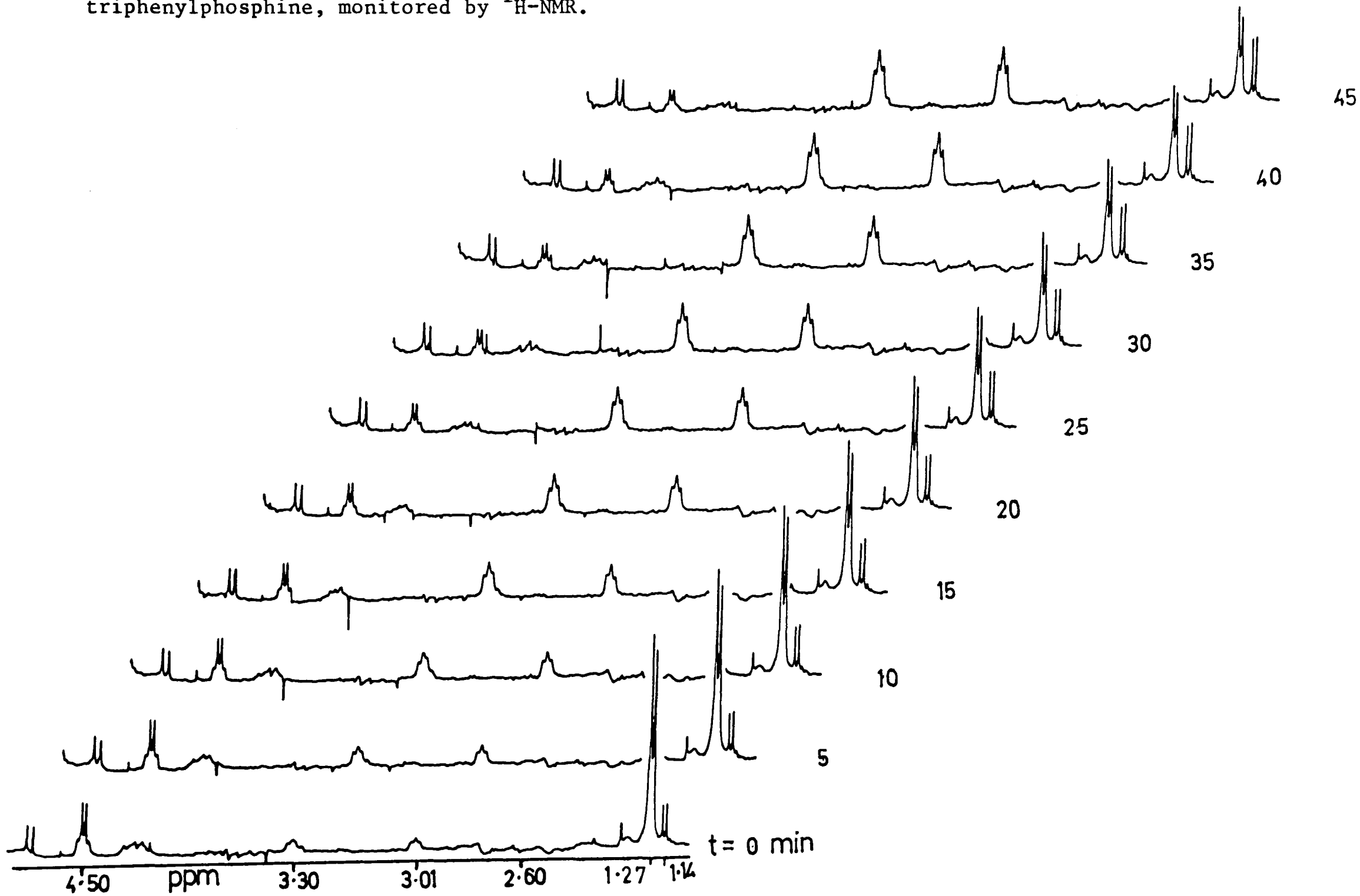
(182)

and 3.35 ppm) was the *n*-isomer *(171)*. The *iso*-acyl complex *(172)* (assigned to resonances at δ 1.06 and 3.3 ppm) was stated to be present in small amounts. This is certainly not the case if the ^{1}H-NMR spectrum is obtained immediately on preparation of the reaction solution and is not consistent with the fact that *iso*-aldehyde is the major hydroformylation product (85%) at 25° and one atmosphere of hydrogen and carbon monoxide. The resonances at δ 3.3 (Ph-C*H*CH$_3$) and δ 1.06 ppm (Ph-CH-C*H*$_3$) assigned to the *iso*-acyl complex *(172)* by Wilkinson, in fact correspond to the *iso*-aldehyde product, 2-phenylpropanal, observed in the experiments reported here.

The effect of excess triphenylphosphine on the reaction of styrene with hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) under carbon monoxide was also investigated by ^{1}H-NMR (Figure II.3.20). In this experiment aldehyde formation was suppressed so that *iso*- to *n*-acyl complex isomerization, although slower, was the dominant reaction pathway. Styrene hydroformylation experiments carried out under analogous conditions show that addition of triphenylphosphine (five equivalents) reduces the reaction rate by a factor of 2.2. Excess phosphine also reduced the line broadening in the acyl complexes *(171)* and *(172)* observed in the initial ^{1}H-NMR experiment (Figure II.3.17). An explanation to account for these observations is that both aldehyde formation and isomerization proceed *via* an initial ligand dissociative step, to a coordinatively

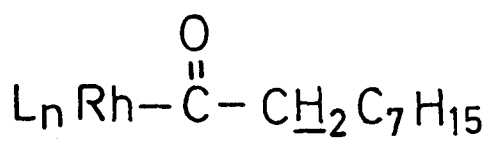
Figure II.3.20

Reaction of $HRh(CO)(PPh_3)_3$ with styrene in benzene under CO, in the presence of five equivalents of triphenylphosphine, monitored by ^1H-NMR.



unsaturated intermediate species, disfavoured by addition of excess ligand.

In a further experiment a solution of oct-1-ene and hydridocarbonyl-*tris*(triphenylphosphine)rhodium (I) under carbon monoxide was monitored by ^{1}H-NMR spectroscopy. A resonance observed at δ 3.45 ppm (triplet, *J* 6 Hz) was attributed to the formation of complex *(183)*; isomerization did not take place.



(183)

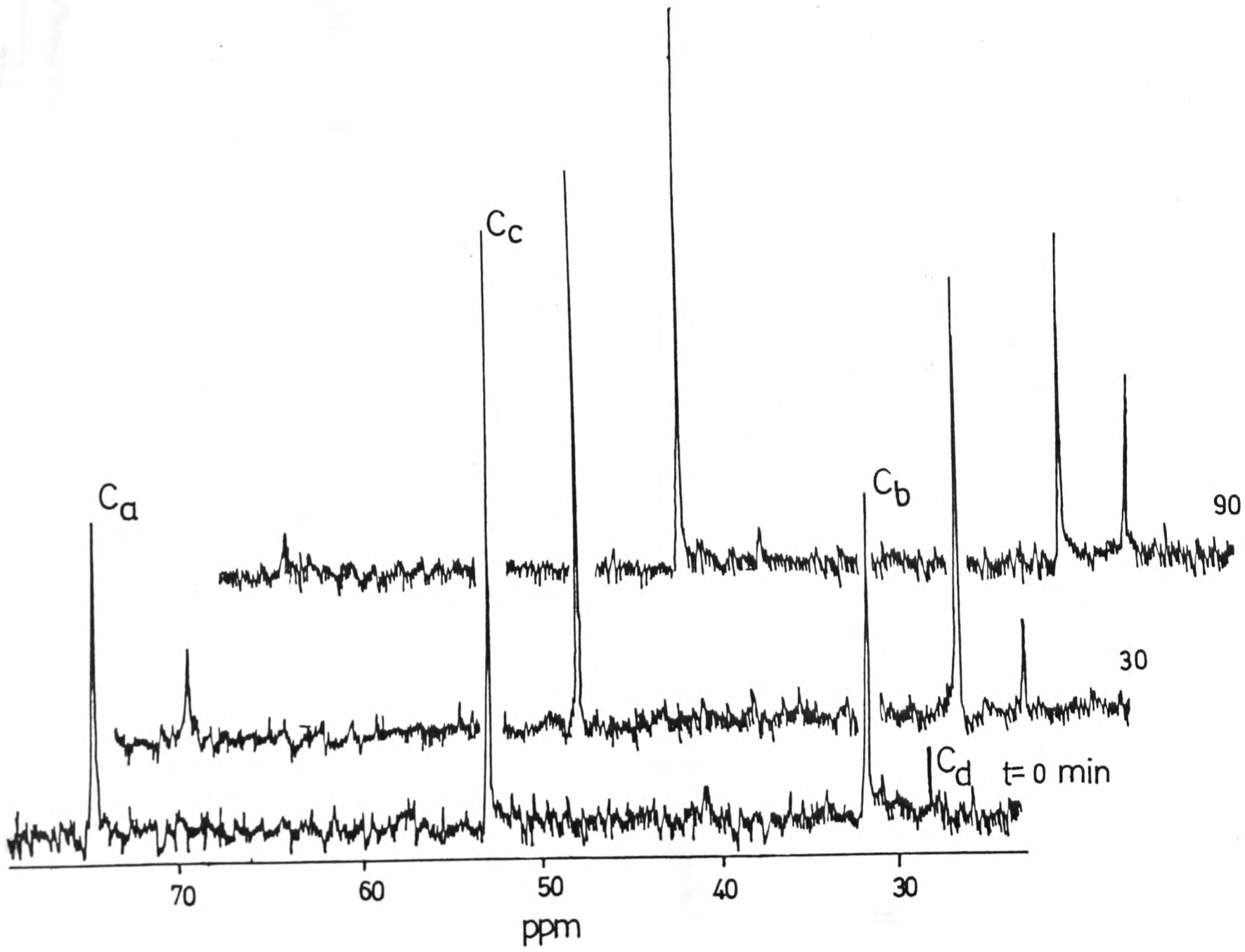
III.3.3.3 *The study of rhodium-acyl complexes by heteronuclear NMR techniques*

In the second part of the study of reactive intermediates under hydroformylation conditions, experiments were carried out employing heteronuclear NMR. The initial experiment performed was the reaction of α-^{13}C-styrene *(157)* with hydridocarbonyl*tris*(triphenylphosphine)rhodium (I) in benzene under carbon monoxide,examined by ^{13}C-NMR spectroscopy (Figure II.3.21). Four ^{13}C-resonances assigned to the *iso* and *n*-acyl complexes *(172)* and *(171)* and the two aldehydes *(176)* and *(175)* were identified by observation of the spectrum at intervals over 2 hours. The initial *i*-/*n*-acyl complex ratio was greater than 7 to 1. ^{13}C-Carbon monoxide, used in place of the ^{12}C-gas, allowed carbonyl-carbon nuclei resonances due to acyl complexes *(172)* and *(171)* and complexes *(143)*, *(145)* and *(146)* to be observed (Figure II.3.22). The NMR data obtained from these experiments and proposed structures are shown in Scheme II.3.12.

The processes identified by the previous ^{1}H-NMR experiments were also observed by ^{13}C-NMR spectroscopy, *i.e.* isomerization of *iso*- to *n*-acyl and formation of *iso*- and *n*-aldehyde from their respective acyl complex precursors. Since no ^{13}C- ^{31}P-couplings were apparent in either carbon

Figure II.3.21

Reaction of $HRh(CO)(PPh_3)_3$ with α-^{13}C-styrene *(157)* in benzene under carbon monoxide, monitored by ^{13}C-NMR (298°K)



$(L_n)Rh\overset{O}{\overset{\|}{C}}\overset{\bullet}{C}_a H(Ph)CH_3$ *(172)*

$(L_n)RhC\,CH_2\overset{\bullet}{C}_b H_2 Ph$ *(171)*

$OHC\overset{\bullet}{C}_c H(Ph)CH_3$ *(176)*

$OHC\,CH_2\overset{\bullet}{C}_d H_2 Ph$ *(175)*

$Ph\overset{\bullet}{C}H=CH_2$ *(157)*

$[\overset{\bullet}{C} = {}^{13}C]$

Figure II.3.22

Reaction of $HRh(CO)(PPh_3)_3$ with (a) ^{13}C-styrene *(157)* or (b) styrene, in benzene under ^{13}C-carbon monoxide, monitored by ^{13}C-NMR (278°K)

$(^{\bullet}C_aO)_2(PPh_3)_2Rh-\overset{O}{\overset{\|}{^{\bullet}C_b}}-CH(Ph)CH_3$ *(172)*

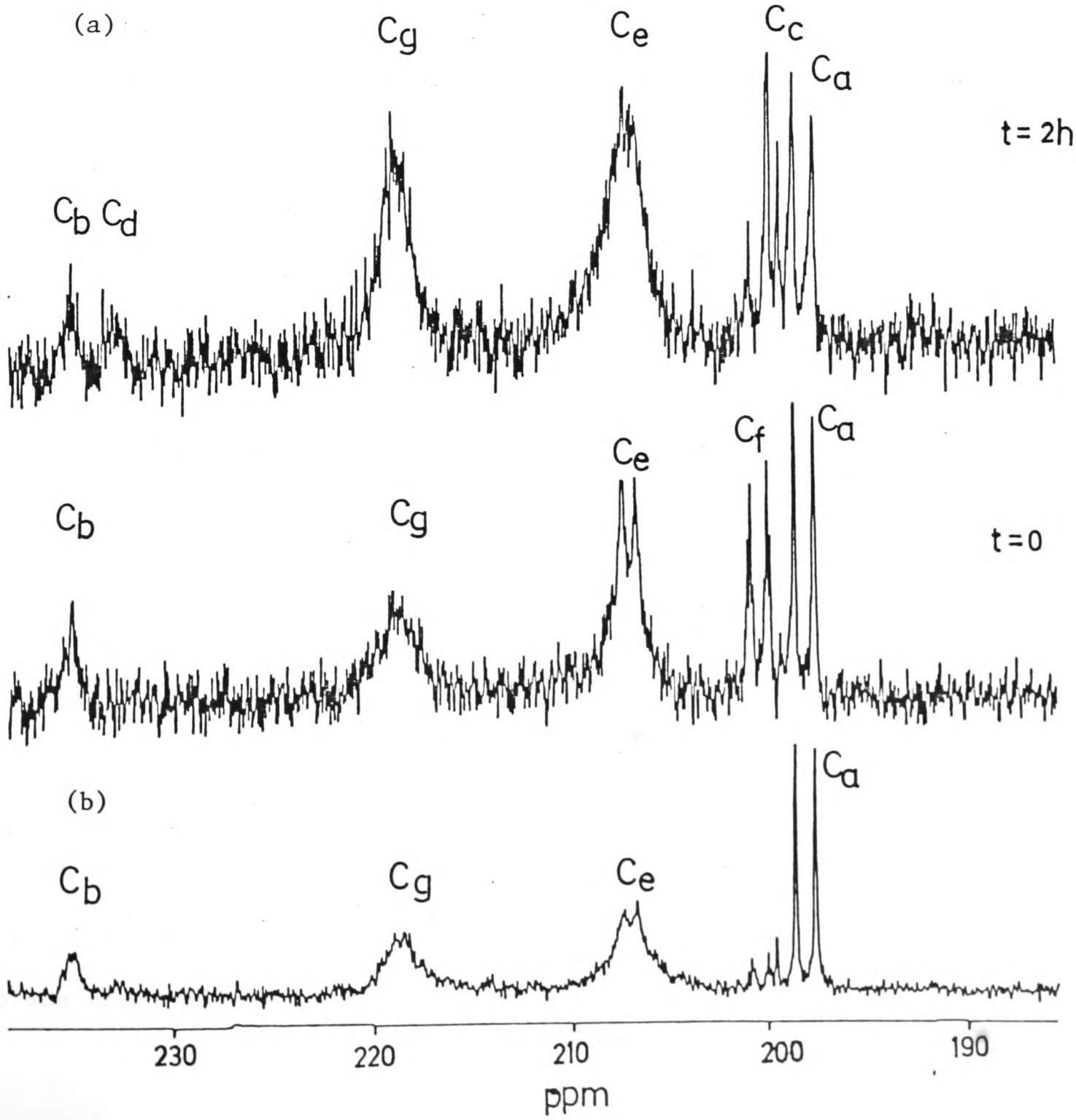
$(^{\bullet}CO)_2(PPh_3)_2Rh-\overset{O}{\overset{\|}{^{\bullet}C_d}}-CH_2{}^{\bullet}CH_2Ph$ *(171)*

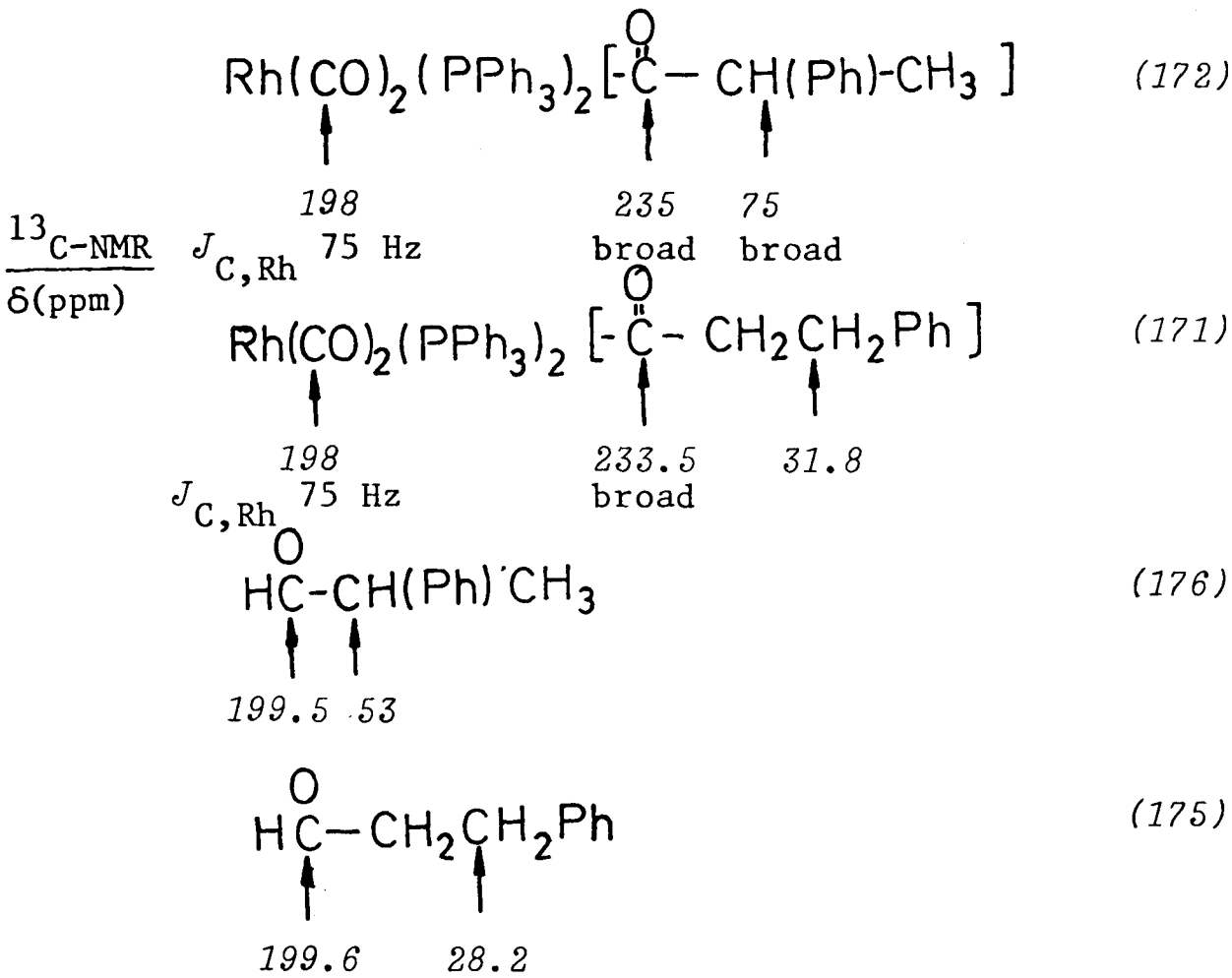
$HRh(^{\bullet}C_eO)(PPh_3)_3$ *(143)*

$HRh(^{\bullet}C_fO)_2(PPh_3)_2$ *(145)*

$Rh_2(^{\bullet}C_gO)_4(PPh_3)_4$ *(146)*

$[^{\bullet} = {}^{13}C]$

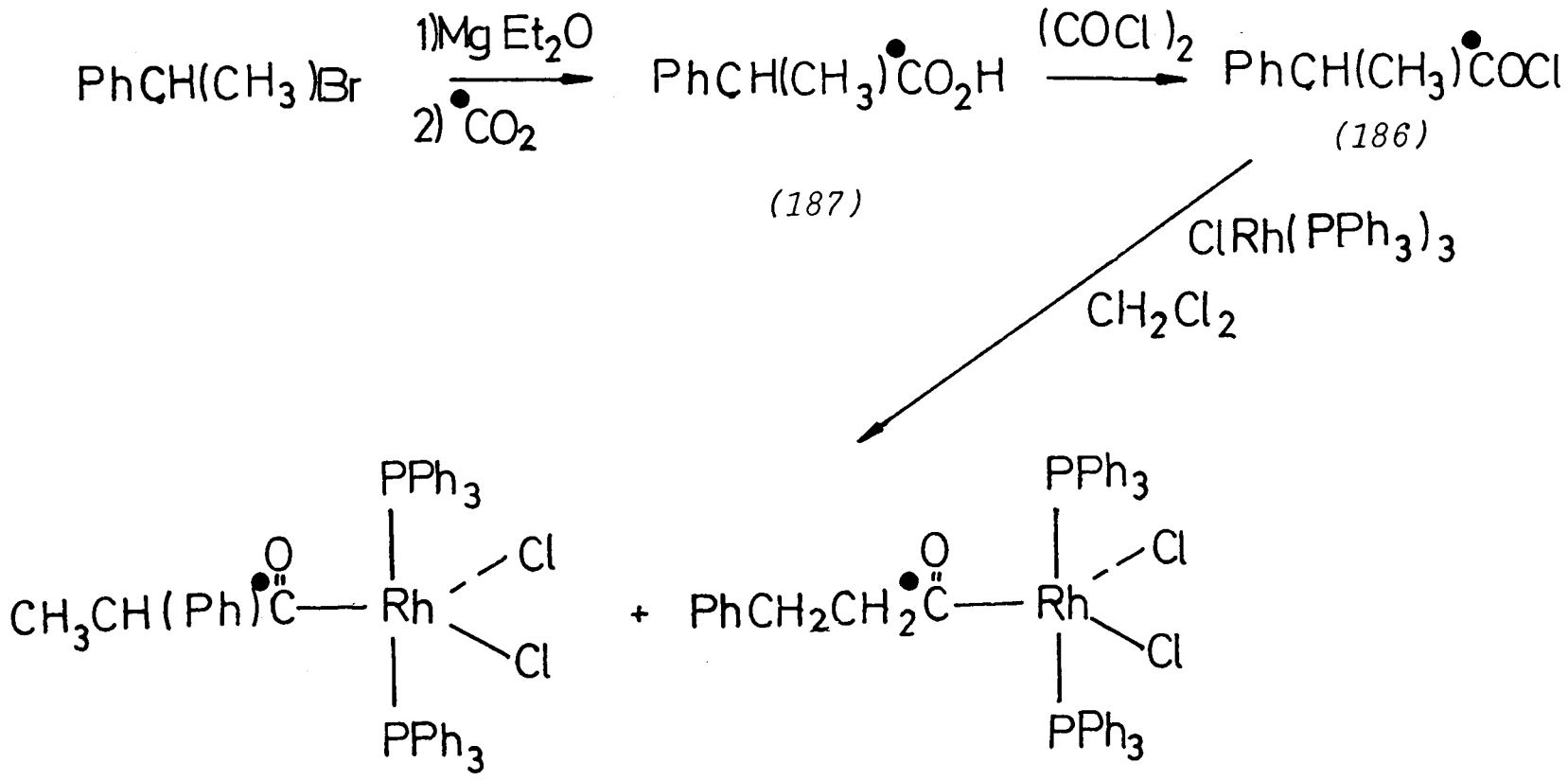


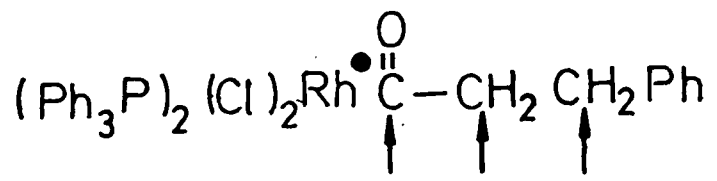


Scheme II.3.12

nucleus of the acyl complex *(171)* and *(172)* (Figure II.3.21) and the ^{13}C-CO acyl-group resonance was clearly line-broadened it was thought that rapid intra-or intermolecular dynamic processes caused time-averaging of the signals. It was not possible to obtain spectra below 279^{o}K due to freezing of the solvent, benzene; changing to toluene appeared to produce less of the rhodium-acyl species *(171)* and *(172)*, however. For these reasons styrene was replaced by oct-1-ene in subsequent experiments.

Stable rhodium acyl complexes *(184)* and *(185)* were prepared for comparison. α-^{13}C-Phenylpropanoyl chloride *(186)*, prepared by the method shown in Scheme II.3.13, was reacted with chloro*tris*(triphenylphosphine)-rhodium (I) *(154)*. This gave a *ca.* 3:1 mixture of the *iso*- and *n*-acyl complexes *(184)* and *(185)* indicating that acyl-group isomerization had taken place under the reaction conditions. Figure II.3.23 shows the



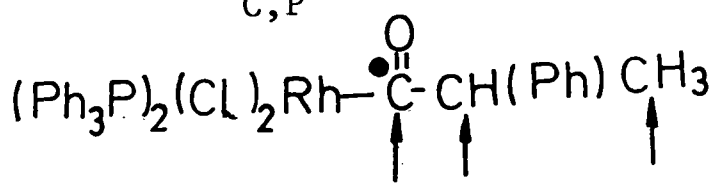


^{1}*H-NMR* δ(ppm) *3.15 2.63*

^{13}*C-NMR* δ(ppm) *209.9 54.7 33.3*

$J_{C,Rh}$ *27* $J_{C,C}$ *32 Hz*

$J_{C,P}$ *6 Hz*



^{1}*H-NMR* δ(ppm) *4.70 1.11*

^{13}*C-NMR* δ(ppm) *213.5 63.5*

$J_{C,Rh}$ *28* $J_{C,C}$ *34 Hz*

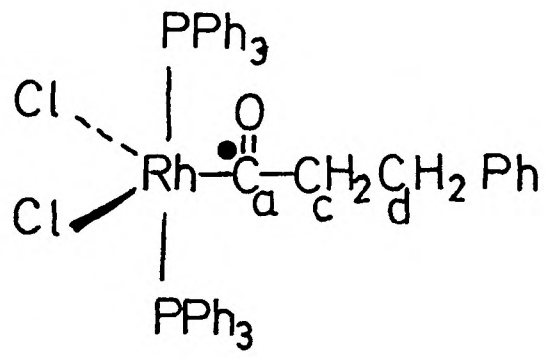
$J_{C,P}$ *6 Hz*

[• = ^{13}C]

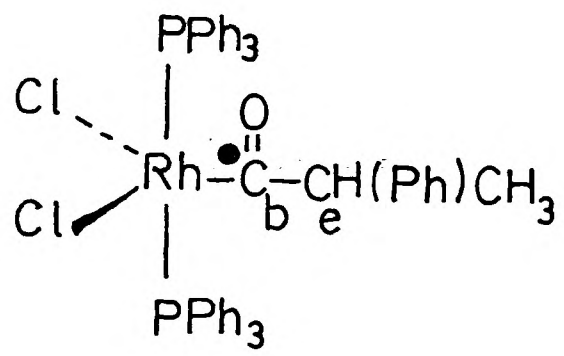
Scheme II.3.13

Figure II.3.23

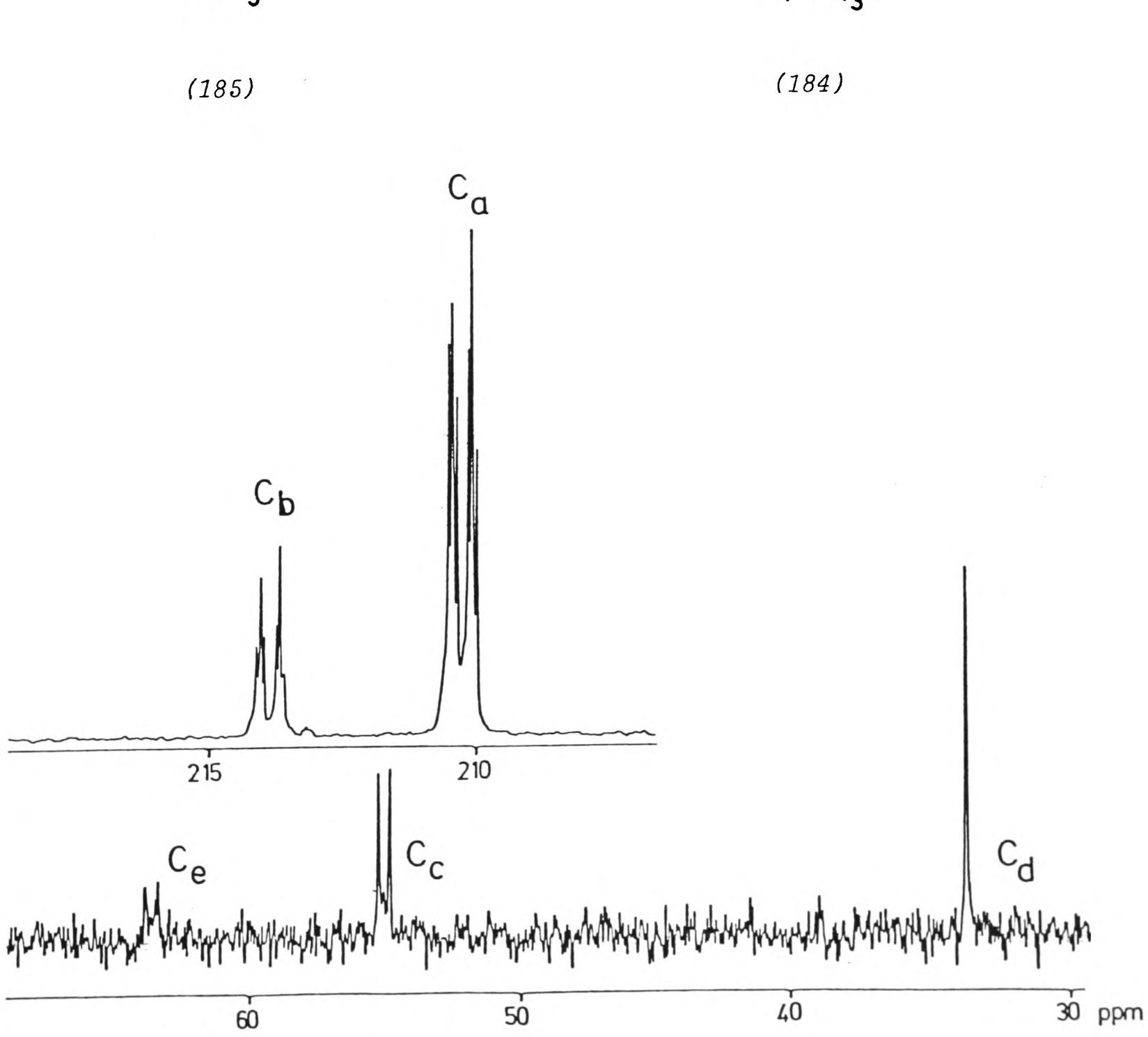
^{13}C-NMR spectrum of rhodium-acyl complexes *(185)* and *(186)* in chloroform-d_3



(185)



(184)



^{13}C-NMR spectrum of the mixture of complexes *(184)* and *(185)*. The chemical shifts and coupling constants are shown in Scheme II.3.13 and confirm the structures of species *(184)* and *(185)*; no dynamic processes were observed.

The reaction of octene with hydridocarbonyl*tris*(triphenylphosphine)-rhodium (I) *(143)* under ^{13}C-carbon monoxide in toluene produced the temperature dependent ^{13}C-NMR spectrum illustrated in Figure II.3.24. Comparison with experiments employing styrene as substrate showed the linear acyl-rhodium complex *(183)* is formed preferentially and in sufficient concentration for convenient NMR observation. Figure II.3.25 depicts the acyl- and metal- ^{13}C-carbonyl resonances at the highest (279^{o}K) and lowest (243^{o}K) probe temperatures used in this experiment; integration of these signals indicated a 1:2 stoichiometry of acyl- and metal-carbonyl groups. The lowest temperature conveniently attainable at 75 MHz (WH 300) was 243^{o}K because the Oxford machine is fitted with a wide-bore probe; since the ^{13}C-NMR spectrum of the acyl-complex *(183)* was still line-broadened at this temperature a similar experiment was conducted at 100 MHz (WH 400) and 193^{o}K (Figure II.3.26).† At this temperature a dimer-free sample of the complex *(183)* appears to be stable over several hours. Examination of the ^{13}C-resonance at δ 198.5 ppm showed double triplet fine structure ($J_{C,Rh}$ 75 Hz, $J_{C,P}$ 20 Hz) indicating ^{13}C-coupling to one rhodium and two phosphorus atoms. The resonance at δ 233.5 ppm, more complex than previously observed, was a doublet of double doublets, due to three different ^{13}C-couplings (J 77, 20 and 8 Hz). The structure proposed on the basis of this NMR evidence is shown below.

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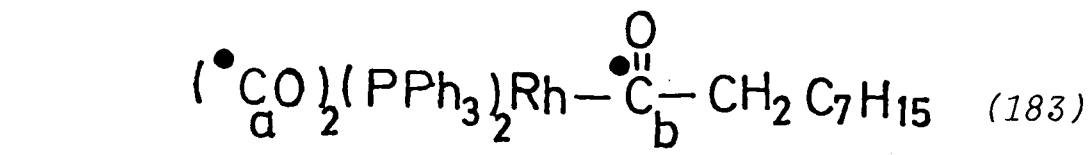
† I would like to acknowledge the assistance of Dr O. Howarth and Dr E. Curzon, University of Warwick and S.E.R.C. in obtaining these spectra.

Figure II.3.24

Reaction of $HRh(CO)(PPh_3)_3$ with oct-1-ene in toluene under ^{13}C-carbon monoxide, monitored by ^{13}C-NMR



(183)

[• = ^{13}C]

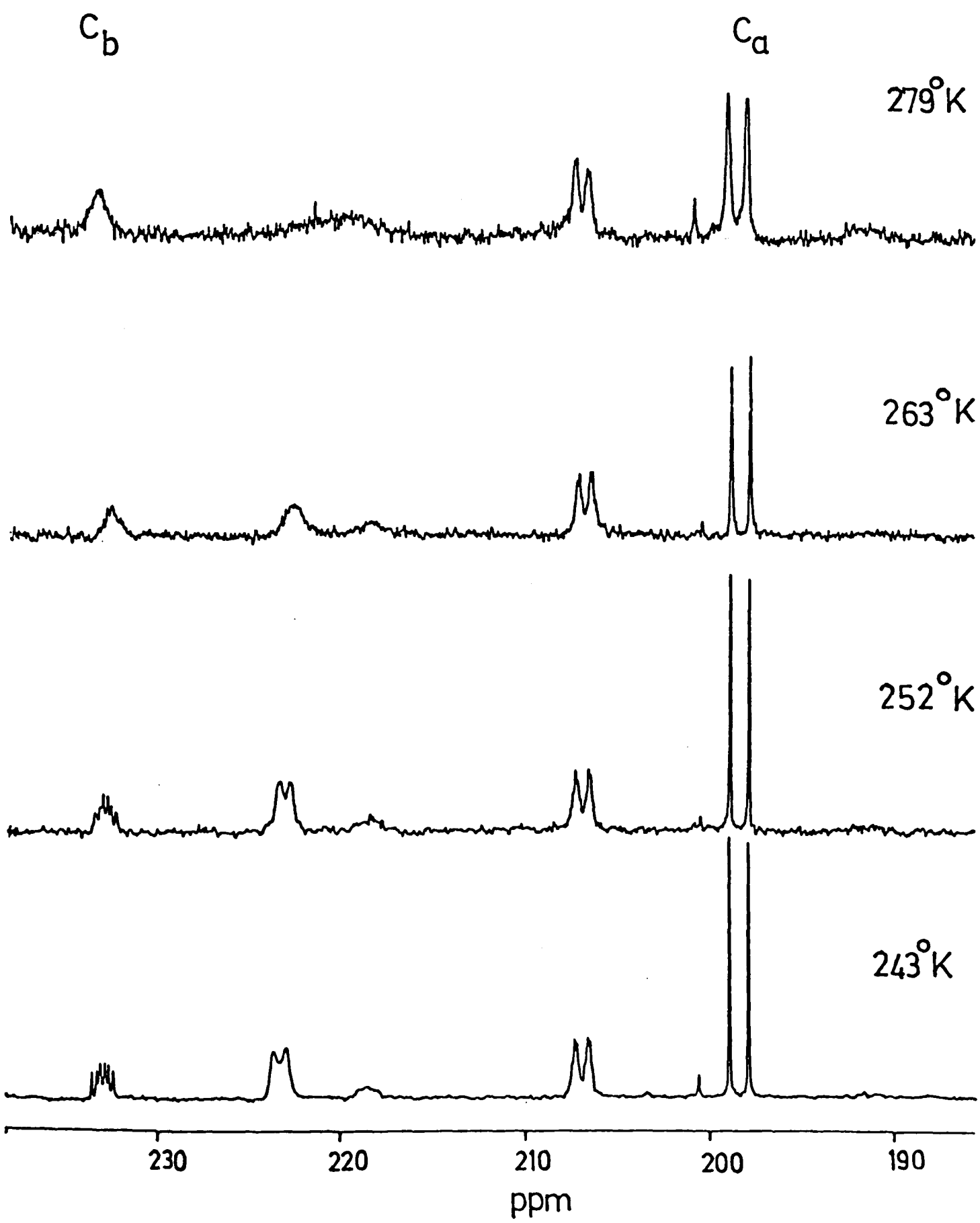


Figure II.3.25

^{13}C-NMR (75 MHz) spectrum of rhodium-acyl complex *(183)* in toluene

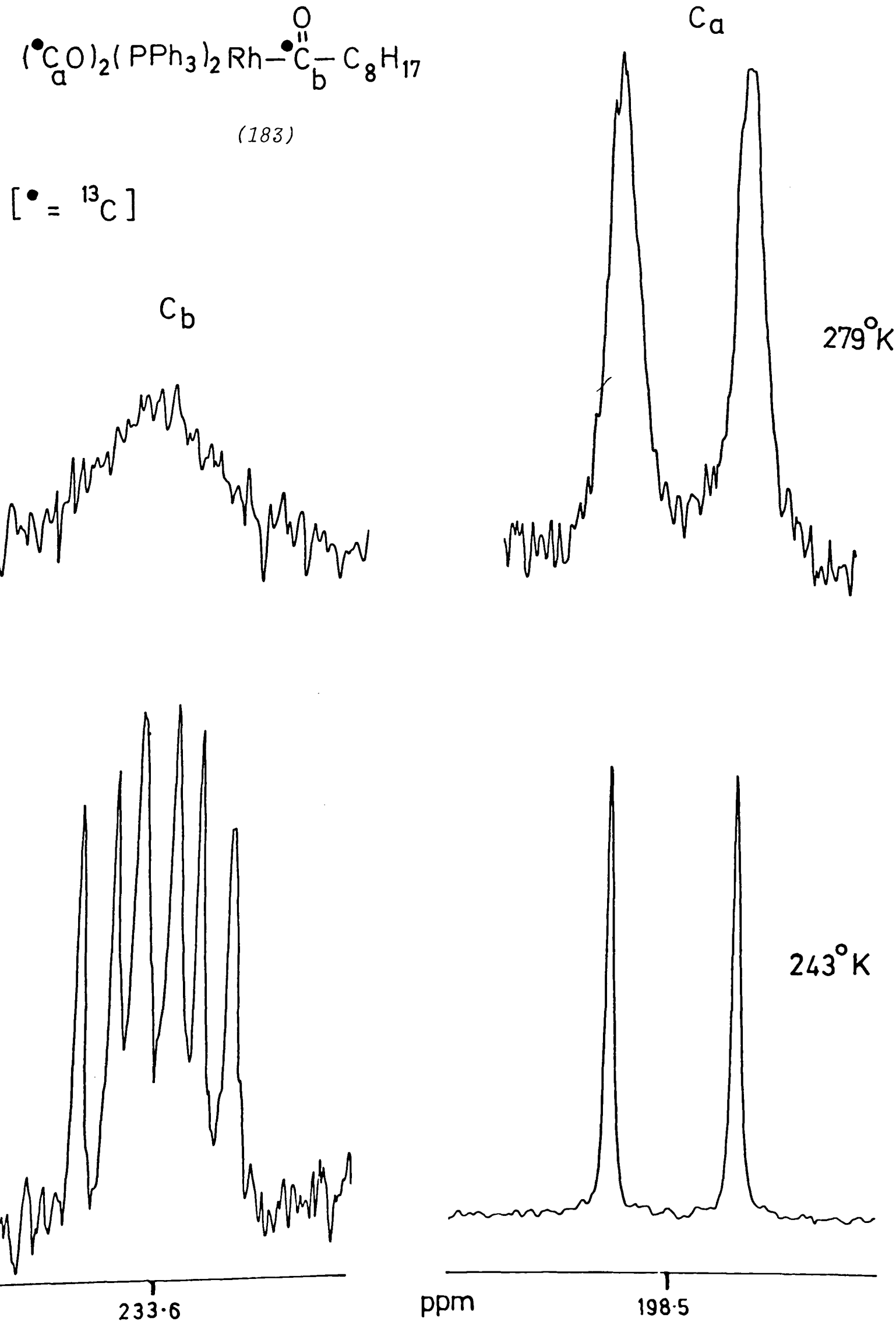
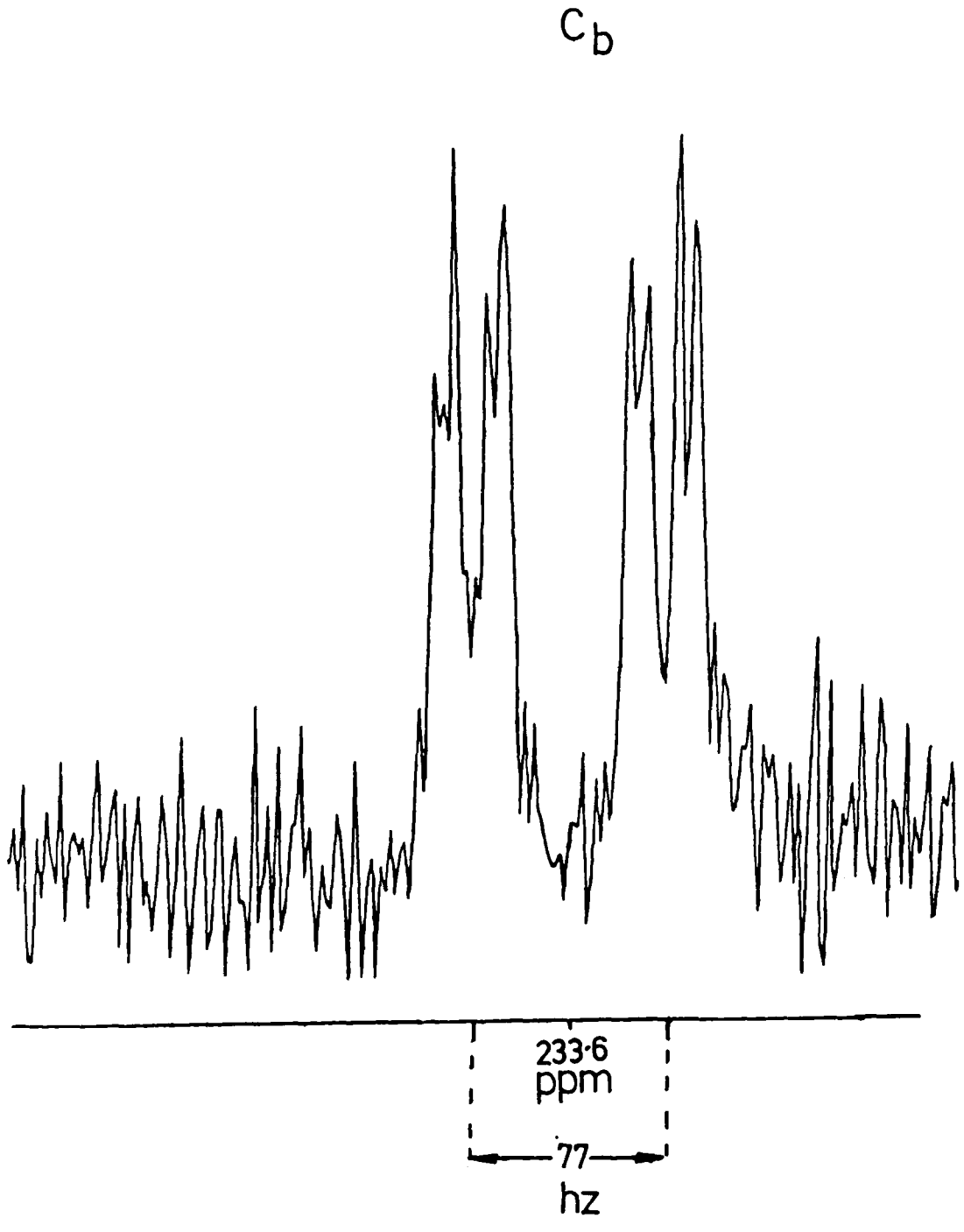
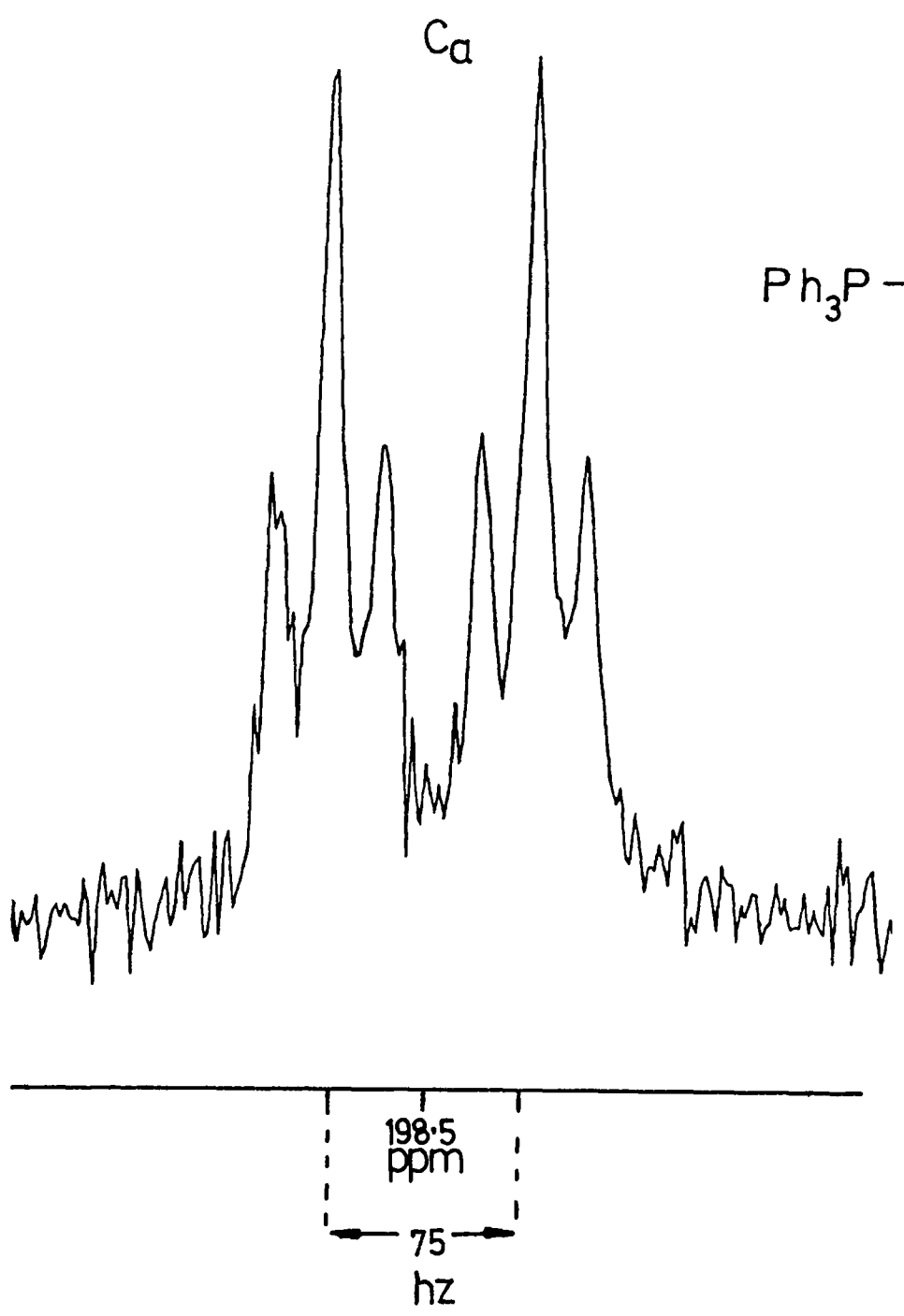
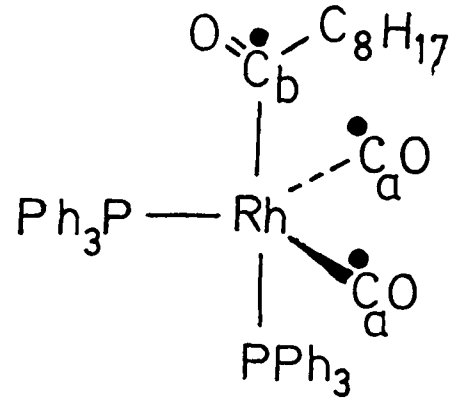


Figure II.3.26

^{13}C-NMR (100 MHz) spectrum of rhodium-acyl complex *(183)* in toluene at 193°K

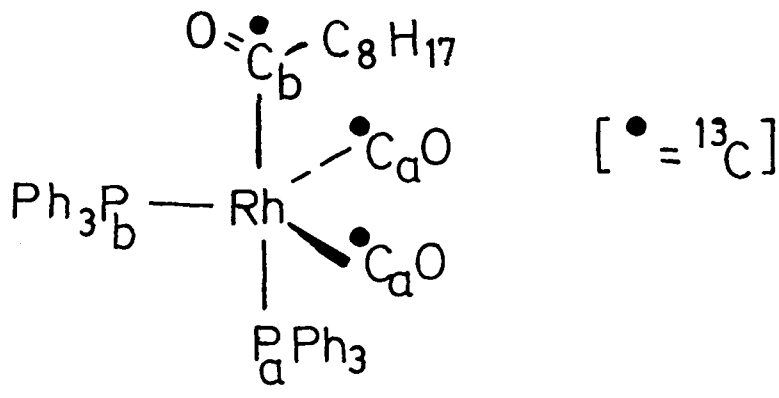






[• = ^{13}C]

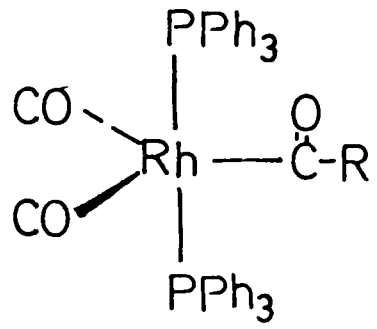
(183)



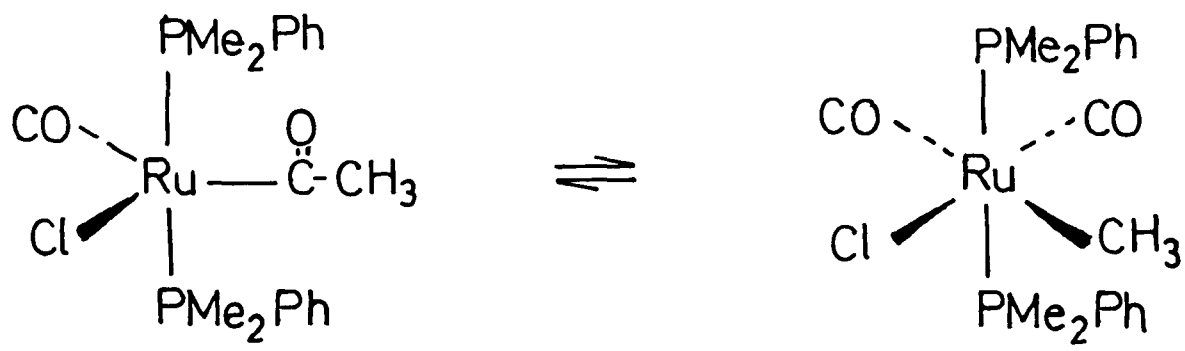
(183)

The acetyl ^{13}C-CO group, therefore, shows one large coupling to the *trans*-phosphorus atom (J_{C_b,P_a} 77 Hz) and two smaller couplings to rhodium ($J_{C_b,Rh}$ 20 Hz) and a *cis*-phosphorus nucleus (J_{C_b,P_b} 8 Hz). ^{13}C-^{13}C coupling is less than or equal to the natural line-width at this temperature (J_{C_a,C_b} ~ 3 Hz). *Trans*-^{13}C-Rh-^{31}P couplings of *ca.* 80 Hz have been reported by Brown and co-workers.[143] Employing α-^{13}C-decene *(161)* in place of octene produced a more complex acyl ^{13}CO-resonance with a further coupling of *ca.* 20 Hz, consistent with α,β ^{13}C-^{13}C coupling constant values. A value of $J_{C,C}$ 32 Hz was obtained for the stable acyl-rhodium complex *(185)*. The ^{13}C-atom α to the carbonyl group of the acyl species *(183)* resonated at δ 67 ppm and was line-broadened (*ca.* 40 Hz linewidth) over the temperature range examined (193-278°K). This is to be expected if it experiences a substantial coupling to the *trans*-phosphine (P_a) and to rhodium giving a complex multiplet.

The acyl complex *(183)* observed in these experiments has been proposed as part of the catalytic cycle for olefin hydroformylation (see Scheme I.3.2, Chapter I, Section 3). Previous research workers[144] have attributed the stereochemistry shown below to this type of complex; this cannot be consistent with the NMR results obtained here. Possible mechanisms which may account for the dynamic processes observed in



complex *(183)* are discussed as follows. Firstly, a Berry-type intramolecular rotational process,[145] invoked to account for dynamic processes in some five-coordinate organometallic molecules,[146] would lead to averaging of ^{13}C-^{31}P couplings at the higher temperature limit, which does not occur. Secondly, there is precedent for interconversion of acyl- and alkyl-metal complexes, for example the acylruthenium complex *(187)* was shown[147] to generate the alkylruthenium complex *(188)* reversibly; this was attributed to the *trans*-labilizing influence of the acetyl ligand. In the octene experiment, however, no

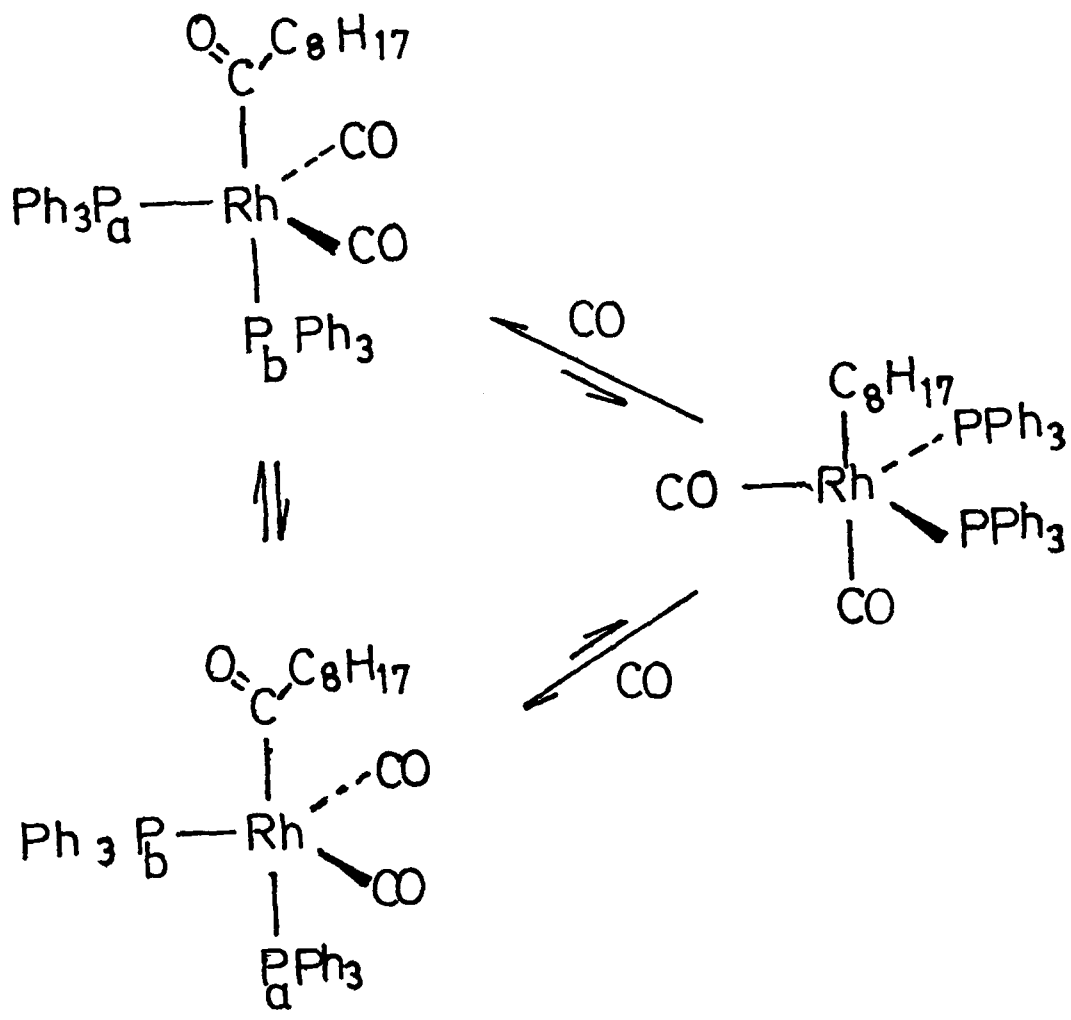


(187) *(188)*

resonance attributable to a metal-alkyl complex was observed indicating that any equilibrium between complex *(183)* and a metal-alkyl complex would have to favour the acyl-rhodium species *(183)* at the lower temperature (193°K).

The data is best interpreted in terms of rapid phosphine isomerization at lower temperatures leading first to loss of the smaller P_a coupling

to C_b and both P_a and P_b coupling to C_b. At higher temperatures the acyl carbon loses its rhodium coupling and becomes broad, implying dissociation of carbon monoxide from the metal. This is accounted for in Scheme II.3.14 and suggests that alkyl-acyl interconversions are rapid on the NMR time-scale at room temperature.



Scheme II.3.14

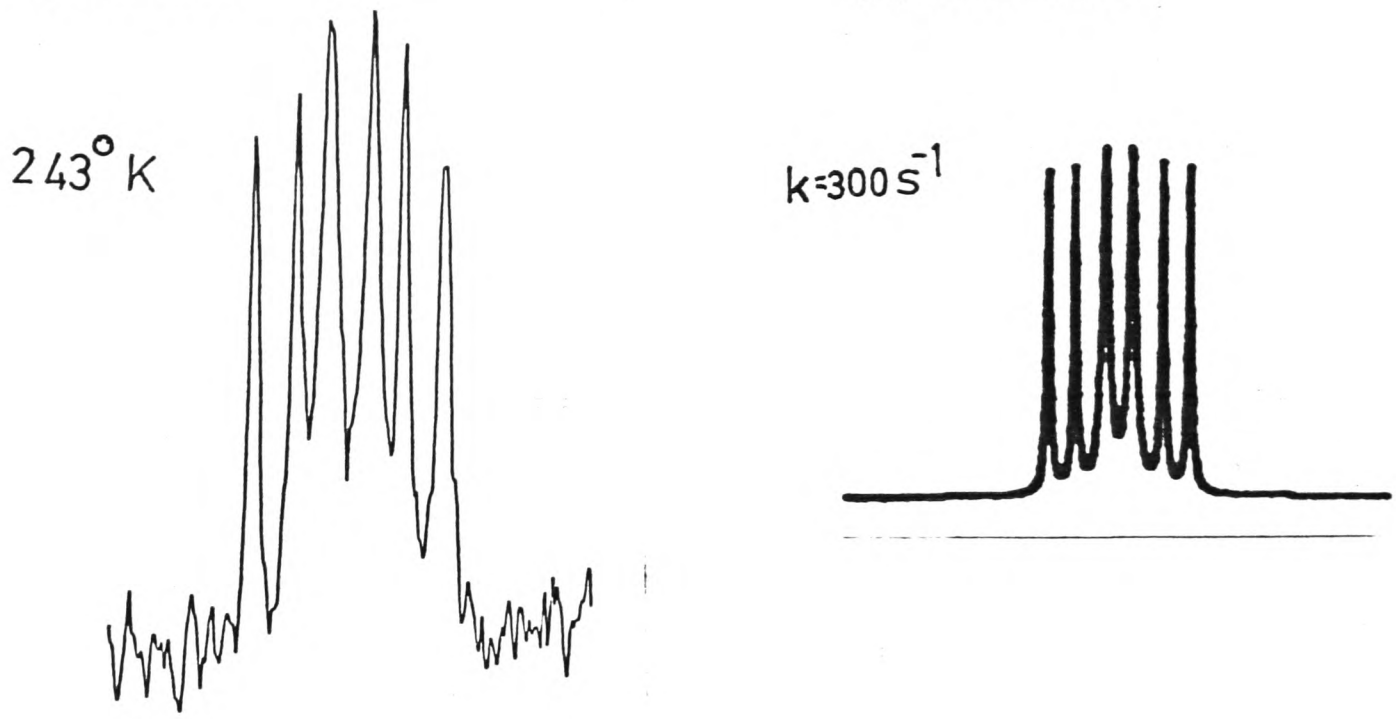
Addendum

An attempt to simulate the dynamic processes occurring in acyl complex *(183)* at lower temperatures (see Scheme II.3.14) corresponds very closely to the experimental spectra (overleaf).

^{13}C-NMR spectrum of acyl complex *(183)*
[*not* to same scale]

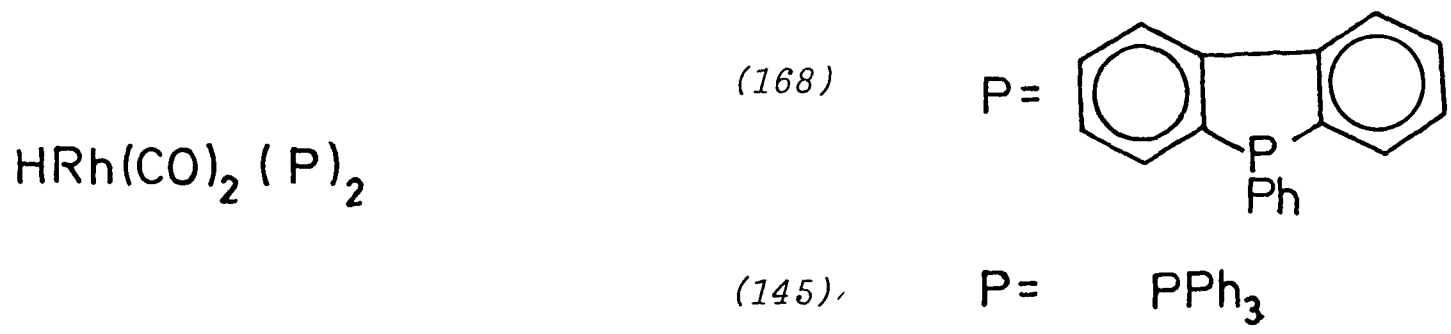
(a) experimental

(b) simulated

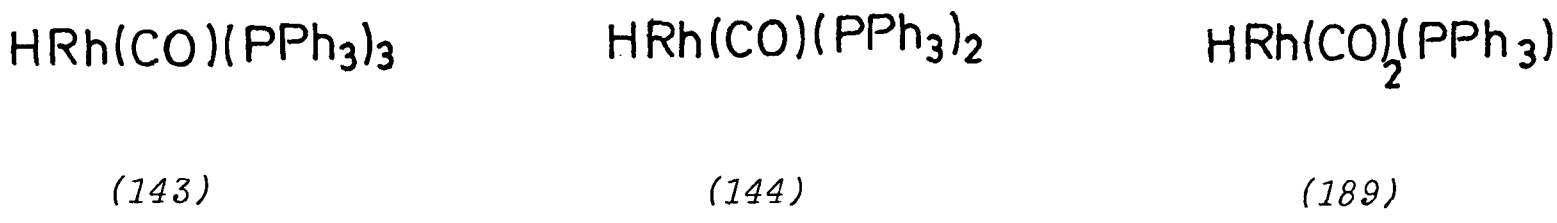


II.3.4. *Summary*

The previous sections describe five new experiments relating to the study of the mechanism of rhodium-catalysed hydroformylation which give new insight into the preferred pathway. Firstly, the dicarbonyl complexes *(145)* and *(168)* have been identified in solution under carbon monoxide or hydrogen and carbon monoxide. The latter was shown to react



selectively with a trapping agent, methylenecyclopropane, at low temperature. With a deficiency of carbon monoxide the triphenylphosphine-derived hydride *(145)* is selectively removed on addition of styrene or octene. No evidence for the formation of any of the coordinatively unsaturated intermediates *(144)* and *(189)* was obtained, and it is

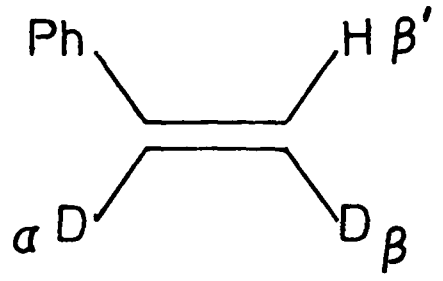


(143) *(144)* *(189)*

concluded that they are present only at very low concentration. The dicarbonyl-hydride *(145)*, like its iridium analogue[132] does not show any appreciable interconversion with the isomeric metal-formyl derivative.[148] Secondly the kinetics of interconversion of carbonyl complexes *(143)* and *(145)* have been examined by saturation transfer ^{31}P-NMR using the pulse sequence *DANTE*, introduced by Freeman and Morris[138]; triphenylphosphine dissociation was shown to be rapid in both cases in carbon monoxide saturated solution at 280°K. The rate of interconversion of the two

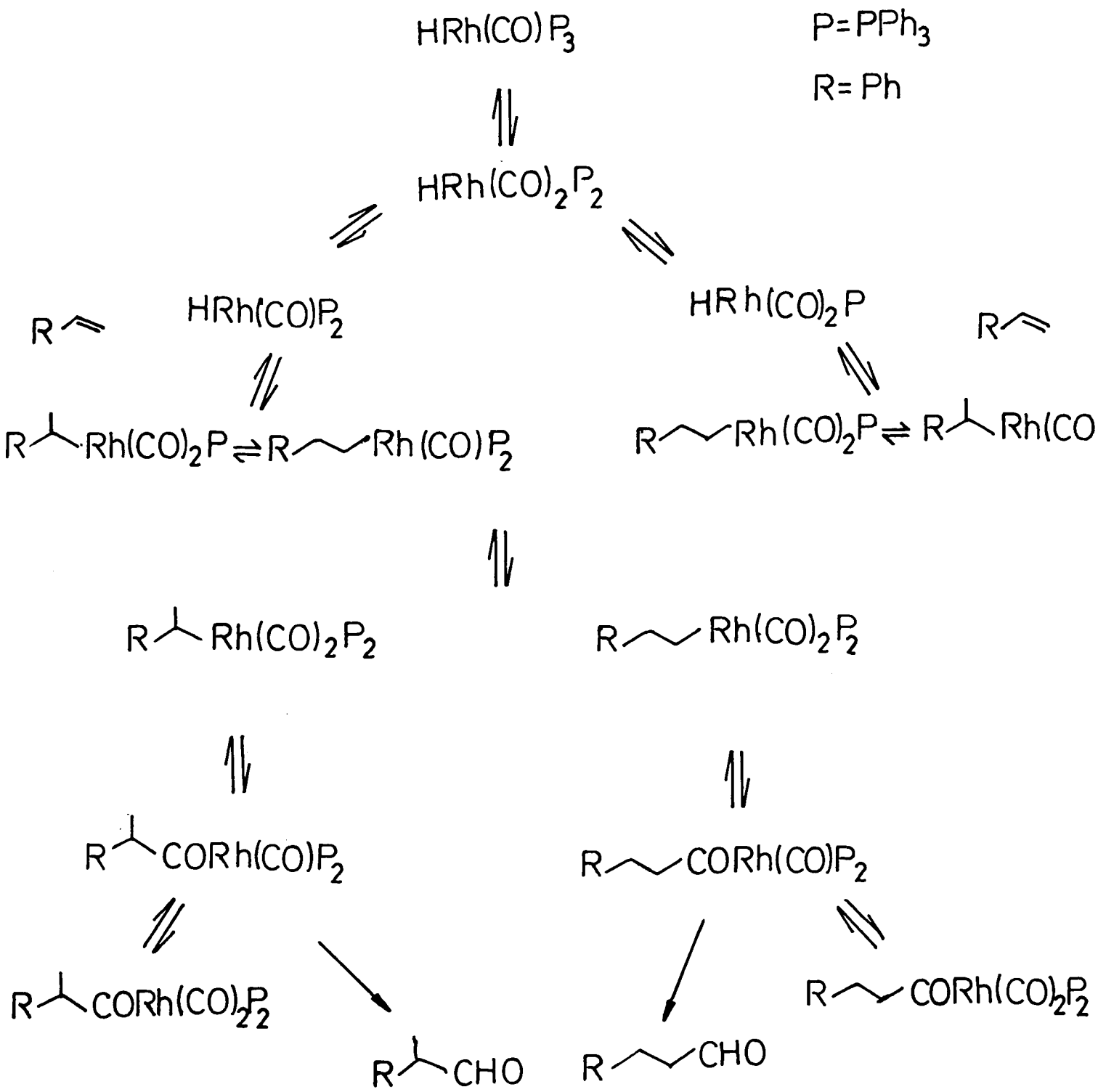
complexes is fast compared with the rate of hydroformylation under ambient conditions; so that none of the catalyst pre-dissociation equilibria are rate-determining.

These experiments suggest, although not conclusively, that the dicarbonyl complex *(145)* is the one which reacts more rapidly with olefins. Treatment of *cis*-1,2-$[^2H]_2$-styrene *(165)* with catalyst *(143)* leads to rapid equilibration of the β- and β′-sites and much slower β′- to α-interconversion. This isomerization is considered to involve the 16-electron complex *(144)* operating by the mechanism shown in Schemes II.3.9 and II.3.10. The reaction is suppressed by triphenylphosphine under conditions where the rate of hydroformylation is decreased by a factor of only 2.2. Under carbon monoxide no isomerization of styrene *(165)* occurs. Nevertheless styrene reacts with the dicarbonyl complex



(165)

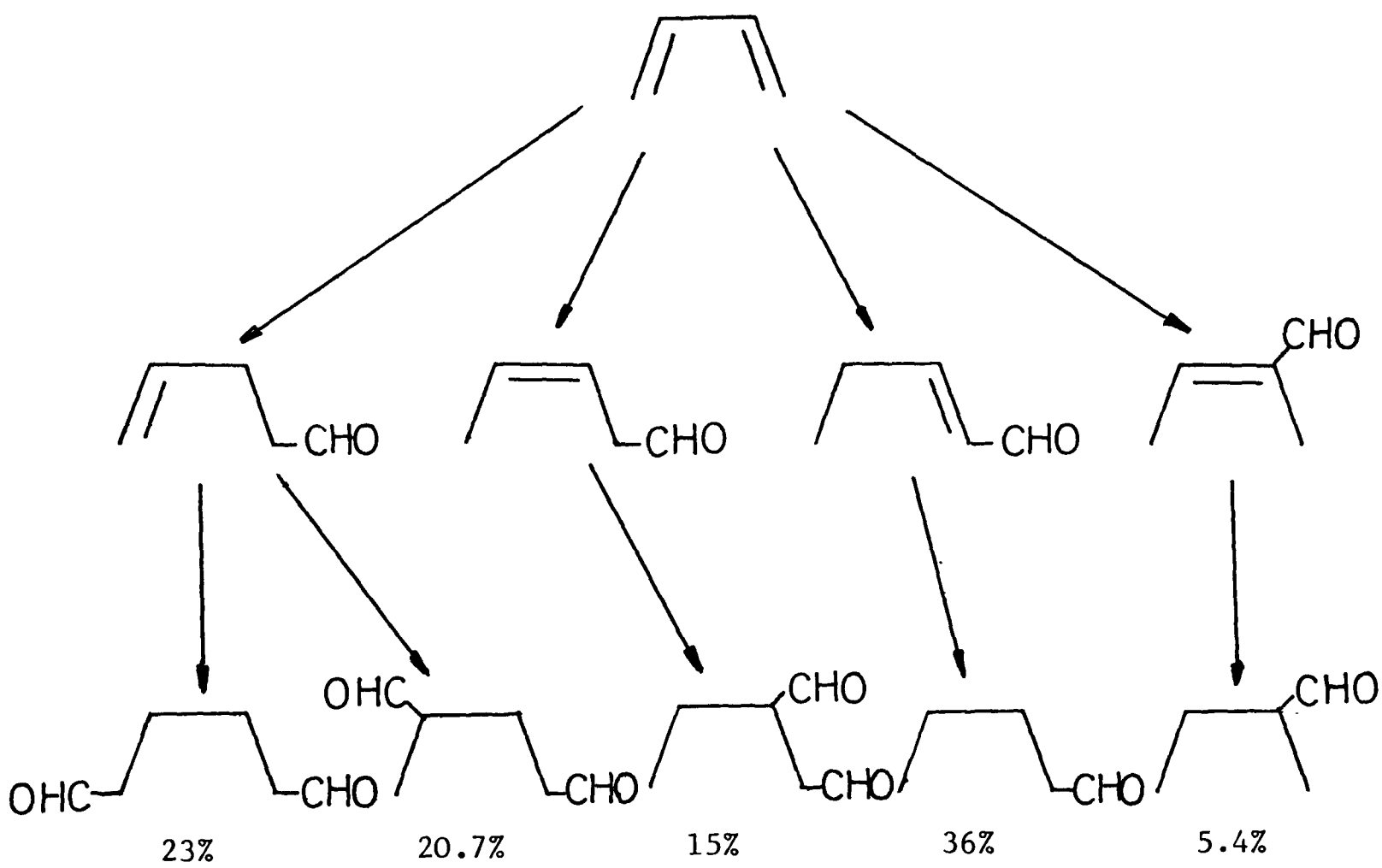
(145) since an acyl-intermediate shown to have structure *(172)* is formed under these conditions. This shows dynamic NMR behaviour best explained in terms of triphenylphsophine isomerization at lower temperatures and acyl-alkyl interconversion at high temperatures where the former is strongly favoured at equilibrium. Finally the acyl complex derived from styrene is > 90% the *iso*-acyl-complex *(172)* initially but rearranges rapidly at ambient temperature to species *(171)*. The set of observations and their relevance to hydroformylation is summarized in Scheme II.3.15.



Scheme II.3.15

II.4. Hydroformylation Studies

An early objective of the project was to determine the effectiveness of *trans*-chelating biphosphine rhodium complexes in hydroformylation of conjugated dienes. It has previously been found that attempted hydroformylation leads to a complex mixture of products (Scheme II.4.1) and that the potentially useful 1,6-hexanedial is only formed in minor amounts.[149,150] This is presumably due to the formation of σ-allyl

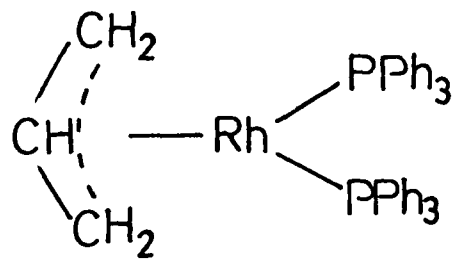


Reaction conditions: 200 atm., 25°, n-Bu_3P modified rhodium catalyst

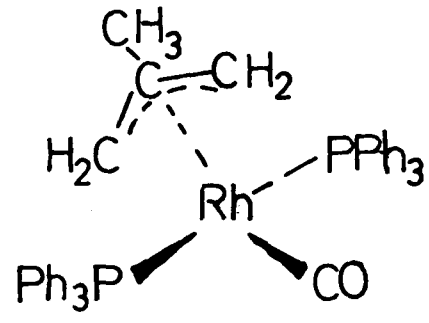
Scheme II.4.1

intermediates which then isomerize to π-allyl complexes thus diverting the course of reaction. Spencer has found likewise[151] that conjugated cyclic dienes give products other than the desired aldehyde.

It was reasoned that a rhodium coordinated rigidly *trans*-chelating biphosphine might confer several advantages in hydroformylation. In the case of conjugated diene hydroformylation, it is unlikely that a σ- to π-allyl (η^1 to η^3) complex interconversion will occur since η^3-allyl rhodium-biphosphine complexes are known to have *cis*-stereochemistry; for example the allylic rhodium complex *(190)* has the structure shown below.[152] A study by Wilkinson and co-workers[152] of the interaction of dienes with hydrido-rhodium or iridium complexes is particularly relevant; hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) reacted with butadiene to give the π-allylic complex *(191)*.



(190)

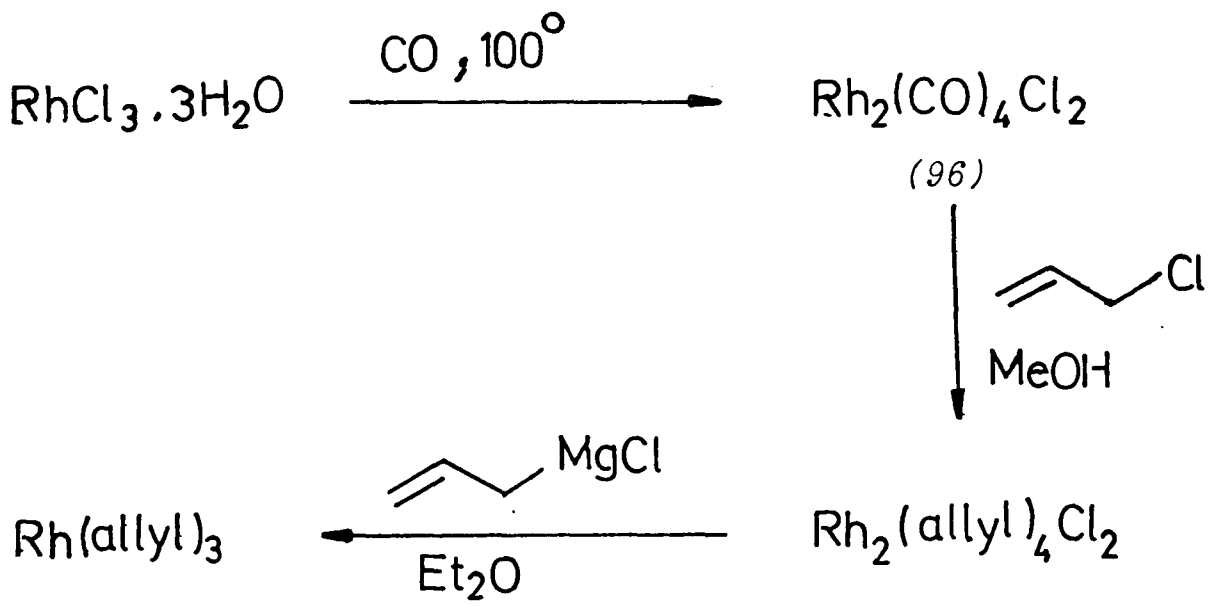


(191)

In addition it should be possible to exert a greater control on the course of the reaction by defining the P-Rh-P orientation as *trans; cis*-chelating phosphines in stoichiometric amounts tend to deactivate hydroformylation catalysts under mild conditions.[153]

Experimental work was largely carried out at the Johnson Matthey Research Centre, Sonning Common as part of the C.A.S.E. scheme and employed a small-scale thermostated reactor capable of operating at

temperatures and pressures not dissimilar to those of the commercial process. The assembly and operation operation of an automatic gas uptake measurement device, capable of monitoring low pressure hydroformylation reactions is described in Appendix B. Generation of the catalyst requires the reaction of a low-valent rhodium complex with the appropriate mono- or biphosphine, and a number of trial experiments suggested that *tris*(allyl)rhodium *(192)* (prepared according to Scheme II.4.2) was an appropriate precursor.

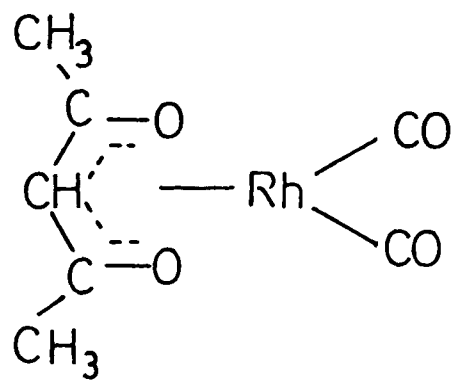


(192) *(193)*

Scheme II.4.2.

For generation of catalytic species under mild conditions it was felt that this procedure was superior to other methods, for example the reaction of cationic mono- or biphosphine rhodium diolefin complexes with triethylamine, or the *in situ* preparation from complexes such as dicarbonyl(2,4-pentanedionato-*O,O'*-)rhodium *(194)* and phosphine.

It was quickly found that butadiene was unreactive under these conditions using 5-phenyl-5*H*-dibenzophosphole *(61)* or the rigid biphosphine *(67)*. Even at much higher pressures and temperatures (100



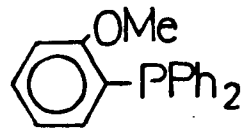
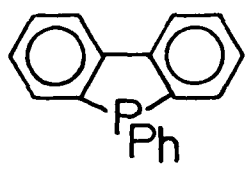
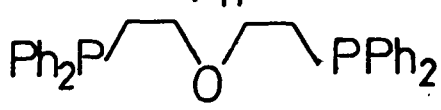
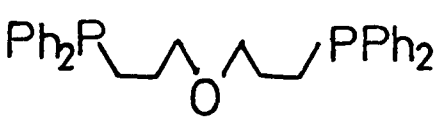
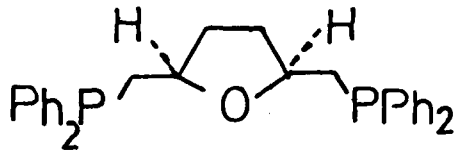
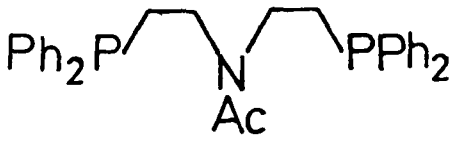
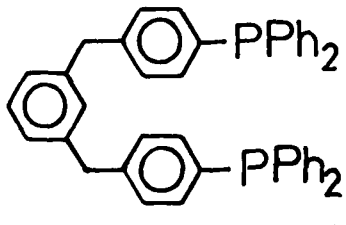
(194)

atmospheres, 100°) the reaction was slow and g.c. analysis of the products showed predominant formation of monoaldehydes. An identifiable amount of 1,6-hexanedial was produced but insufficient to encourage further work. At this point efforts were concentrated on hydroformylation studies at medium and low pressures employing oct-1-ene and styrene as olefinic substrates. Results are recorded in Tables II.4.1 and II.4.2 and are discussed subsequently.

Hydroformylation of mono-olefins employing rhodium-triphenylphosphine catalysts has been extensively studied[18] and factors affecting *n-/iso-* aldehyde product ratios are now well understood. In the reaction catalysed by hydridocarbonyl*tris*(triphenylphosphine)rhodium (I), this ratio is sensitive to many factors including triphenylphosphine concentration and relative proportions of hydrogen and carbon monoxide. Wilkinson and co-workers have made an extensive study of rhodium catalysed hydroformylation at ambient temperatures and low pressure.[18] High straight to branched aldehyde product ratios and rapid hydroformylation were found for $>$1:1 H_2:CO mixtures at 1 atmosphere. The presence of excess triphenylphosphine increases the product ratio at the expense of the reaction rate. A significant conclusion was reached, however

Table II.4.1.

Hydroformylation of oct-1-ene

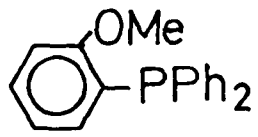
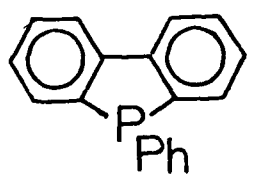
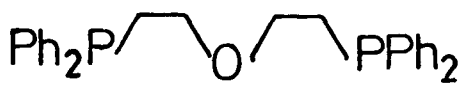
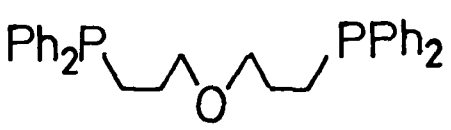
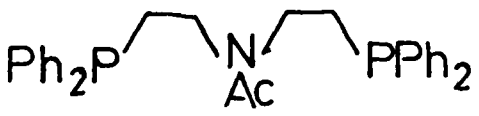
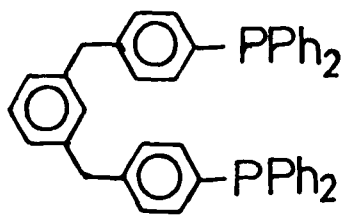
	Catalyst Precursor	Phosphine	Approx relative rate	% n-isomer
1.	$Rh(allyl)_3$	2 PPh_3	10.0	71 (77)[a] (77)[b]
2.	$Rh(acac)(CO)_2$	2 PPh_3	5.8	71
3.	$Rh(acac)(CO)_2$	65 PPh_3	6.4	83
4.	$Rh(allyl)_3$	2 	10.9	71
5.	$Rh(allyl)_3$	2 	5.9	77
6.	$Rh(allyl)_3$		3.2	90[c,d] (79)[e]
7.	$Rh(allyl)_3$		4.3	75 (71)[f]
8.	$Rh(allyl)_3$		2.9	80
9.	$Rh(allyl)_3$		3.1	81 (82)[g]
10.	$Rh(allyl)_3$		9.8	75

Reaction conditions: 1:1 H_2/CO, 100°, 80 psi, 300 ppm rhodium in toluene (15 ml) and oct-1-ene (1 ml)

[a] Hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) procatalyst, 25°, 1 atm.; [b] cationic diolefin complex *(85)* procatalyst, 30°, CH_2Cl_2; [c] average of three separate runs; [d] 5:1 H_2 /CO gave 93% *n*-isomer; [e] cationic diolefin complex *(90)*, procatalyst 25°, 1 atm; [f] cationic diolefin complex *(91)*, procatalyst, 25°, 1 atm; [g] cationic diolefin complex *(93)* procatalyst, 25°, 1 atm. [b,e,f,g] in presence of NEt_3.

Table II.4.2.

Hydroformylation of styrene

	Catalyst Precursor	Phosphine	Approx relative rate	% n-isomer
1.	$Rh(allyl)_3$	2 PPh_3	10.0	51 (17)[a] (10)[b] (6)[c]
2.	$Rh(acac)(CO)_2$	2 PPh_3	8.0	52
3.	$Rh(acac)(CO)_2$	65 PPh_3	5.1	29
4.	$Rh(allyl)_3$	2 	4.9	52
5.	$Rh(allyl)_3$	2 	5.1	42
6.	$Rh(allyl)_3$		5.3	35 (12)[d]
7.	$Rh(allyl)_3$		3.3	31
8.	$Rh(allyl)_3$		4.7	34
9.	$Rh(allyl)_3$		6.3	46 (19)[e]

Reaction conditions: 1:1 H_2/CO, 100°, 80 psi, 300 ppm rhodium in toluene (15 ml) and styrene (1 ml).

[a] 25°, 1 atm, $PhCH_3$; [b] Hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) procatalyst, 25°, 1 atm, $PhCH_3$; [c] hydrido*tetrakis*(triphenylphosphine)-rhodium(I) procatalyst, 25°, 1 atm, $PhCH_3$; [d] cationic diolefin complex *(90)* procatalyst, 25°, 1 atm, CH_2Cl_2; [e] 25°, 1 atm, $PhCH_3$, NEt_3.

that increased temperatures and gas pressures compensate for the lowered rate of reaction. Subsequent similar studies by other workers [154] at higher pressures and temperatures confirmed this.

The dependences of rate of hydroformylation and *n*-/*iso*-aldehyde ratio on reaction variables have been summarized by Merola.[155]

$$\text{Rate} \propto [\text{olefin}]^1 [\text{Rh}]^1 [\text{H}_2]^1 [\text{CO}]^{-1} [\text{PPh}_3]^1$$

$$\frac{n\text{-aldehyde}}{i\text{-aldehyde}} \propto [\text{PPh}_3]^1 [\text{CO}]^{-1} [\text{Rh}]^0$$

Commercial hydroformylation plants achieve the required high *n*-/*iso*-ratios by operating at high concentrations of triphenylphsophine and low partial pressures of carbon monoxide.[6]

In this project the hydroformylation of oct-1-ene was studied first (Table II.4.1). The reactions catalysed by rhodium-triphenylphosphine complexes proceeded as expected to give 71% of the *n*-isomer irrespective of whether the catalyst was prepared by *in situ* reaction of *tris*(allyl)-rhodium *(192)* or dicarbonyl(2,4-pentanedionato-*O,O'*-)rhodium *(194)* with triphenylphosphine. The latter complex, however, only caused reaction after an induction period, presumably dependent on displacement of the acetylacetonate ligand and formation of a rhodium-hydride complex to initiate the catalytic cycle. Induction periods have been reported for other rhodium catalysts.[17] The reactions carried out at 25° and 1 atmosphere employed hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* or bicyclo [2.2.1]hepta-2,5-diene*bis*(triphenylphosphine)rhodium(I) tetrafluoroborate *(85)* as catalyst precursors and produced similar isomer ratios. Excess phosphine at the higher pressure and temperature increased the proportion of *n*-isomer in a similar manner to that described by Hughes and Unruh.[154] The 2-methoxyphenyldiphenylphosphine derived catalyst produced an identical product ratio to the corresponding

triphenylphosphine complex, whereas the use of a dibenzophosphole ligand *(61)* slightly increased the proportion of *n*-nonanal formed. The latter phosphine *(61)* is recognized as a ligand of strong donor ability and steric rigidity compared with triphenylphosphine;[22] these factors may account for the increased *n-/i*-ratio.

A quite different series of results was obtained using chelating biphosphines. At room temperature and atmospheric pressure the cationic diolefin complexes of biphosphines *(63)*, *(64)* and *(66)* gave unexceptional isomer ratios and the rates of reaction were *ca.* ten times slower than the corresponding monophosphine complex *(85)*. At the higher pressure and temperature, rates were more similar to those reactions involving monophosphine complexes, but considerable variations in isomer ratio were obtained. The phosphinoether *(63)* is particularly interesting since mole equivalence with *tris*(allyl) rhodium produced *n-/iso*-ratio better than that of complex *(194)* with sixty-five equivalents of triphenylphosphine. Biphosphine *(67)* (designed to be rigidly *trans*-chelating) appears to behave as a mono-phosphine, although *trans*-chelate complexes have been characterized (see Chapter II, Sections 1 and 2). Side reactions such as hydrogenation or olefin isomerization were not competitive in any of the reactions investigated.

In a subsequent period spent at Johnson Matthey, a further series of oct-1-ene hydroformylations were carried out using a catalyst derived from *tris*(allyl)rhodium *(192)* and 1,5-*bis*(diphenylphosphino)-3-oxapentane *(63)*, and *n-/i*-aldehyde ratios are recorded in Table II.4.3. The slight reduction in the isomer ratio (entry 3, Table II.4.3.) with that obtained previously (entry 6, Table II.4.1) was attributed to differences in the composition of the hydrogen and carbon monoxide gas mixture. The highest isomer ratios were obtained using a temperature of 80^{o}, 100 psi and a 5:1 hydrogen to carbon monoxide mixture. Under these conditions, however, olefin

hydrogenation was an equivalent reaction pathway.

Table II.4.3.

Hydroformylation of oct-1-ene employing a rhodium-phosphine catalyst derived from 1.5-*bis*(diphenylphosphino)-3-oxapentane *(63)* and *tris*-(allyl)rhodium *(192)*

1:1 H_2/CO

Entry	Temperature (C)	Pressure (psi)	% *n*-isomer
1	60	100	86
2	80	80	82
3	80	100	84
4	80	120	86
5	100	100	85

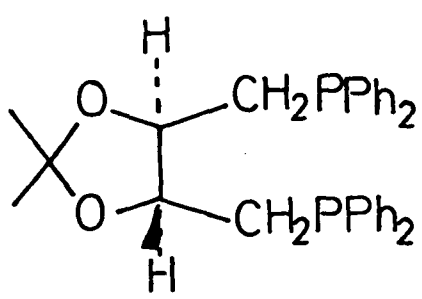
5:1 H_2/CO

6	60	100	91
7	80	100	94

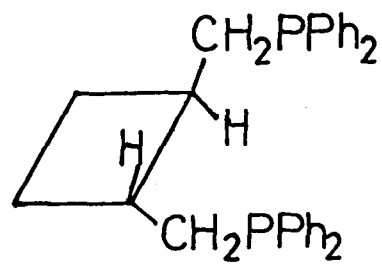
Reaction conditions: 300 ppm rhodium in toluene (15 ml) and oct-1-ene (1.0 ml)

Sanger,[153] and Hughes and Unruh[154] have recently investigated hex-1-ene hydroformylation catalysed by rhodium complexes of mono- and biphosphines. In both studies the catalysts were prepared by *in situ* reaction of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) with a mono- or chelating biphosphine; thus the exact composition of the catalyst is difficult to ascertain. The maximum amount of *n*-aldehyde for hydroformylations employing triphenylphosphine at 100° and *ca.* 100 psi was 94% and required a PPh_3:Rh ratio of 955:1. The best chelating

biphosphines investigated were those having rigid *trans*-conformations, for example (+)-[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)*bis*(methylene)] - *bis*diphenylphosphine *(195)* (DIOP) and *trans*-1,2-*bis*(diphenylphosphinomethyl)cyclobutane *(196)* produced 83% and 87% of the *n*-isomer respectively [P⁀P:Rh=2:1, 100°, 100 psi].



(195) (DIOP)



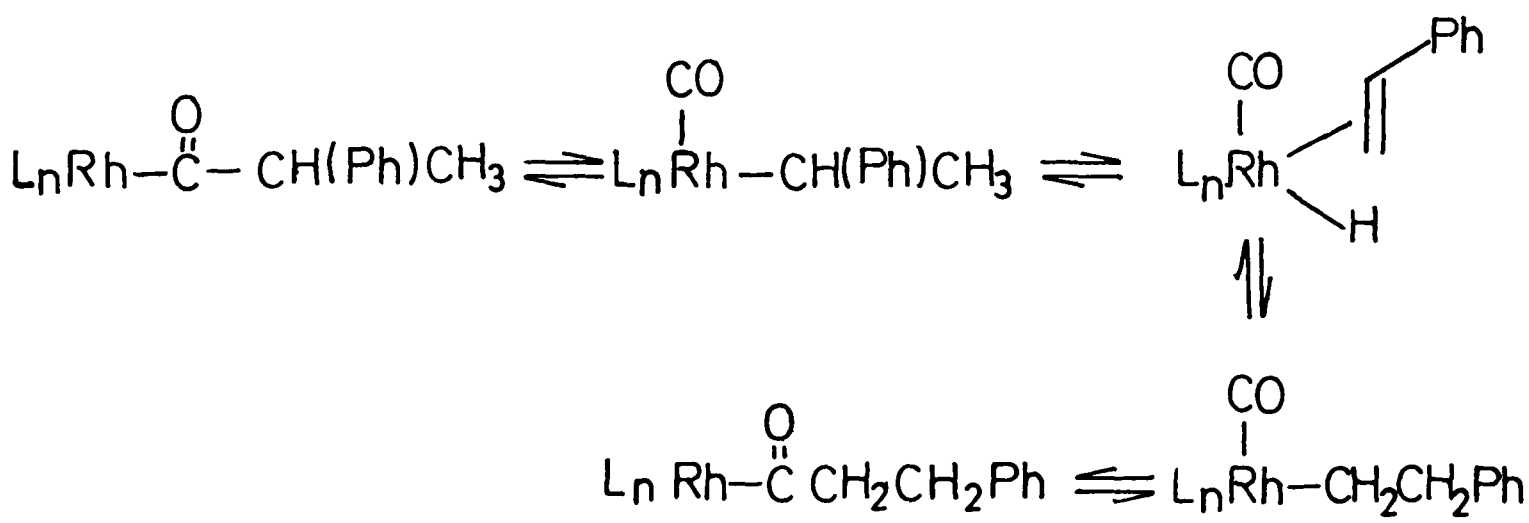
(196)

The phosphinoether *(63)*, therefore, compares very favourably with other chelating phosphines, particularly regarding the use of rhodium complexes of 1:1 rhodium to biphosphine stoichiometry. The proportion of *n*-isomer produced (*ca.* 90%) by employing complexes of 1,5-*bis*(diphenylphosphino)-3-oxapentane is also comparable with reactions using a large excess of triphenylphosphine. The steric requirement of rigidly *trans*-chelating biphosphines may explain the preference for the formation of linear aldehyde products; it is, however, not clear whether the biphosphine *(63)* is *trans*-chelated at all times in the reaction cycle.

The other olefinic substrate investigated was styrene (Table II.4.2). Styrene is different from octene because the *iso*-aldehyde, 2-phenylpropanal, is the major hydroformylation product, reflecting superior stability of σ-benzyl complexes. This contrasts with the stability of styrene

derived acyl complexes (see Chapter II, section 3), where the linear species is the more stable. The contrast between low and medium pressure hydroformylation is also marked. Under ambient conditions a very high proportion of the *iso*-product is formed, and *n*-/*i*-ratio is relatively insensitive to the nature of the phosphine; reaction rates are similar to those obtained for oct-1-ene. The results obtained at higher temperature and pressure differ in that the *n*-/*iso*- is close to 1:1 in many cases. Both *tris*(allyl)rhodium and dicarbonyl(2,4-pentanedionato-*O*,*O*'-)rhodium procatalysts lead to very similar isomer ratios and reaction rates. Addition of excess phosphine causes a reduction in the proportion of *n*-isomer formed, as does the use of rhodium-biphosphine derived catalysts.

Equilibrium constants at the various intermediate stages are not known and it is possible that the data obtained for styrene reflects a reversible isomerization of intermediate species (Scheme II.4.2), otherwise trends might be very similar to octene. The competing pathway by which a rhodium-acyl complex reductively eliminates aldehyde on reaction with hydrogen will be dominant in the case of oct-1-ene if *n*- to *iso*-acyl complex isomerization is not competitive.



Scheme II.4.2.

CHAPTER III - EXPERIMENTAL

CHAPTER III - EXPERIMENTAL

Instrumentation

^{1}H - Nuclear magnetic resonance spectra were obtained on either a Perkin-Elmer R24 (60 MHz), a Perkin-Elmer R32 (90 MHz) or a Bruker WH 300 (300.13 MHz) instrument. Chemical shifts (δ) are expressed in parts per million (ppm) from tetramethylsilane. ^{13}C - NMR spectra were recorded on Bruker WH 90 (22.63 MHz) Bruker WH 300 (75.47 MHz) and Bruker WH 400 (100 MHz) pulsed Fourier-transform spectrometers; chemical shifts (δ) are quoted relative to tetramethylsilane. ^{31}P - NMR spectra were also recorded on Bruker WH 90 (36.43 MHz), Bruker WH 300 (121.5 MHz) and Bruker WH 400 (162 MHz) instruments; chemical shifts are quoted relative to external phosphoric acid (85%). 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, and mult. = multiplet. NMR solvents are as indicated.

For variable temperature spectra ($< 20^{o}$) the following methods were employed:

Bruker WH 90: The sample was cooled to the required temperature in the probe by nitrogen gas (precooled by heat exchange with liquid nitrogen). Calibration of the temperature was carried out by standard procedures based on the relative chemical shifts of the hydroxyl and methyl protons.

Bruker WH 300 and WH 400: the sample was cooled to the required temperature by cold nitrogen gas produced by direct boil-off from a reservoir of liquid nitrogen. Temperature calibration was effected by the method described above.

In both cases the samples were allowed to equilibrate at the required temperature for at least 5 min prior to obtaining the NMR spectra.

Infra-red spectra were recorded either as nujol mulls, on potassium bromide discs or in the stated solvent, using a Perkin-Elmer 257-spectrometer. The following abbreviations are used:- v.s. = very strong, s = strong, m = medium and w = weak.

Ultra-violet spectra were recorded on a Unicam SP 800 A spectrophotometer in 1 cm cells as solutions in the solvents indicated. Extinction coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses after the absorption).

Mass spectra were recorded on Varian MAT CH7 and VG Micromass 16F spectrometers (in field-desorption or electron-impact mode as indicated). *m/e* values (followed in parantheses by the percentage abundance) are given for the molecular ion and the base peak.

Microanalyses were performed under the supervision of Dr F B Strauss. Melting points were determined on a Reichert-Kofler block and are uncorrected. Temperatures are quoted in degrees centigrade throughout unless otherwise stated.

Techniques and materials

Silica gel for column chromatography was 40-60 micron grade. Thin layer chromatography (t.l.c) was performed on 0.2 mm thick E. Merck silica plates 60F-254; preparative thin layer chromatography was performed on plates (20 cm x 20 cm x 1 mm) coated with E. Merck silica gel (60 $PF_{254+366}$) prepared by Mr R Prior. Analytical gas-liquid chromatography employed a Pye series 104 chromatograph at *ca.* 100^{o}, using a 2 m column of 3% Carbowax 20M on Chromasorb W with a nitrogen eluent. Preparative g.l.c. was carried out on a Pye series 104 A chromatograph at *ca.* 150^{o} with a 5 mm column of 5% Carbowax on Chromasorb W.

All reactions involving phosphines, organometallic complexes and other air-sensitive compounds were conducted under an argon atmosphere using standard vacuum-line techniques and Schlenck glassware. All transfers of liquids and solutions of air- or moisture-sensitive materials were carried out with dried, inert gas purged syringes fitted with stainless steel needles or with thin steel tubing. Argon was purified by successive passage through liquid paraffin, concentrated sulphuric acid, potassium hydroxide pellets and glass wool.

Commercial solvents were distilled prior to use from an appropriate drying agent according to standard procedures. Dichloromethane, chloroform, carbon tetrachloride and ethyl acetate were distilled from phosphorus pentoxide and stored over predried molecular sieves (4A), ethanol and methanol from magnesium turnings. All hydrocarbons were distilled from phosphorus pentoxide or sodium wire and then stored over molecular sieves Linde (4A); pyridine and triethylamine were distilled from barium oxide and calcium hydride respectively: both were kept over potassium hydroxide pellets. Diethyl ether (referred to as ether throughout the text) dioxan and tetrahydrofuran were freshly distilled from sodium wire employing sodium benzophenone ketyl as an indicator. Dimethyl sulphoxide was distilled from calcium hydride under reduced pressure. All water used in reactions was deionized ($\lambda < 10^{-6}$ ohmcm^{-1}).

Hydrogen and carbon monoxide (1:1 mixture) and carbon monoxide gases were obtained from Air Products Ltd. ^{13}C-Carbon monoxide (5 litre cylinder) and Barium ^{13}C-carbonate and deuterium gas employed in the preparation of substrates and for NMR studies came from Prochem Ltd. Rhodium trichloride trihydrate and dicarbonyl(2,4-pentanedionato-O,O^{1}) rhodium (I) were obtained by a generous loan from Johnson Matthey Ltd.

Only representative procedures for the preparation of organometallic complexes for NMR analysis or for catalytic hydroformylation at high and low pressures are given; full data otherwise are recorded in the Results and Discussion.

III.1. Synthesis of Phosphines and their Rhodium Complexes

III.1.1 *Synthesis of Phosphines*

Phenylmagnesiumbromide [125]

Bromobenzene (32.0 g, 0.2 mol) was added to a suspension of magnesium turnings (5.5 g, 0.23 mol) in ether (100 ml, dried and distilled) such that gentle boiling under reflux was maintained throughout the addition. After stirring (30 min) the mixture was filtered under argon to give a solution of phenylmagnesiumbromide (1.7 M, estimated by titration) in ether.

Tetraphenylphosphonium bromide (60) [87]

Phenylmagnesiumbromide (60 ml, 0.1 mol, 1.7 M solution in ether prepared as above) was added dropwise to a suspension of cobalt (II) chloride (1.3 g, 5.5 mmol), triphenylphosphine (26.0 g, 0.1 mol) and bromobenzene (31.4 g, 0.2 mol) in ether (150 ml). The mixture was stirred (12 h), boiled under reflux (3 h), cooled and aq. hydrobromic acid (200 ml, 25% solution) added slowly, and the aqueous layer separated. Evaporation *in vacuo* gave a yellow solid which on recrystallization from water yielded tetraphenylphosphonium bromide *(60)* as white crystals (21.0 g, 50%), m.p. 285-287° (lit.,[156] 288°); ^{31}P-NMR δ(MeOH) 23.3; $\nu_{max.}$ (nujol) 1585(w), 1440(s), 1105(s), 988(w), and 725(s) cm^{-1}; $\lambda_{max.}$ 225 (33,800), 261 (3,990), 267 (4,980), and 275 (3,990) nm.

5-Phenyl-5H-dibenzophosphole (61) [157]

n-Butyllithium (60 ml, 1.55 M solution in hexane, 0.039 mol) was added dropwise to a stirred solution of diethylamine (10.0 g, 0.137 mol, dried and distilled), in ether (50 ml) during 15 min at -10°, the volume of the solution reduced to *ca.* one third *(in vacuo)* and ether (50 ml) added. Tetraphenylphosphonium bromide *(60)* (11.5 g, 0.027 mol) was added at 0° and the solution was stirred (30 min) and boiled under reflux (2h). On cooling 4 M hydrochloric acid (50 ml) was added very slowly

followed by toluene (50 ml). The organic layer was separated, dried over magnesium sulphate and the solvent removed *(in vacuo)* to leave a white solid which was crystallized from methanol to give 5-Phenyl-5*H*-dibenzophosphole *(61)* as white crystals (3.0 g, 42%) m.p. 89-90° (lit.,[157] 93–94°); ^{31}P-NMR $\delta(CH_2Cl_2)$ -9.5; $\nu_{max.}$ (nujol) 1435(s), 1260(w), 1130)w), 1025(w), 750(s), 730(s), and 695(s) cm^{-1}; *m/e* 259 ($\underline{M}^+$, 100%).

1,5-Bis*(methanesulphonyloxy)-3-oxapentane* (68)

Methane sulphonyl chloride (12 g, 0.105 mol) was added dropwise to a stirred solution of 3-oxapentane-1,5-diol (5 g, 0.047 mol) and triethylamine (10.6 g, 0.105 mol) in ether (100 ml) at 0°. The mixture was stirred for 3 h at 0° and left overnight. Solvent was removed *in vacuo* and then water (75 ml) and dichloromethane (75 ml) added. The aqueous layer was separated, extracted further with dichloromethane (75 ml) and the extracts combined, and dried over magnesium sulphate. Removal of solvent and crystallization of the residue from ethanol gave 1,5-*bis*(methane-sulphonyloxy)-3-oxapentane *(68)* as white needles m.p. 58-59° (lit.,[158] 54-55°); ^{1}H-NMR $\delta(CDCl_3)$ 3.05(6H, s, OSO_2CH_3), 3.78(4H, mult., CH_2O), and 4.36(4H, mult., CH_2OSO_2); $\nu_{max.}$ ($CHCl_3$) 3030(w), 1355(vs), 1175(vs), 1145(m), 1035(m), 970(m), and 925(m) cm^{-1}.

Lithium diphenylphosphide [92]

Finely cut lithium metal (0.5 g, 0.045 mol) was added to a stirred degassed solution of triphenylphosphine (6.0 g, 0.023 mol) in tetrahydrofuran (75 ml) under argon. The mixture was stirred (4h) at 20°, after which the dark red solution was filtered in order to remove excess lithium metal. Addition of 2-chloro-2-methyl-propane (2.1 g, 0.023 mol) to the filtrate and warming to 40° for 5 min destroyed the phenyl lithium formed in the

course of the reaction and produced a solution of lithium diphenylphosphide (0.3 M) in tetrahydrofuran.

1,5-Bis*(diphenylphosphino)*-3-*oxapentane* (63)

1,5-*Bis*(methanesulphonyloxy)-3-oxapentane *(68)* (3.0 g, 0.011 mol) was added to a stirred solution of lithium diphenylphosphide (0.3 M in tetrahydrofuran (50 ml), prepared as above) at -78° during 5 min, allowed to warm to 20° and stirred for a further 12 h. Degassed water (25 ml) and toluene (75 ml) were added, the organic layer separated, dried ever magnesium sulphate and filtered. Solvent was removed from the filtrate *in vacuo* to leave a light yellow oil (4.7 g, 93%), which was further purified by chromatography in toluene on a short florisil column to give 1,5-*bis*(diphenylphosphino)-3-oxapentane *(63)* as a viscous oil; ^{1}H-NMR δ($CDCl_3$) 2.2 (4H, mult., CH_2P), 3.3 (4H, mult., CH_2O) and 7.0-7.5 (20H, mult., aromatic *H*); ^{31}P-NMR δ(CH_2Cl_2) -20.9; $\nu_{max.}$ ($CHCl_3$) 3070(w), 3000(m), 2940(m), 2860(m) 1480(m), 1435(s), and 1100(s) cm^{-1}.

4-Oxaheptane-1,7-diol (69)[159]

A mixture of 1,3-propanediol (180 g, 2.37 mol) and sodium metal (7 g, 0.33 mol) was heated at 70° for 1 h. 1-Chloro-3-hydroxypropane (31 g, 0.33 mol) was added with stirring to the above solution at 100° during 30 min; the mixture was then heated for a further 1 h at 100° and 2 h at 130°. On cooling and filtering, the filtrate was distilled *in vacuo* to give a fraction b.p. 84-90°/0.05 mm Hg (lit.,[159] 90-95°/0.5 mm Hg) (10.5) which was 4-oxaheptane-1,7-diol *(69)* ; ^{1}H-NMR δ($CDCl_3$) 1.78(4H, q *J* 6 Hz, C-CH_2-C), 3.55(4H, t *J* 6 Hz, CH_2O) and 3.66 (4H, t *J* 6 Hz, CH_2O).

1,7-Bis*(methanesulphonyloxy)-4-oxaheptane* (70)

Methane sulphonyl chloride (5.5 g, 0.048 mol) was added dropwise to a stirred solution of 4-oxaheptane-1,7-diol (3.0 g, 0.022 mol) and

triethylamine (5.0 g, 0.049 mol) in ether (dried, 75 ml) at 0° during 15 min. After stirring for 12 h at 20°, the solvent was removed *in vacuo*, water (50 ml) and dichloromethane (50 ml) were added, and the aqueous layer separated. After extraction with dichloromethane (50 ml), the combined organic layers were dried under magnesium sulphate. Removal of solvent *in vacuo* gave 1,7-Bis*(methanesulphonyloxy)-4-oxaheptane* (70) as a yellow oil (6.0 g, 94%); ^{1}H-NMR δ($CDCl_3$) 2.0 (4H, quintet *J* 6 Hz, CCH_2C, 3.0 (6H, s, OSO_2CH_3), 3.50 (4H, t, *J* 6 Hz, CH_2O) and 4.3 (4H, t, *J* 6 Hz, CH_2O); $\nu_{max.}$ ($CHCl_3$) 3020(w), 1355(vs), 1175(vs), 1120(m), and 950(s) cm^{-1}.

The material was used without further purification.

1,7-Bis*(diphenylphosphino)-4-oxaheptane* (64)

1,7-*Bis*(methanesulphonyloxy)-4-oxaheptane *(70)* 2.0 g, 6.9 mmol) was added to a stirred solution of lithium diphenylphosphide [(0.3 M), prepared as described previously from lithium metal (0.3 g), triphenylphosphine (4.0 g, 15.3 mmol) and 2-chloro-2-methylpropane (1.4 g) in tetrahydrofuran (50 ml)] at -78° during 5 min. The mixture was allowed to warm to 20° and stirred for a further 3 h. Degassed water (25 ml) and toluene (75 ml) were added to the organic layer which was separated, and dried over magnesium sulphate. Solvent was removed *in vacuo* to leave a light yellow oil (2.5 g, 78%) which crystallized on trituration with cold methanol (*ca.* 10 ml). Recrystallization from methanol gave *1,7*-Bis *(diphenylphosphino)-4-oxaheptane* (64) as a white solid, m.p. = 75-77° (Found: C, 76.6; H, 6.6; P, 13.0%; $C_{30}H_{32}OP_2$ requires C, 76.6; H, 6.9; P, 13.2%); ^{1}H-NMR δ($CDCl_3$) 1.4-2.5 (8H, mult, CH_2P and CCH_2C), 3.4 (4H, t, *J* 7 Hz, CH_2O) and 7.0-7.4 (20H, bs, aromatic *H*); ^{31}P-NMR δ (CH_2Cl_2) -15.0; $\nu_{max.}$ ($CHCl_3$) 3070(m), 3000(m), 2940(m), 2860(m), 1480(m), 1435(s) and 110(s) cm^{-1} *m/e* 470 (M^+, 80%), and 108(100).

cis-2,5-Bis*(hydroxymethyl)tetrahydrofuran* (71)[160]

A solution of potassium permanganate (72.0 g, 0.455 mol) in acetone (2000 ml) and water (200 ml) was added dropwise to a vigorously stirred solution of hexa-1,5-diene(25.0 g, 0.304 mol) in acetone (200 ml) and water (40 ml). During the addition a constant stream of carbon dioxide was bubbled through the reaction mixture. After stirring for 30 min the mixture was filtered, and acetone removed from the filtrate *in vacuo*. The aqueous residue was extracted with light petroleum and dichloromethane (100 ml each), the aqueous layer separated and the volume reduced *in vacuo* to leave *cis*-2,5-*bis*(hydroxymethyl) tetrahydrofuran *(71)* (17.4 g, 43%) as a yellow oil; ^{1}H-NMR (D_2O) 1.4-2.4 (4H, mult., CH_2CH_2), 3.50-3.60 (4H, mult., CH_2OH) and 3.85-4.30 (2H, mult., C*H*). The material was used without further purification.

cis-2,5-Bis*(toluenesulphonyloxymethyl)tetrahydrofuran* (72)[161]

A solution of toluenesulphonylchloride (56.0 g, 0.293 mol) in pyridine (60 ml) was added dropwise to a stirred solution of *cis*-2,5-bis(hydroxymethyl)-tetrahydrofuran *(71)* (17.4 g, 0.132 mol) in pyridine (125 ml) at 0°C. The mixture was stirred for 3 h at 20°, then left for 12 h, poured onto water (2000 ml) and the white solid collected by filtration. Recrystallization from ethanol gave *cis*-2,5-*bis*(toluene-sulphonyloxymethyl)tetrahydrofuran *(72)* (19.4 g, 33%) as colourless needles, m.p. 130-132° (lit.,[161] 130.5°); ^{1}H-NMR ($CDCl_3$) δ 1.4 to 2.0 (4H, mult., CH_2CH_2), 2.40 (6H, s, CH_3), 3.8 to 4.2 (6H, mult., CH_2O) and methine *H*), 7.50 (8H, q, aromatic *H*).

Cis-2,5-Bis*(diphenylphosphinomethyl)tetrahydrofuran* (65)

Sodium potassium alloy was prepared by melting a mixture of potassium (1.53 g, 39.2 mmol) and sodium (0.40 g, 17.4 mmol) under argon. Dioxan (70 ml, dried, degassed) and triphenylphosphine (5.0, 19.1 mmol) were

added and the mixture stirred for 2 h. A solution of *cis*-2,5-*bis*(toluenesulphonyloxymethyl)tetrahydrofuran *(72)* (4.18 g, 9.5 mmol) in toluene (50 ml) was added, and after stirring (10 min) was filtered through celite and solvent removed *in vacuo* to leave cis-*2,5*-bis*(diphenylphosphinomethyl)tetrahydrofuran* (65) (4.2 g, 94%) as a colourless oil which crystallized on standing (*ca.* 4 weeks) to give a white solid m.p. 63-64° (Found: C, 76.9; H, 6.8; P, 12.95% Calc. for $C_{30}H_{30}OP_2$: C, 76.9; H, 6.45; P, 13.2%): ^{1}H-NMR δ($CDCl_3$) 1.4 to 2.6 (8H, br. mult., CH_2CH_2 and CH_2P), 3.7 to 3.9 (2H, mult., methine*H*), 7.0 to 7.7 (20 H, mult, aromatic*H*); ^{31}P-NMR δ(CH_2Cl_2) -23.5; *m/e* 468 ($\underline{M}^+$, 90%), 183(100).

N-*Acetyl-1,5*-bis*(diphenylphosphino)-3-azapentane* (66)

METHOD A

1,5-Bis*(diphenylphosphino)-3-azapentane hydrochloride* (74)[94]

1,5-Dichloro-3-azapentane hydrochloride *(73)* (1.0 g, 5.6 mmol) was added to a stirred solution of lithium diphenylphosphide [(1.12 mmol), prepared as described previously from lithium metal (0.3 g) triphenylphosphine and 2-Chloro-2-methylpropane (1.2 ml) in tetrahydrofuran (50 ml)]at -78° during 5 min. The mixture was stirred for 4 h at 20° and then hexane (20 ml) and aqueous sodium hydroxide (20 ml 10% solution) were added, and stirred (10 min). The aqueous layer was separated, acidified with 2M aq. hydrochloric acid and shaken vigorously to give a white solid; this was collected by filtration and recrystallization from acetonitrile gave 1,5-*bis*(diphenylphosphino-3-azapentane hydrochloride) *(74)* (2.4 g, 90%) as white needles, m.p. 172-174° (lit.,[94] 174-175.5°); ^{1}H-NMR δ($CDCl_3$) 2.4 to 3.4 (8H, mult., CH_2N and CH_2P), 7.1 to 7.8 (20H, bs, aromatic *H*) and 10.1 (2H, s, $\overset{\oplus}{N}H_2$); ^{31}P-NMR δ(CH_2Cl_2) -19.2.

METHOD B

Bis*(1,5-methanesulphonyloxy)*-N-*methanesulphonyl-3-azapentane* (75)

Methane sulphonyl chloride (4.6 ml, 60.0 mmol) was added dropwise to a stirred solution of *Bis*(2-hydroxyethyl)amine (2.1 g, 20.0 mmol) in pyridine at 0^{o}, and kept at 0^{o} for 48 h. The mixture was poured onto ice (150 g), acidified (pH_3) with conc. hydrochloric acid and extracted with dichloromethane (3 x 50 ml). The organic layers were separated, dried (magnesium sulphate) and the solvent removed *in vacuo* to leave a white solid which on recrystallization from ethanol gave *bis*(1,5-methanesulphonyloxy)-*N*-methanesulphonyl-3-aza-pentane *(75)* (1.32 g) m.p. = 111-114^{o} (lit.,[162] 114-115^{o}); ^{1}H-NMR δ(DMSO-d_6) 3.02 (3H, s, NSO_2CH_3), 3.18 (6H, s, OSO_2CH_3), 3.58 (4H, t *J* 6 Hz, NCH_2), 4.32 (4H, t *J* 6 Hz, OCH_2).

1,5-Bis*(diphenylphosphino)*-N-*methanesulphonyl-3-azapentane* (76)

1,5-*Bis*(methanesulphonyloxy)-*N*-methanesulphonyl-3-azapentane *(75)* (500 mg, 1.47 mmol) was added to a stirred solution of lithium diphenyl-phosphide [prepared as previously described from lithium metal (400 mg) triphenylphosphine (1.6 g) and 2-chloro-2-methylpropane in tetrahydro-furan (50 ml)] at -78^{o}, and stirred for 4 h at 20^{o}. Water and dichloro-methane (10 ml of each, degassed) were added and the organic layer separated, dried and evaporated *in vacuo*. The resulting solid (0.4 g) was recrystallized from methanol to give 1,5-*bis*(diphenylphosphino)-*N*-methanesulphonyl-3-azapentane *(76)* as white needles, m.p. 94-95^{o} (lit.,[92] 98-100^{o}) ^{1}H-NMR $\delta(CDCl_3)$ 2.0 to 2.4 (4H, mult., CH_2P), 2.7 (3H, s, NSO_2CH_3), 3.1 to 3.5 (4H, mult, CH_2N), 7.1 to 7.6 (20H, mult., aromatic *H*); ^{31}P-NMR $\delta(CH_2Cl_2)$ -19.8.

1,5-Bis*(diphenylphosphino)-3-azapentane*

Bis-(1,5-diphenylphosphino)-*N*-methanesulphonyl-3-azapentane *(76)* (0.35 g, 0.67 mmol) and Red-al (Aldrich, 70% solution of sodium *bis*(2-methoxyethoxy)aluminium hydride in toluene (2 ml, 6.9 mmol)) together with excess toluene (2 ml, dried) were boiled under reflux for 3 h and then stirred for a further 24 h. Water (25 ml) was added and the mixture extracted with chloroform (2 x 25 ml). The organic layers were separated, dried (magnesium sulphate) and evaporated. The resulting oil (*ca.* 0.1 g) was treated with 6 M hydrochloric acid (5 ml) and solvent removed *in vacuo*. ^{1}H-NMR and ^{31}P-NMR of the residue were found to be identical to those of the amine hydrochloride prepared by Method A.

N-*Acetyl*-bis*(1,5-diphenylphosphino)-3-azapentane* (66)

A mixture of *bis*(1,5-diphenylphosphino)-3-azapentane hydrochloride *(74)* (1.85 g, 3.9 mmol) 4 N sodium hydroxide (50 ml) and hexane (50 ml) were shaken until the solid material had dissolved. The hexane layer was separated, dried (magnesium sulphate) and evaporated *in vacuo*. The colourless oily residue was dissolved in dichloromethane (25 ml) and acetic anhydride (0.5 g, 4.9 mmol) in dichloromethane (10 ml) added dropwise during 5 min. The solution was stirred for 1 h and then evaporated *in vacuo* to leave *N*-acetyl-*bis*(1,5-diphenylphosphino)-3-azapentane *(66)* (1.65 g, 97%) as a colourless oil which crystallized on standing (3 months) to give a white solid m.p. 78-80°; ^{1}H-NMR $\delta(CDCl_3)$ 1.8 (3H, s, CH_3) 2.0 to 2.4 (4H, mult., CH_2P), 3.0 to 3.5 (4H, mult., CH_2N) and 7.0 to 7.5 (20H, bs, aromatic *H*); ^{31}P-NMR $\delta(CH_2Cl_2)$ -19.3 and 20.5.

1,3-Bis*(4-bromobenzoyl)benzene* (80)

A mixture of isophthaloyl chloride *(78)* (5.0 g, 24.6 mmol), aluminium

trichloride (12.0 g, 90.2 mmol) and bromobenzene (25 ml) was heated at 100° for 30 min. After cooling the dark brown solution was poured onto ice (500 g) and the solid formed was collected by filtration and washed with water (500 ml) and ether (250 ml). Drying *in vacuo* and recrystallization from toluene gave an off-white solid (8.8 g) which was shown to be (by ^{1}H-NMR) a mixture (*ca.* 3:1) of two compounds. The major (faster running) component was separated by preparative t.l.c (eluent: dichloromethane) to give *1,3-bis(4-bromobenzoyl)benzene* (80) as white platelets, m.p. 224-6° (Found: C, 53.85; H, 2.7; Br, 36.1. $C_{20}H_{12}O_2Br_2$ requires: C, 54.1; H, 2.7; Br, 36.0%); ^{1}H-NMR $\delta(CDCl_3)$ 7.6 (9H, mult.) 8.01 (2H, dd, *J* 7.8 and 1.50 and 8.15 (H, t, *J* 1.5); $\nu_{max.}$ (nujol) 1660(vs), 1265(s), 1065(m), 1000(s), 840(s) 735(s) and 700(m) cm^{-1}; *m/e* 438, 440, 442 ($\underline{M}^+$, 100%).

The material was used without further purification.

1,3-Bis*(4-bromobenzyl)benzene* (82)

A mixture of 1,3-*bis*(4-bromobenzoyl)benzene *(80)* (4.0 g, 75% mixture prepared as above) and 3-oxapentane-1,5-diol (25 ml) was heated at 120° until homogeneous. Hydrazine hydrate (3.0 ml, 61.8 mmol) was added, the solution boiled under reflux for 1 h and potassium hydroxide (3.0 g, 53.6 mmol) added during 10 min. The reaction flask was set up for distillation and boiled for 1 h. On cooling the residual mixture was poured onto aq. hydrochloric acid (200 ml, 20%) and extracted with dichloromethane (3 x 75 ml). The organic layers were combined, dried (magnesium sulphate) and evaporated *in vacuo* to leave a yellow oil (3.4 g) which crystallized on standing. Recrystallization from ethanol gave *1,3*-bis*(4-bromobenzyl)benzene* (82) as white needles, m.p. 69.5 to 71° (Found: C, 58.0; H, 3.8; Br, 38.6%. $C_{20}H_{20}Br_2$ requires: C, 57.7; H, 3.9; Br, 38.4%); ^{1}H-NMR $\delta(CDCl_3)$ 3.9(4H, s, CH_2) and 6.9 to 7.5(12H, mult.,

aromatic *H*); *m/e* 418 (40%), 416(70), 414(40) and 165(100).

1,3-Bis*(4-diphenylphosphinobenzyl)benzene* (67)

n-Butyllithium (5.0 ml, 1.55 M solution in hexane, 7.75 mmol) was added dropwise to a stirred solution of 1,3-*bis*(4-bromobenzyl)benzene *(82)* (1.55 g, 3.73 mmol) in ether (40 ml, dried and degassed) at 0^{o} under argon. The solution was stirred for 30 min at 0^{o}, chlorodiphenylphosphine (1.64 g, 7.45 mmol) was added dropwise during 10 min, and the mixture allowed to warm to 20^{o}. After stirring for a further 30 min, filtration and evaporation of the filtrate *in vacuo* left a yellow oil (1.63 g). This material was purified by flash chromatography on silica (eluent: 30% dichloromethane in hexane) to give *1,3*-bis*(4-diphenylphosphinobenzyl)benzene* (67) as a colourless oil which crystallized on standing; mp 48-49^{o} (Found: C, 83.8; H, 6.3; P, 9.9%. $C_{44}H_{36}P_2$ requires C, 84.3; H, 5.8; P, 9.9%); ^{1}H-NMR $\delta(CDCl_3)$ 3.9(4H, s, CH_2), 7.0 to 7.4 (32H, mult., aromatic *H*); ^{31}P-NMR $\delta(CH_2Cl_2)$ -5.4; *m/e* 627 ($\underline{M}^{+}$, 100%).

III.1.2. *Synthesis of Organorhodium complexes*

Di-μ-chlorobis(bicyclo[2.2.1]*hepta-2,5-diene)dirhodium(I)* (83)a[99]

A mixture of rhodium trichloride trihydrate (1.4 g, 5.3 mmol), bicyclo[2.2.1]hepta-2,5-diene (4.0 ml, 37 mmol) ethanol (20 ml) and water (2 ml) was stirred under argon for 2 d. The yellow precipitate was collected by filtration, washed twice with aqueous ethanol and dried *in vacuo* to give di-μ-chloro*bis*(bicyclo[2.2.1]hepta-2,5-diene)-dirhodium(I) *(83)a* (0.8 g, 60%), m.p. (dec) 240-242^{o} (lit.[99] 240^{o}); $\nu_{max.}$ (CS_2) 3060(m), 3000(m), 2960(m), 2920(m), 2855(m), 1307(s), 1171(m), 1029(m), 932(m), 882(m), 721(m), and 680(s) cm^{-1}. The material was used without further purification.

*Di-μ-chloro*bis*(cycloocta-1,5-diene)dirhodium(I)* (83)b[100]

A mixture of rhodium trichloride trihydrate (1.0 g, 3.8 mmol), cycloocta-1,5-diene (2.0 ml, 16.3 mmol) and ethanol (30 ml) was boiled under reflux for 3 h. The yellow precipitate was collected by filtration, washed twice with aqueous ethanol and dried *in vacuo* to give di-μ-chloro*bis*(cycloocta-1,5-diene)dirhodium(I) *(83)b* (0.75 g, 80%), m.p. (dec) 253-255° (lit.,[100] 256°); $\nu_{max.}$ (CS_2) 1325(s), 1301 (s), 1297(m), 1210(m), 1172(s), 1153(s), 1076(w), 993(s), 961(s), 866(s), 817(s), and 795(m) cm^{-1}.

Bis*(bicyclo*[2.2.1]*hepta-2,5-diene)rhodium(I) tetrafluoroborate* (84)[101]

A mixture of di-μ-chloro*bis*(bicyclo[2.2.1]hepta-2,5-diene)dirhodium (I) *(83) a* (0.28 g, 0.61 mmol), bicyclo[2.2.1]hepta-2,5-diene (0.3 ml, 2.78 mmol), silver tetrafluoroborate (0.3 g, 1.54 mmol) and dichloromethane (5 ml) was stirred for 10 min. Filtration, and addition of the filtrate to ether (30 ml, dried) resulted in a brick red precipitate; this was separated by Craig-tube filtration, washed (3 x with ether) and dried *in vacuo* to give *bis*(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate *(84)* (0.32 g, 72%), m.p. 157-159° (lit.,[101] 157-158°); ^{1}H-NMR δ($CDCl_3$) 1.56(4H, s, CH_2), 4.19(4H, s, C*H*), 5.53(8H, d, C*H*=C*H*); $\nu_{max.}$($CHCl_3$); 1053(s) and 1038(s) cm^{-1}.

Bicyclo[2.2.1]*hepta-2,5-diene*-bis*(triphenylphosphine)rhodium(I) tetrafluoroborate* (85)[163]

A mixture of di-μ-chloro*bis*(bicyclo[2.2.1]hepta-2,5-diene)-dirhodium (I) *(83)a* (0.1 g, 0.22 mmol) in dichloromethane (2 ml) triphenylphosphine (0.25 g, 0.95 mmol) and sodium tetrafluoroborate (0.08 g, 0.73 mmol) in water (2 ml) was stirred under argon for 15 min. The organic layer was separated, added to ether (25 ml, dried) and the orange precipitate

was separated by filtration. Washing with ether (10 ml) and drying *in vacuo* gave bicyclo[2.2.1]hepta-2,5-diene-*bis*(triphenylphosphine)-rhodium(I) tetrafluoroborate *(85)* (1.16 g, 89%); ^{1}H-NMR δ($CDCl_3$) 1.50 (2H, s, CH_2), 4.10(2H, s, C*H*), 4.54(4H, s, C*H*=C*H*), 7.33 (30H, bs, aromatic*H*); ^{31}P-NMR δ (CH_2Cl_2) 31.0, $J_{P,Rh}$ 156 Hz.

Bis*(triphenylphosphine)-cycloocta-1,5-diene rhodium(I) tetrafluoroborate* (86)[163]

A mixture of di-μ-chloro*bis*(cycloocta-1,5-diene)dirhodium(I) *(83)b* (0.10 g, 0.2 mmol), sodium fluoroborate (0.08 g, 0.73 mmol), triphenylphosphine (0.30 mg, 1.15 mmol), water (2 ml) and dichloromethane (5 ml) was vigorously stirred for 15 min under argon. The organic layer was separated, washed with water (2 x 2 ml) dried and magnesium sulphate reduced to *ca.* 1 ml *in vacuo* and added to ether (30 ml). The resulting orange-yellow precipitate was collected by filtration, washed with ether (2 x 10 ml) and dried *in vacuo* to give the complex *(86);* ^{1}H-NMR δ (CD_2Cl_2) 2.2 to 2.5 (8H, mult., CH_2CH_2), 4.6(4H, s, C*H*=C*H*) and 7.3 (30H, bs, aromatic *H*); ^{31}P-NMR δ (CH_2Cl_2) 27.7, $J_{P,Rh}$ 144 Hz.

Bicyclo[2.2.1]*hepta-2,5-diene*-bis*(2-methoxyphenyldiphenylphosphine)-rhodium(I) tetrafluoroborate* (87)

A solution of *bis*(bicyclo[2.2.1]hepta-2,5-diene *(84)* (0.08 g, 0.27 mmol) and 2-methoxyphenyldiphenylphosphine *(59)* (0.130 mg, 0.44 mmol) in tetrahydrofuran (2 ml) was stirred under argon for 10 min; the yellow-orange complex was precipitated by addition of the solution to ether (30 ml). Separation by Craig-tube filtration, washing with ether (2 x 10 ml) and drying *in vacuo* gave *bicyclo*[2.2.1]*hepta-2,5-diene*-bis-*(2-methoxyphenyldiphenylphosphine)rhodium(I) tetrafluoroborate* (87). (0.15 g, 79%), m.p. (dec.) 143-144° (Found: C, 61.6; H, 5.0; P, 6.8% $C_{45}H_{42}O_2P_2RhBF_4$ requires: C, 62.9; H, 4.9; P, 7.15%); ^{1}H-NMR δ(CD_2Cl_2)

1.3 to 1.7 (4H, mult., $-CH_2-$ and $-CH-$), 3.85(6H, s, OCH_3), 4.25 (4H, d, $CH=CH$) and 6.8 to 7.7 (28H, mult., aromatic *H*); ^{31}P-NMR δ (CH_2Cl_2) 24.8, $J_{P,Rh}$ 156 Hz; *m/e* (field desorption) 779 ($\underline{M}^+$).

Bicyclo[2.2.1]*hepta-2,5-diene*bis*(5-phenyl-5H-dibenzophosphole) rhodium(I) tetrafluoroborate* (88)

5-Phenyl-5*H*-dibenzophosphole *(61)* (0.25 g, 0.96 mmol) was dissolved in warm methanol (10 ml) under argon and a filtered solution of *bis*(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate *(84)* (0.18 g, 0.48 mmol) in methanol (2 ml) added. On standing for *ca.* 4 h at 0°, red crystals were deposited; these were collected by filtration, washed with a small amount of cold methanol and dried *in vacuo* to give *bicyclo*[2.2.1]*-hepta-2,5-diene*bis*(5-phenyl-5H-dibenzophosphole)rhodium (I) tetrafluoroborate (88)* (0.25 g, 65%), m.p. (dec) 190° (Found: C, 64.5; H, 4.5; P, 7.3%. $C_{43}H_{34}P_2RhBF_4$ requires: C, 64.4; H, 4.3; P, 7.7%); ^{1}H-NMR δ(CD_2Cl_2) 1.67 (2H, s, CH_2), 4.13(2H, s, CH), 4.93(4H, s, $CH=CH$) and 7.3(26H, mult., aromatic *H*); ^{31}P-NMR δ(CH_2Cl_2) 22.0 $J_{P,Rh}$ 152 Hz; *m/e* (field desorption) 715 (M^+).

Bicyclo[2.2.1]*hepta-2,5-diene*-bis*(1,5-diphenylphosphino)pentanerhodium(I) tetrafluoroborate* (89)[164]

Di-μ-chloro*bis*(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) *(83)a* (0.095 g, 0.2 mmol) and silver tetrafluoroborate (0.080 g, 0.4 mmol) were stirred in acetone (2 ml) under argon. *Bis*(1-5,diphenylphosphino)-pentane *(62)* (0.180 g, 0.4 mmol) was added and the mixture stirred for 10 min, filtered and the filtrate added to ether (30 ml). The orange precipitate was collected by filtration washed (3 x with ether) and dried *in vacuo* to give bicyclo[2.2.1]hepta-2,5-diene-*bis*(1,5-diphenyl-phosphino)pentanerhodium(I) tetrafluoroborate *(89)* (0.24 g, 82%); ^{1}H-NMR

$\delta(CDCl_3)$ 1.50(2H, s, CH_2), 1.6 to 2.6(10H, mult., $PCH_2CH_2CH_2P$), 4.0 (2H, s, *CH*), 4.5(4H, mult., *CH*=*CH*), and 7.4(20H, bs, aromatic *H*); ^{31}P-NMR $\delta(CH_2Cl_2)$ 16.7, $J_{P,Rh}$ 152 Hz.

Bicyclo[2.2.1]*hepta-2,5-diene-1,5-*bis*(diphenylphosphino)-3-oxapentane-rhodium(I) tetrafluoroborate* (90)[93]

Bis(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate *(84)* (0.22 g, 0.59 mmol) in methanol (2 ml) was added to a degassed solution of 1,5-*bis*(diphenylphosphino)-3-oxapentane *(63)* (0.26 g, 0.59 mmol) in methanol (4 ml) which was stirred for 5 min, and then left to stand at -30° for 8 h. Collection of the red crystals by filtration and drying *in vacuo* gave bicyclo[2.2.1]hepta-2,5-diene-1,5-*bis*(diphenylphosphino)-3-oxapentanerhodium(I) tetrafluoroborate *(90)* as red-orange crystals (0.31 g, 72%); ^{1}H-NMR $\delta(CDCl_3)$ 1.52(2H, s, CH_2), 2.55 (4H, mult., CH_2P), 3.7(4H, mult., CH_2O), 3.94(2H, s, *CH*), 4.39(4H, mult., *CH*=*CH*) and 7.55 (20H, bs, aromatic); ^{31}P-NMR $\delta(CH_2Cl_2)$ 18.1, $J_{P,Rh}$ 156 Hz.

Bicyclo[2.2.1]*hepta-2,5-diene-1,7-*bis*(diphenylphosphino)-4-oxaheptane rhodium(I) tetrafluoroborate* (91)

A solution of *bis*-bicyclo[2.2.1]hepta-2,5-dienerhodium(I) tetrafluoroborate *(84)* (0.09 g, 0.24 mmol) and 1,7-*bis*(diphenylphosphino)-4-oxaheptane *(64)* (0.113 g, 0.24 mmol) in dichloromethane (2 ml) was stirred under argon for 10 min. Addition to ether (25 ml), separation of the precipitate by Craig-tube filtration and washing with ether (3 x 10 ml) yielded 0.17 g (95%) of the complex. Recrystallization from methanol/water gave *bicyclo*[2.2.1]*hepta-2,5-diene-1,7-*bis*(diphenylphosphino)-4-oxaheptanerhodium(I) tetrafluoroborate dihydrate* (91) as red-orange crystals, m.p. (dec.) 144° (Found: C, 56.1; H, 5.4; P, 8.1%. $C_{37}H_{40}OP_2RhBF_4 \cdot 2H_2O$ requires: C, 56.4; H, 5.6; P, 7.85%); ^{1}H-NMR $\delta(CD_2Cl_2)$ 1.5 (2H, s, CH_2),

1.6 to 2.3 (8H, mult., CH_2CH_2P), 3.1(4H, mult., CH_2O), 4.0(2H, s, *CH*) and 4.5(4H, s, *CH*=*CH*); ^{31}P-NMR δ(CH_2Cl_2) 22.3, $J_{P,Rh}$ 154; *m/e* (field desorption) 666 ($\underline{M}^+$, 100%).

Bicyclo[*2.2.1*]*hepta-2,5-diene*-cis-2,5-bis(*diphenylphosphinomethyl*)-*tetrahydrofuranrhodium(I) tetrafluoroborate* (92)

Cis-2,5-*bis*(diphenylphosphinomethyl)tetrahydrofuran *(65)* (0.26 g, 0.56 mmol) and di-μ-chloro*bis*(bicyclo[2.2.1]hepta-2,5-dienedirhodium(I) *(83)a* (0.13 g, 0.28 mmol) were stirred in methanol (25 ml) under argon for 30 min. The mixture was filtered and sodium tetrafluoroborate (3.5 g) in water (15 ml) slowly added. The resulting orange precipitate was collected by filtration, washed three times with aqueous methanol and dried *in vacuo* to give bicyclo[2.2.1]hepta-2,5-diene-*cis*-2,5-*bis*-(diphenylphosphinomethyl)tetrahydrofuranrhodium(I) tetrafluoroborate *(92)* (0.22 g, 53%); ^{1}H-NMR δ(CD_2Cl_2) 1.38(2H, s, CH_2), 1.40 to 2.80 (8H, mult., CH_2CH_2, CH_2P), 3.75(2H, bs =CH-*CH*), 4.07(4H, mult., *CH*=*CH*), 4.20 to 4.50 (2H, mult., *CH*), 7.3 to 7.6(20H, bs, aromatic *H*); ^{31}P-NMR δ (CH_2Cl_2) 15.0, $J_{P,Rh}$ 154 Hz.

N-*Acetyl-1,5*-bis(*diphenylphosphino*)-*3-azapentane-bicyclo*[*2.2.1*]*hepta-2,5-dienerhodium(I) tetrafluoroborate* (93)

A mixture of *bis*(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate *(84)* (0.087 g, 0.23 mmol), *N*-acetyl-1,5-*bis*(diphenylphosphino)-3-azapentane *(66)* (0.113 g, 0.23 mmol) and tetrahydrofuran (1 ml) was stirred for 10 min under argon. The orange solid (collected by filtration) was washed with ether (3 x 10 ml) and dried *in vacuo* gave N-*methyl-1,5*-bis(*diphenylphosphino*)-*3-azapentane-bicyclo*[*2.2.1*]*hepta-2,5-dienerhodium(I) tetrafluoroborate* (93) (0.19 g), m.p. (dec.) 187° (Found: C, 58.5; H, 5.8; P. 7.8%. $C_{37}H_{39}NOP_2RhBF_4$ requires: C, 58.1; H, 5.1; P, 8.1%); ^{1}H-NMR δ (CD_2Cl_2) 1.50(2H, s, CH_2), 1.61(3H, s, OCH_3), 2.0 to 3.8 (8H, mult., CH_2P

and CH_2N), 3.85(2H, s, *CH*), 4.43 (4H, mult., *CH*=*CH*), 4.50(20H, bs, aromatic *H*); ^{31}P-NMR δ(CH_2Cl_2) 28.8 and 19.2, $J_{P,Rh}$ 154 Hz and $J_{P,P}$ 35 Hz; ν_{max} (CH_2Cl_2) 3060(w), 1650(vs), 1435(s), and 1060(s) cm^{-1}.

Bicyclo[2.2.1]*hepta-2,5-diene-1,3*-bis*(4-diphenylphosphinobenzyl)-benzenerhodium(I) tetrafluoroborate* (94)

A solution of *bis* bicyclo[2.2.1]hepta-2,5-diene rhodium(I) tetrafluoroborate *(84)* (0.067 g, 0.18 mmol) and 1,3-*bis*(4-diphenylphosphinobenzyl)benzene (0.112 g, 0.18 mmol) in dichloromethane (2 ml) was stirred under argon for 10 min. Addition to ether (30 ml) precipitated a yellow complex, which was collected by Craig-tube filtration, washed with ether (3 x 10 ml) and dried *in vacuo* to give *bicyclo*[2.2.1]*hepta-2,5-diene-1,3*-bis*(4-diphenylphosphinobenzyl)benzene rhodium(I) tetrafluoroborate (94)* (0.110 g, 68%); ^{1}H-NMR δ($CDCl_3$) 1.4(2H, s, CH_2), 3.8 to 4.1 (6H, mult., *CH* and CH_2), 4.4(4H, s, *CH*=*CH*) and 6.8 to 7.5 (32H, mult., aromatic *H*); ^{31}P-NMR δ (CH_2Cl_2) 29.2, $J_{P,Rh}$ 156 *m/e* (field desorption) 821 ($\underline{M}^+$).

Di-μ-chloro tetracarbonyldirhodium(I) (96)[103]

Rhodium trichloride trihydrate (1.0, 3.8 mmol) was heated at 100° under a constant steam of carbon monoxide (saturated with ethanol) for 6 h. The sublimed product and residue were extracted with dichloromethane, and filtered through celite. Removal of solvent *in vacuo* gave di-μ-chlorotetracarbonyldirhodium(I) *(96)* as orange needles (0.54 g, 73%) m.p. 125-126° (lit.,[103] 124-125°).

Bis(*1,5-bis(diphenylphosphino)-3-oxapentane*)*dicarbonyl-dichlorodirhodium(I)* (95)[102]

Di-μ-chloro-*tetra*(carbonyl)dirhodium(I) (0.068 g, 0.175 mmol) in methanol (8 ml) was added to 1,5-*bis*(diphenylphosphino)-3-oxapentane *(63)*

(0.157 g, 0.355 mmol) in methanol (8 ml) and the mixture stirred 8 h. The yellow complex was collected by Craig-tube filtration, washed three times with methanol(5 ml) and dried *in vacuo* to give di-1,5-*bis*-(diphenylphosphino)-3-oxapentane-dicarbonyl-dichlorodirhodium(I) *(95)* (0.095 g); ^{31}P-NMR $\delta(CH_2Cl_2)$ 22.5, $J_{P,Rh}$ 125 Hz.

Trans-*1,7*-bis*(diphenylphosphino)-4-oxaheptanecarbonylchlororhodium(I)* (97)

A mixture of di-μ-chloro*tetra*(carbonyl)dirhodium(I) *(96)* (0.030 g, 0.077 mmol) and 1,7-*bis*(diphenylphosphine)-4-oxaheptane *(64)* (0.073 g, 0.155 mmol) in methanol (8 ml) was stirred for 4 h. The yellow complex was collected by Craig-tube filtration and washed with a small quantity of methanol to give trans-*1,7*-bis*(diphenylphosphino)-4-oxaheptanecarbonylchlororhodium(I)* (97) (0.075 g), (Found: C, 58.4; H, 5.3; P, 9.7%. $C_{31}H_{32}ClO_2P_2Rh$ requires C, 58.5; H, 5.1; P, 9.7%); ν_{max}(CO) (KBr disc) 1965 cm^{-1}. *m/e* (field desorption) 610 ($\underline{M}^+$ - CO).

1,3-Bis*(4-diphenylphosphinobenzyl)benzenecarbonylchlororhodium(I)* (98)

A mixture of di-μ-chloro*tetra*(carbonyl)dirhodium(I) (0.3 g, 0.77 mmol), 1,3-*bis*(4-diphenylphosphinobenzyl)benzene (0.95 g, 1.52 mmol) and methanol (10 ml) was stirred for 12 h. The yellow solid was collected by Craig-tube filtration, washed with ether (3 x 10 ml) and dried *in vacuo* to give *1,3*-bis*(4-diphenylphosphinobenzyl)-benzenecarbonylchlororhodium(I)* (98) (0.9 g), m.p. (dec) 145°; ^{1}H-NMR $\delta(CDCl_3)$ 3.9(4H, s, CH_2) and 6.9 to 7.9 (32H, mult., aromatic *H*); ^{31}P-NMR $\delta(CH_2Cl_2)$ 28.6, $J_{P,Rh}$ 128 Hz; ν_{CO} 1965 cm^{-1}; *m/e* (field desorption) 792/4 ($\underline{M}^+$)

*Reaction of N-acetyl-1,5-*bis*(diphenylphosphino)-3-azapentane* (66) *with di-μ-chlorotetra(carbonyl)dirhodium(I)* (96).

A solution of N-acetyl-1,5-bis(diphenylphosphino)-3-azapentane *(66)* (0.06 g, 0.12 mmol) and di-μ-chlorotetra(carbonyl)dirhodium(I) *(96)*

(0.025 g, 0.06 mmol) in dichloromethane (5 ml) was stirred for 30 min. Ethanol (50 ml) was then added and the off-white precipitate collected by Craig-tube filtration and dried *in vacuo* to give a light yellow complex *(99)*: ^{31}P-NMR(CH_2Cl_2) δ 20.6, $J_{P,Rh}$ 124 Hz; ν_{max}(CO) (KBr disc) 1970, 1620, 1480 and 1430 cm^{-1}.

Trans-bis*(triphenylphosphine)carbonylchlororhodium(I)* (100)[104]

A solution of di-μ-chloro*tetra*(carbonyl)dirhodium(I) *(96)* (1.30 g, 3.3. mmol) and triphenylphosphine (3.5 g, 13.3 mmol) in toluene (25 ml) was stirred for 5 min. Ethanol (20 ml) was added and the yellow crystals collected by filtration, washed with ether and dried *in vacuo* to give *trans-bis*(triphenylphosphine)carbonylchlororhodium(I) *(100)* (4.3 g, 95%), m.p. 194-196° (lit.,[104] 195-197°); ^{31}P-NMR δ($CHCl_3$) 29.8, $J_{P,Rh}$ 127 Hz; $\nu_{max.}$ 1960(s), 1480(s), 1440(s), 1100(s), 750(s) and 700(s) cm^{-1}.

III.2. Preparation of organometallic complexes for NMR studies described in Chapter II, Section 2.

III.2.1. *Hydrogenation of* bis*(phosphine)diolefin rhodium(I) complexes in methanol: dihydrides and solvent adducts*

(A) ^{31}*P-NMR:*

A suspension of bicyclo [2.2.1]hepta-2,5-diene *bis*(triphenylphosphine)-rhodium(I) tetrafluoroborate *(85)* (30 mg, 0.038 mmol) in methanol (1.8 ml) in an 8 mm NMR tube was thoroughly degassed by three successive freeze-thaw cycles under argon. The NMR tube was attached to a vacuum line *via* a septum-capped adaptor and was narrowed before use to facilitate sealing. The tube was evacuated, hydrogen admitted and vigorously agitated until the characteristic orange colour of the diene complex was discharged (1 to 5 min). The tube was then sealed and the ^{31}P-NMR spectrum obtained by loading the 8 mm tube within a 10 mm tube into the NMR spectrometer. D_2O was used as the external lock signal in the space between the tubes.

(B) ^{1}*H-NMR:*

A suspension of bicyclo [2.2.1]hepta-2,5-diene *bis*(triphenylphosphine)-rhodium(I) tetrafluoroborate *(85)* (10 mg, 0.013 mmol) in methanol-d_4 in a 5 mm NMR tube was thoroughly degassed by three freeze-thaw cycles under argon. In this case the NMR tube was attached to the vacuum line *via* a fine needle which pierced the septum cap. The tube was evacuated, hydrogen admitted and vigorously agitated until the orange colour of the diene complex was discharged (1 to 5 min) at which stage a light-yellow brown solution typically remained.

In a related experiment, the reduction of bicyclo [2.2.1]hepta-2,5-diene-1,5-*bis*(diphenylphosphino)-3-oxapentanerhodium(I) tetrafluoroborate *(90)* by hydrogen deuteride was achieved in a similar manner as described above.

Hydrogen deuteride was generated in a closed system by the slow addition of cold methanol (0.8 ml) to lithium aluminium deuteride (84 mg, 2 mmol).

The NMR spectra of other rhodium-phosphine complexes were obtained in an analogous manner, with the exception that CD_3OD was the lock signal of choice for low temperature work.

III.2.2. *Reaction of* bis*(phosphine)diolefin rhodium(I) complexes with hydrogen and carbon monoxide in dichloromethane.*

(A) ^{31}*P-NMR:*

A solution of *bis*(triphenyphosphine)cycloocta-1,5-dienerhodium(I) tetrafluoroborate *(86)* (30 mg, 0.036 mmol) in dichloromethane (1.8 ml) in an 8 mm NMR tube was thoroughly degassed by three freeze-thaw cycles under argon. The tube was evacuated and hydrogen and carbon monoxide (1:1 mixture) was admitted *via* a septum cap and fine needle; the tube was agitated vigorously to effect dissolution and equilibration. The ^{31}P-NMR spectrum was obtained by the method described in III.4.1. *(A)*. The effect of triethylamine (25 mg, 0.25) on the initial ^{31}P-NMR spectrum was also observed.

(B) ^{1}*H-NMR:*

A solution of *bis*(triphenylphosphine)cycloocta-1,5-dienerhodium(I) tetrafluoroborate *(86)* (10 mg, 0.012 mmol) in dichloromethane-d_2 (0.5 ml) in a 5 mm NMR tube was thoroughly degassed by three freeze-thaw cycles under argon. The tube was evacuated and hydrogen and carbon monoxide (1:1 mixture) was admitted *via* a septum cap and fine needle and the tube agitated. The ^{1}H-NMR spectrum of the complex thus obtained showed no hydridic resonances in the range δ=0 to -25 ppm.

The NMR spectra of other diolefin rhodium-phosphine complexes were obtained using similar methods to those described above.

III.3. Mechanistic Studies

III.3.1. *Synthesis of Rhodium-Phosphine Complexes*

*Hydridocarbonyl*tris*(triphenylphosphine)rhodium(I)* (143)[121]

Solutions of rhodium trichloride trihydrate (0.26 g, 1 mmol) in ethanol (20 ml), aq. formaldehyde (40% solution), and potassium hydroxide (0.8 g) in ethanol (20 ml) were added successively to a stirred boiling solution of triphenylphosphine (2.6 g, 10 mmol) in ethanol (100 ml). The mixture was boiled under reflux for 10 min, the solid collected by filtration and washed with ethanol, water, ethanol and hexane to give hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (0.82 g, 90%) as a yellow solid, m.p. 122-123° (lit.,[121] 120-122°); $\nu_{max.}$ (nujol) 2093(w), 1989(s) and 1440(s) cm^{-1}.

Hydrido(^{13}*C-carbonyl)*tris*(triphenylphosphine)rhodium(I)* (153)

A solution of chloro*tris*(triphenylphosphine)rhodium(I) *(154)* (0.4 g, 0.43 mmol) in toluene (20 ml) was stirred under an atmosphere of ^{13}C-carbon monoxide (Prochem, 92% enriched in ^{13}C) during 1 h. Ethanol (50 ml) was added, the golden-yellow precipitate collected by Craig-tube filtration, and washed with ethanol (50 ml) to give *trans-bis*-(triphenylphosphine)(^{13}C-carbonyl)chlororhodium(I) (0.25 g, 84%); $\nu_{max.}$ 1915 cm^{-1}. A mixture of this latter complex (0.25 g, 0.36 mmol), triphenylphosphine (0.375 g, 1.43 mmol) and ethanol (25 ml) was heated to 80° and a filtered solution of sodium borohydride (0.125 g, 3.29 mmol) in ethanol (15 ml) was added dropwise during 10 min. After boiling under reflux for a further 10 min the yellow complex was separated by Craig-tube filtration, washed with ethanol and hexane to give hydrido(^{13}C-carbonyl)-*tris*(triphenylphosphine)rhodium(I) *(153)* (0.336 g, 86%), m.p. 118-120° lit.,[121] 120-122°); $\nu_{max.}$ 2029 and 1891 cm^{-1}.

*Chloro*tris*(triphenylphosphine)rhodium(I)* (154)[122]

A solution of rhodium trichloride trihydrate (0.5 g, 1.91 mmol) in ethanol (20 ml) was added to a solution of triphenylphosphine (3.0 g, 11.5 mmol) in ethanol (80 ml) and the mixture boiled under reflux for 30 min. The burgundy-red solid was collected by Craig-tube filtration, washed with ether (25 ml) and dried *in vacuo* to give chloro*tris*(triphenylphosphine)rhodium(I) *(154)* (1.4 g, 80%), m.p.157-158° (lit.,[122] 157-158°)

*Hydrido*tetrakis*(triphenylphosphine)rhodium(I)* (155)[123a]

Solutions of rhodium chloride trihydrate (0.26 g, 1.0 mmol) in ethanol (20 ml) and potassium hydroxide (0.4 g, 7.1 mmol) in ethanol were added successively to a stirred refluxing solution of triphenylphosphine (2.62 g, 10 mmol) in ethanol (80 ml) and the mixture boiled under reflux for 10 min. On cooling to 30° the orange solid was collected by filtration, washed with ethanol, water and ethanol and dried *in vacuo* to give hydrido*tetrakis*(triphenylphosphine)rhodium(I) *(155)* (0.74 g, 64%); ^{1}H-NMR δ (C_6D_6) 7.0 to 7.5 (60H, mult., aromatic *H*) and -8.3 (1H, bs, Rh*H*); ^{31}P-NMR δ($PhCH_3$) 58.2, $J_{P,Rh}$ 188 Hz; $\nu_{max.}$(nujol) 2150(w), 1440(s), 1090(s), 750(s), and 700(s) cm^{-1}.

*Hydrido*tetrakis*(5-phenyl-5*H*-dibenzophosphole)rhodium(I)* (156)[123b]

Rhodium trichloride trihydrate (0.017 g, 0.065 mmol) and 5-phenyl-5*H*-dibenzophosphole *(61)* (0.38 mmol) in ethanol (4 ml) were boiled under reflux for 30 min, during which time a yellow solid was formed. Sodium borohydride (0.040 g, 1.1 mmol) was dissolved in ethanol (2 ml), the solution filtered and added to the above reaction mixture which was heated for a further 30 min. The orange solid was collected by filtration, washed with ether (10 ml) and dried *in vacuo* to give hydrido*tetrakis*(5-phenyl-

5-*H*-dibenzophosphole)rhodium(I) *(156)* (0.088 g); ^{1}H-NMR δ($CDCl_3$) 6.8 to 8.5 (52H, mult., aromatic *H*) and -10.6 (1H, mult., Rh*H*); ^{31}P-NMR δ($PhCH_3$) 27.6, $J_{P,Rh}$ 166 Hz; $\nu_{max.}$ (KBr disc) 1440(s), 750(s), 720(s), 700(m).

III.3.2. *Synthesis of Olefinic Substrates*

α-^{13}*C-Benzoic acid* (158).[165]

A mixture of ^{13}C-carbon dioxide [generated in a closed system from ^{13}C-barium carbonate (6 g, 0.030 mol) and conc. sulphuric acid] and phenylmagnesium bromide [50 ml (0.043 mol) of a 0.86 M solution in ether, prepared as previously described from magnesium turnings (3 g), bromobenzene (20 g) and ether (200 ml)] was vigorously stirred at -50°. When the uptake of carbon dioxide had ceased, the mixture was allowed to warm to 20° and water (6 ml) and conc. hydrochloric acid (6 ml) were added. The ethereal layer was separated and extracted with aq. 4 M sodium hydroxide (5 x 20 ml); the extract was acidified (conc. hydrochloric acid) and the mixture further extracted with ether (2 x 75 ml). The organic layer was separated, dried (magnesium sulphate) and solvent removed *in vacuo* to give a white solid. Recrystallization from water gave α-^{13}C-benzoic acid *(158)* (2.35 g, 64%), m.p. 122-123° (lit.,[165] 122°)

α-^{13}*C-Benzyl alcohol* (159)

A solution of ^{13}C-benzoic acid *(158)* (3.35 g, 0.028 mol) in ether (dried, 50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (2.0 g, 0.053 mol) in ether (100 ml) at 0°. The mixture was then boiled under reflux for 2 h, cooled to 0° and water (5 ml) slowly added, followed by aq. 4 M sodium hydroxide (5 ml) and water (10 ml). The suspension was filtered and solvent was removed from the filtrate *in vacuo* to leave α-^{13}C-benzyl alcohol *(159)* (2.45 g, 82%) as a yellow

oil; ^{1}H-NMR δ($CDCl_3$) 2.65 (1H, bs, O*H*), 4.55 (2H, d, $J_{C,H}$ 72 Hz, $^{13}CH_2$), 7.25 (5H, bs, aromatic *H*). The material was used without further purification.

α-^{13}*C-Benzaldehyde* (160) [126]

Nitrogen dioxide (*ca.* 10 g) was added to a solution of ^{13}C-benzyl alcohol *(159)* (2.45 g, 0.023 mol) in dichloromethane (50 ml) at -15°, and the solution allowed to warm to 20° during 3 h, and left for 12 h at 20°. The solvent was evaporated *in vacuo* and the residue dissolved in ether (50 ml), washed with aq. sodium hydrogen carbonate (50 ml) and the organic layer separated. Removal of the solvent *in vacuo* and distillation of the residue (bath temp. 70-75°/10 mm Hg) gave α-^{13}C-benzaldehyde *(160)* (1.50 g, 63%); ^{1}H-NMR δ($CDCl_3$) 7.2 to 7.9 (5H, mult., aromatic *H*) and 9.9 (1H, d, $J_{C,H}$ 87Hz, C*H*O).

α-^{13}*C-Styrene* (157)

Dimethylsulphoxide (20 ml) was added to sodium hydride (2.7 g, 50% dispersion in oil - washed thrice with petrol and dried *in vacuo*) and the mixture heated at 70° for 1 h to produce a solution of (methylsulphinyl)methyl sodium (2.8 M) in dimethylsulphoxide.[128]

(Methylsulphinyl)methyl sodium (2.7 ml, 7.5 mmol, solution in dimethylsulphoxide prepared as above) was added to methyltriphenylphosphonium bromide (3.6 g, 10 mmol) and dimethylsulphoxide (10 ml) and the mixture left for 5 min. α-^{13}C-Benzaldehyde *(160)* (0.5 g, 4.7 mmol) in 2-methylbutane (3 ml) was added and the reaction mixture stirred vigorously for 10 min, then left for 10 min. 2-Methylbutane was separated and the residue extracted further with 2-methylbutane (3 x 5 ml); the extracts were warmed (*ca.* 40°) to evaporate solvent and the residue distilled (bath temp. 30-40°/10 mm Hg) to give α-^{13}C-styrene *(157)* (0.38 g, 80%);

^{1}H-NMR $\delta(CDCl_3)$ 5.1 to 5.9 ($2\frac{1}{2}$H, mult., CH_2 and $\frac{1}{2}{}^{13}CH$), 7.3 (5H, mult., aromatic *H*) and 7.5 to 7.7 ($\frac{1}{2}$H, mult., $\frac{1}{2}{}^{13}CH$).

α-*^{13}C-Decanoic acid* (162)

A mixture of ^{13}C-carbon dioxide [generated in a closed system from ^{13}C-barium carbonate (6.0 g, 0.0303 mol) and concentrated sulphuric acid] and nonylmagnesium bromide [(0.04 mol, 60 ml of a 0.65 M solution) prepared by the procedure described for phenyl-magnesium bromide from nonyl bromide (15 g, 0.072 mol) and magnesium turnings (5 g) in ether (100 ml)] was vigorously stirred at -50°. When the uptake of carbon dioxide had ceased, the mixture was stirred for 3 h at 0°, and water (6 ml) and concentrated hydrochloric acid (6 ml) added. The organic layer was separated and extracted with 4 M sodium hydroxide (3 x 75 ml); this extract was acidified (concentrated hydrochloric acid) and further extracted with ether (2 x 75 ml) . After combining and drying the extracts over magnesium sulphate the solvent was evaporated *in vacuo* to leave α-^{13}C-decanoic acid *(162)* (5.05 g, 92%) m.p. 28.5-30° (lit.,[166] 30-31°) ^{1}H-NMR ($CDCl_3$) 0.5 to 2.0 (17H, mult., CH_2 and CH_3), 2.35 (2H, t, *J* 7 Hz $-CH_2{}^{13}CO_2H$) and 10.6 (1H, s, CO_2H).

α-*^{13}C-1-Decanol* (163).

A solution of α-^{13}C-decanoic acid *(162)* (5.05 g, 0.029 mol) in ether (50 ml) was added dropwise to a suspension of lithium aluminium hydride (2.5 g, 0.065 mol) in ether (50 ml) at 0° during 30 min. The mixture was stirred at 0° for ½ h then boiled under reflux (3 h), cooled to 0° and water (5 ml), 4 M NaOH (10 ml) and water (10 ml) added. After filtration and washing the filter-cake with ether (100 ml) the solvent was evaporated to give α-^{13}C-1-decanol *(163)* (4.6 g, *ca.* 100%) as a colourless oil; ^{1}H-NMR ($CDCl_3$) 0.8 to 2.0 (19H, mult., CH_2 and CH_3)

2.35 (1H, bs, O*H*) and 3.55 (2H, doublet t, $J_{^{13}CH}$ 140 and $J_{H,H}$ 6 Hz, $^{13}CH_2OH$). The material was used without further purification.

α-*^{13}C-1-decene* (161)[129]

A solution of α-^{13}C-1-decanol *(163)* (1.6, 0.01 mol) and hexamethylphosphorus triamide (10 ml) was heated and the fraction distilling between 170 and 225° was collected. Water (10 ml) and 2-methylbutane (50 ml) were added to the distillate and shaken; the organic layer was separated, dried (magnesium sulphate) and warmed *(ca.* 40°) to remove solvent. The residue was distilled (bath temp 80-90°/10 mm Hg, lit.,[167] 75-78°/30 mm Hg) to give α-^{13}C-1-decene (1.4 g, 60%) as a colourless liquid; ^{1}H-NMR ($CDCl_3$) 0.91 (3H, t, CH_3), 1.16 to 1.50 (12H, mult., CH_2), 2.06 (2H, mult., $CH_2C{=}C$), 5.00 (2H, mult., $J_{^{13}CH}$ *ca.* 155 Hz, $=^{13}CH_2$) and 5.81 (1H, mult., $-CH{=}^{13}CH_2$).

Bicyclo [2.2.1]*hepta-2,5-diene*-bis*(methyldiphenylphosphine)rhodium(I) tetrafluoroborate* (164)[168]

A mixture of di-μ-chloro-*bis*(bicyclo [2.2.1] hepta-2,5-diene)dirhodium(I) *(83a)* (0.288 g, 0.62 mmol), sodium fluoroborate (0.150 g, 1.36 mmol) and acetone (10 ml) was stirred for 5 min under argon. Methyldiphenylphosphine (0.500 g, 2.5 mmol) was slowly added and after stirring for a further 5 min the mixture was filtered. Ethanol (5 ml) and ether (100 ml) were added to the filtrate and the red-orange complex was collected by filtration; washing with ether (30 ml) and drying *in vacuo* gave bicyclo [2.2.1]-hepta-2,5-diene-*bis*(methyldiphenylphosphine)rhodium(I) tetrafluoroborate *(164)* (0.390 g); ^{1}H-NMR δ($CDCl_3$) 1.55 (6H, d, *J* 7 Hz, PCH_3), 1.70 (2H, bs, CH_2), 3.95 (2H, mult., C*H*), 4.45 (4H, mult., C*H*=C*H*) and 7.35 (20 H, mult., aromatic *H*).

cis-α,β-$[^2H]_2$-*Styrene* (165)

A solution of phenyacetylene (1.0 g, 9.8 mmol) and bicyclo[2.2.1]hepta-2,5-diene-*bis*(methyldiphenylphosphine)rhodium(I) tetrafluoroborate *(164)* (0.05 g, 0.073 mmol) in 2-methoxyethanol (10 ml) was thoroughly degassed by three freeze-thaw cycles under argon. The reaction vessel was evacuated, deuterium admitted and the solution was stirred at 20° until the required uptake of gas was achieved *(ca.* 230 ml in 4 h). Water (20 ml) was added and the mixture extracted with 2-methylbutane (3 x 10 ml). The extracts were combined, dried (magnesium sulphate) and warmed (*ca.* 40°) to remove solvent. The residue was distilled to give *cis*-α,β-$[^2H]_2$-Styrene *(165)* (*ca.* 0.5 ml) as the sole product. b.p. 40-50°/10 mm Hg; ^{1}H-NMR δ($CDCl_3$) 5.70(1H, t, C*H*) and 7.30(5H, mult., aromatic *H*).

Methylenecyclopropane (166)[131]

Potassium metal (4.0 g, 0.1 mol, small portions) was added to liquid ammonia (*ca.* 200 ml, dried and distilled) at -78°; the resulting dark blue solution was stirred (30 min) and iron(III) nitrate (*ca.* 0.1 g) added. Tetrahydrofuran (100 ml) was added to the dark suspension and excess ammonia allowed to evaporate during 2 h; 3-Chloro-2-methylpropene (9.0 g, 0.1 mol) in tetrahydrofuran (100 ml) was then introduced dropwise at 65° at such a rate that gas evolution occurred at a controllable rate. The distillate was passed through aq. sulphuric acid (20%, 100 ml) and collected in a trap at -80° to give methylenecyclopropane *(166)* (*ca.* 0.5 g); ^{1}H-NMR δ(C_7D_8) 0.3 (2H, mult., CH_2) and 4.8 (2H, mult., olefinic CH_2). The material was stored as a sealed sample in toluene.

III.3.3. *Preparation of Rhodium-Phosphine Species for NMR Studies*

(A) ^{31}*P-NMR:*

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (35 mg, 0.038 mmol) in toluene (1.8 ml) in an 8 mm NMR tube was thoroughly degassed by three freeze-thaw cycles under argon. The tube was evacuated, carbon monoxide admitted *via* a septum cap pierced by a fine needle and then vigorously agitated (*ca.* 1 to 2 min). The ^{31}P-NMR spectrum was obtained by loading the 8 mm tube inserted in a 10 mm tube into the NMR spectrometer. D_2O was used as the external lock signal in the space between the tubes.

(B) ^{1}*H-NMR:*

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (10 mg, 0.011 mmol) in toluene-d_8 (0.5 ml) in a 5 mm NMR tube was thoroughly degassed by three freeze-thaw cycles under argon. The tube was evacuated, and carbon monoxide admitted *via* a septum cap and fine needle. The sample was then agitated vigorously (*ca.* 1 to 2 min) before immediate recording of the NMR spectrum.

(C) ^{13}*C-NMR:*

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (35 mg, 0.038 mmol) in toluene-d_8 (1.8 ml) in an 8 mm NMR tube was prepared for NMR analysis in a manner similar to that described in III.3.3. *(A)* with the exception that ^{13}C-carbon monoxide was used in place of the ^{12}C-labelled gas.

Other samples for ^{31}P-, ^{1}H- or ^{13}C-NMR analysis were prepared analogously.

III.3.4. *Preparation of Rhodium-Phosphine Species for NMR Studies in the Presence of Olefinic Substrates*

The olefinic substrates employed in these studies were styrene, α-^{13}C-styrene *(157)*, *cis*-α,β-$[^2H]_2$-styrene *(165)*, Oct-1-ene, and α-^{13}C-dec-1-ene *(161)*.

(A) ^{31}P-NMR and ^{13}C-NMR:

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) (35 mg, 0.038 mmol) in toluene-d_8 (1.8 ml) (lock signal) in an 8 mm NMR tube was degassed by three freeze-thaw cycles under argon. The tube was evacuated and ^{13}C-carbon monoxide admitted *via* a septum cap and fine needle. The tube was agitated vigorously for 3 min and α-^{13}C-styrene *(157)* (0.1 g, 0.96 mmol) was introduced into the NMR tube *via* a microsyringe and fine needle. The tube was agitated for a further 1 min, placed inside a 10 mm tube and the NMR spectrum obtained immediately.

(B) ^{1}H-NMR:

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (10 mg, 0.011 mmol) in benzene-d_6 (0.5 ml) (lock signal) in a 5 mm NMR tube was degassed by three freeze-thaw cycles under argon. The tube was evacuated and carbon monoxide admitted *via* a septum cap and fine needle. The tube was agitated (3 min) and styrene (25 mg, 0.24 mmol, freshly obtained by preparative gas chromatography of commercial material) added; the NMR spectrum was recorded immediately.

1-Bromo-1-phenylethane

A solution of styrene (20.0 ml, 0.175 mol) in hydrobromic acid (100 ml, 45% w/v solution in glacial acetic acid) was stirred for 12 h at 20°, poured on to water (250 ml) and extracted with dichloromethane (2 x 150 ml). The extracts were combined, washed with saturated aqueous

sodium hydrogen carbonate solution (3 x 100 ml) dried (magnesium sulphate) and evaporated *in vacuo*. The residual oil was distilled to give 1-bromo-1-phenylethane (30.0 g, 84%), b.p. 95-98°/15 mm Hg (lit.,[169] 78-82°/10 mm Hg); ^{1}H-NMR δ($CDCl_3$) 2.0 (3H, d, *J* 6 Hz, CH_3), 5.15 (1H, q, *J* 6 Hz, C*H*) and 7.1 to 7.6 (5H, mult., aromatic *H*).

α-^{13}*C-2-Phenylpropanoic acid*[187]

1-Bromo-1-phenylethane (17.5 g, 0.095 mol) was added dropwise to a suspension of magnesium turnings (8.0 g, 0.33 mol) in ether (100 ml) and the mixture then boiled under reflux (1 h). Filtration under argon gave a solution of 1-phenylethylmagnesium bromide in ether (0.7 M, estimated by titration.

A mixture of ^{13}C-carbon dioxide [generated in a closed system from ^{13}C-barium carbonate (5.0 g, 25.5 mmol) and concentrated sulphuric acid] and 1-phenylethylmagnesium bromide (50 m., 0.7 M, 35 mmol, solution in ether prepared as above) was vigorously stirred at -50°. When the uptake of carbon dioxide had ceased the mixture was allowed to warm to 20° and water (6 ml) and concentrated hydrochloric acid (6 ml) were added. The organic layer was separated and extracted with 4 M sodium hydroxide (3 x 75 ml); the extract was acidified (concentrated hydrochloric acid) and the mixture extracted with ether (2 x 75 ml). The organic layer was separated, dried over magnesium sulphate and solvent removed *in vacuo* to leave a yellow oil. This was distilled giving α-^{13}C-2-phenylpropanoic acid *(187)* b.p. 80-82°/0.1 mm Hg (lit.,[170] 144-147°/11 mm Hg); ^{1}H-NMR δ($CDCl_3$) 1.50 (3H, dd, $J_{H,H}$ 6 Hz and $J_{H,C}$ 7 Hz, CH_3), 3.70 (1H, dq, $J_{H,H}$ 7 Hz and $J_{H,C}$ 7 Hz, C*H*) and 7.2 (5H, bs, aromatic *H*).

Bis*(triphenylphosphine)dichlororhodium(III) acyl complexes* (184) *and* (185)

A solution of α-^{13}C-2-phenylpropanoic acid (0.725 g, 4.84 mmol) and oxalyl chloride (0.650 g, 5.12 mmol) in toluene was stirred for 1 h. Solvent was removed by evaporation *in vacuo*, chloro*tris*(triphenylphosphine)rhodium(I) *(154)* (1.50 g, 1.62 mmol) in dichloromethane (20 ml) added and the mixture stirred for 24 h. Addition of ethanol precipitated a golden-yellow complex which was collected by filtration and dried *in vacuo*. ^{1}H- and ^{13}C-NMR showed this to be a 3:1 mixture of *bis*(triphenylphosphine)dichloro-α-^{13}C-3-phenylpropanoylrhodium(III) *(185)* ^{1}H-NMR δ($CDCl_3$) 2.65 (2H, mult., CH_2), 3.15 (2H, mult., CH_2), ^{13}C-NMR δ($CDCl_3$) 33.3 (1C, s, CH_2), 54.7 (1C, d, CH_2) and 209.9 (1C, mult., *C*O) and *bis*(triphenylphosphine)dichloro-α-^{13}C-2-phenylpropanoylrhodium(III) *(184)* ^{1}H-NMR δ($CDCl_3$) 1.11 (3H, mult., CH_3) and 4.70 (1H, mult., C*H*); ^{13}C-NMR δ($CDCl_3$) 63.5 (1C, d, *C*H) and 213.5 (1C, mult., *C*O).

III.4. Hydroformylation Studies: High and Low Pressures

Di-μ-chlorotetra(allyl)dirhodium(III) (193)[171]

Water (0.25 ml) was added to a solution of di-μ-chlorotetracarbonyl-dirhodium(I) (0.1 g, 0.26 mmol) and 3-chloropropene (0.25 ml, 3.07 mmol) in methanol (1 ml) nad the mixture left for 4 h. Collection of the yellow crystals by filtration and drying *in vacuo* gave *di*-μ-chlorotetra-(allyl)dirhodium(III) *(193)* (0.076 g, 67%), m.p. 180-185° (lit.,[171] 180-185°).

Tris*(allyl)rhodium(III)* (192)

A mixture of 3-chloropropene (0.8 g, 10.5 mmol), magnesium turnings (0.3 g, 12.3 mmol) and ether (15 ml, dried and distilled) was stirred for 3 h at 0° to give a solution of allylmagnesium chloride in ether (0.15 M, by titration).

Di-μ-chlorotetra(allyl)dirhodium(III) (0.076, 0.17 mmol) was added to a solution of allylmagnesium chloride [3 ml (0.45 mmol) of a 0.15 M solution in ether]. The resultant mixture was stirred under argon for 30 min, cooled to -40°, water (2 ml) added and shaken for 2 min. The organic layer was separated, dried over magnesium sulphate, evaporated to dryness under reduced pressure, and the residue sublimed [40-50°(bath temp)/ 0.1 mm Hg]to give *tris*(allyl)rhodium(III) *(192)* (0.055 g, 72%) m.p. 79-84° (lit.,[171] 80-85°); ^{1}H-NMR δ($CDCl_3$) 1.68 (1H, d, *J* 11.5 Hz), 2.65 (1 H, d, *J* 11.5 Hz), 2.82 (1 H, d, *J* 6.3 Hz,) 3.04 (1H, d, *J* 7.2 Hz), 4.01 (1 H, mult.,allyl C*H*)and 5.39(1 H, mult., allyl C*H*).

III.4.1. *High pressure reactions (⩾ 4 atmospheres)*

Hydroformylations employing mono- and biphosphines prepared in the course of this project were examined at the Johnson Matthey Research Centre, Sonning Common.

(A) Butadiene

Reactions involving 1,3-butadiene as substrate were performed in a thermostated Baskerville autoclave capable of operating at pressures up to *ca.* 120 atmospheres and temperatures to 150°, with a rate of stirring of 500 r.p.m. Hydrogen: carbon monoxide ratios of 1:1 were used.

1,3-butadiene (11.5 g, 0.21 mol), dicarbonyl (2,4-pentanedionato-*O,O'*)rhodium(I) (112.7 mg, 0.42 mmol) and 5-phenyl-5*H*-dibenzophosphole *(61)* (218 mg, 0.84 mmol) in toluene (150 ml) were placed in the autoclave. The solution was carefully degassed by pressurizing under nitrogen, and the autoclave then pressurized with hydrogen and carbon monoxide to 100 atm. and brought to the required temperature (100°) by an external electrical heater; stirring was then commenced. The pressure was maintained throughout the course of the reaction; after five hours the autoclave was cooled and the solution analysed by g.l.c. with reference to an authentic sample of 1,6-hexanedial.

Other experiments involving butadiene were carried out in a similar fashion.

(B) Oct-1-ene and Styrene

Reactions involving oct-1-ene and styrene were performed in a Davey minireactor capable of operating at pressures up to *ca.* 10 atmospheres and temperatures up to 150°. Stirring was maintained throughout the course of the reaction so that mass transfer between gas and solution was not rate limiting (*ca.* 1500 r.p.m). Hydrogen and carbon monoxide were supplied as 1:1 and 5:1 mixtures.

Tris(allyl)rhodium (9.9 mg, 0.044 mmol) and triphenylphosphine (23.1 mg, 0.088 mmol) were dissolved in a solution of oct-1-ene (1.0 ml) in toluene

(15.0 ml). The resulting solution, containing 300 p.p.m. rhodium, was introduced into the reactor by suction *via* a fine syringe needle. Degassing was achieved by pressurization-depressurization of the reactor three times under nitrogen. The reactor was then heated (electrically) to 100°, pressurized to 80 p.s.i. and stirring commenced. The time required for the pressure to drop by 5 p.s.i. was recorded by an automatically operated timer, after which the reactor was manually repressurized to 80 p.s.i; this procedure was repeated until the reaction was essentially complete. The reaction solution was expelled from the reactor by nitrogen pressure and analysed by g.c. with reference to authentic aldehydes.

The procedures used for other rhodium procatalysts and styrene were similar to that described above.

III.4.2. *Low pressure reactions (1 atmosphere)*

A solution of hydridocarbonyl*tris*(triphenylphosphine)rhodium(I) *(143)* (40 mg, 0.044 mmol) and styrene (0.1 ml, 0.091 g, 0.875 mmol) in toluene (2.0 ml) was degassed by three freeze-thaw cycles under argon. The apparatus was evacuated and hydrogen and carbon monoxide (1:1 mixture) was admitted and stirring commenced. Gas uptake was measured throughout the course of the reaction; a constant temperature of 28° was maintained by means of a thermostated water jacket which surrounded the reaction vessel. When the uptake of hydrogen/carbon monoxide had ceased the solution was analysed by g.c with reference to authentic samples of 2- and 3-phenylpropanal.

Analogous procedures were used for other experiments described in Chapter II. Sections 2 and 3.

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APPENDIX A

DANTE *Experiment simulation programs for a Hewlett-Packard HP 85 minicomputer*

(i) Two site system (irradiation of site 1)

```
10 DIM P(200,3),P$[33]
20 DISP "ENTER NO.OF POINTS:200
   MAX "
21 INPUT W
22 IF W>200 THEN 20
23 DISP "INPUT DATA FROM TAPE?Y
   /N"
24 INPUT R$[1,32]
25 IF UPC$(P$[1,1])="N" THEN 50
26 IF UPC$(R$[1,1])#"Y" THEN 23
27 DISP "FILE NAME?"
28 INPUT R$
29 ASSIGN# 1 TO R$
30 FOR I=1 TO W
31 READ# 1 ; P(I,1),P(I,2),P(I,
   3)
32 DISP USING 190 ; P(I,3),P(I,
   1),P(I,2)
33 NEXT I
34 GOTO 150
50 FOR I=1 TO W
60 DISP "S1(";I;")S2(";I;")TIME
   (";I;")(SECS)"
61 INPUT P(I,1),P(I,2),P(I,3)
62 NEXT I
63 DISP "DONE"
64 DISP "STORE DATA ON TAPE?"
65 INPUT R$[1,32]
66 IF UPC$(R$[1,1])="N" THEN 15
   0
67 IF UPC$(R$[1,1])#"Y" THEN 64
68 DISP "FILE NAME"
69 INPUT R$
70 CREATE R$,3,100
71 ASSIGN# 1 TO R$
72 FOR I=1 TO W
73 PRINT# 1 ; P(I,1),P(I,2),P(I
   ,3)
74 NEXT I
75 ASSIGN# 1 TO *
80 GOTO 140
140 DISP "DONE"
150 DISP "PRINT DATA:Y/N"
160 INPUT P$[1,32]
170 IF UPC$(R$[1,1])="N" THEN 24
    0
180 IF UPC$(P$[1,1])#"Y" THEN 17
    0
190 IMAGE DD DDD.5X,DDD.DD,3X,DD
    D.DD
200 PRINT "TIME(SECS)  SITE1
    SITE2"
210 FOR I=1 TO W
220 PRINT USING 190 ; P(I,3),P(I
    ,1),P(I,2)
230 NEXT I
240 CLEAR
250 DISP "RELAXATION RATES OF 1
    AND 2"
260 INPUT R1,R2
```

```
270 PRINT "R1=";R1;"R2=";R2
280 DISP "EQUIL.VALUES OF 1 AND
    2"
290 INPUT M1,M2
300 PRINT "M1=";M1;"M2=";M2
310 DISP "INITIAL VALUES OF 1 AN
    D 2"
320 INPUT I1,I2
330 PRINT "I1=";I1;"I2=";I2
340 DISP "RATE CONSTANT IN UNITS
     OF SEC-1"
350 INPUT K
360 PRINT "k=";K
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,I1,M1+.1*
    M1
470 XAXIS 0,1,0,T
480 YAXIS 0,M1/10.0,M1
481 GOSUB 3000
482 GOSUB 9000
490 PENUP
500 MOVE 0,I1
510 A=I1
511 B=I2
520 FOR X=2.5 TO N STEP 2 5
530 A=A+D1*(R1*(M1-A)-K*A+K*B*M1
    /M2)
540 B=B+D1*(R2*(M2-B)-K*B*M1/M2+
    K*A)
550 A1=A
551 B1=B
560 A1=A1+D1*(R1*(M1-A1)-K*A1+K*
    B1*M1/M2)
570 B1=B1+D1*(R2*(M2-B1)-K*B1*M1
    /M2+K*A1)
580 A2=A1
581 B2=B1
590 A2=A2+D1*(R1*(M1-A2)-K*A2+K*
    B2*M1/M2)
600 B2=B2+D1*(R2*(M2-B2)-K*B2*M1
    /M2+K*A2)
610 A3=A2
611 B3=B2
620 A3=A3+D1*(R1*(M1-A3)-K*A3+K*
    B3*M1/M2)
630 B3=B3+D1*(R2*(M2-A3)-K*B3*M1
    /M2+K*A3)
640 A=(A+2*A1+2*A2+A3)/6
650 B=(B+2*B1+2*B2+B3)/6
660 DRAW X/N*T,A
670 NEXT X
671 BEEP
```

```
711 PAUSE
720 DISP "COPY? Y/N"
721 INPUT R$[1,32]
730 IF UPC$(R$[1,1])="N" THEN 76
    0
740 IF UPC$(R$[1,1])#"Y" THEN 72
    0
745 PRINT "VARIATION OF A WITH T
    IME"
750 GRAPH
751 COPY
760 GCLEAR
770 SCALE -T/20,T+T/10,-M2/10,M2
780 XAXIS 0,1,0,T
790 YAXIS 0,M2/10,0,M2
791 GOSUB 3060
792 GOSUB 2040
800 PENUP
810 MOVE 0,I2
820 A=I1
830 B=I2
840 FOR X=2.5 TO N STEP 2.5
850 A=A+D1*(R1*(M1-A)-K*A+K*B*M1
    /M2)
860 B=B+D1*(R2*(M2-B)-K*B*M1/M2+
    K*A)
870 A1=A
880 B1=B
890 A1=A1+D1*(R1*(M1-A1)-K*A1+K*
    B1*M1/M2)
900 B1=B1+D1*(R2*(M2-B1)-K*B1*M1
    /M2+K*A1)
910 A2=A1
920 B2=B1
930 A2=A2+D1*(R1*(M1-A2)-K*A2+K*
    B2*M1/M2)
940 B2=B2+D1*(R2*(M2-B2)-K*B2*M1
    /M2+K*A2)
950 A3=A2
960 B3=B2
970 A3=A3+D1*(R1*(M1-A3)-K*A3+K*
    B3*M1/M2)
980 B3=B3+D1*(R2*(M2-B3)-K*B3*M1
    /M2+K*A3)
990 A=(A+2*A1+2*A2+A3)/6
1000 B=(B+2*B1+2*B2+B3)/6
1010 DRAW X/N*T,B
1020 NEXT X
1021 BEEP
1051 PAUSE
1060 DISP "COPY? Y/N"
1061 INPUT R$[1,32]
1070 IF UPC$(R$[1,1])="N" THEN 1
     120
1080 IF UPC$(R$[1,1])#"Y" THEN 1
     060
1090 PRINT "VARIATION OF B WITH
     TIME"
1099 GRAPH
1100 COPY
```

```
1110 GCLEAR
1120 DISP "NEW VALUES?"
1130 INPUT R$[1,32]
1140 IF UPC$(R$[1,1])="N" THEN 1
     170
1150 IF UPC$(R$[1,1])#"Y" THEN 1
     120
1160 GOTO 240
1170 DISP "END"
1180 GOTO 4020
2000 REM "PLOT CROSS"
2005 FOR I=1 TO N
2010 MOVE P(I,3),P(I,1)
2020 LABEL "+"
2025 NEXT I
2030 RETURN
2040 REM "PLOT CROSS"
2045 FOR I=1 TO N
2050 MOVE P(I,3),P(I,2)
2060 LABEL "+"
2065 NEXT I
2070 RETURN
3000 REM "LABEL1"
3010 FOR X=0 TO T STEP 1
3020 MOVE X,(-M1)/15
3030 LABEL VAL$(X)
3040 NEXT X
3050 RETURN
3060 REM "LABEL2"
3070 FOR X=1 TO T STEP 1
3080 MOVE X,(-M2)/15
3090 LABEL VAL$(X)
4000 NEXT X
4010 RETURN
4020 END
```

(ii) Three site system (irradiation of site 1)

```
 10 DIM P(50,4),R$[32]
 20 DISP "ENTER NO.OF POINTS:50
    MAX."
 30 INPUT W
 40 IF W>50 THEN 20
 50 DISP "INPUT DATA FROM TAPE?Y
    /N"
 60 INPUT R$[1,32]
 70 IF UPC$(R$[1,1])="N" THEN 17
    0
 80 IF UPC$(R$[1,1])#"Y" THEN 50
 90 DISP "FILE NAME?"
100 INPUT R$
110 ASSIGN# 1 TO R$
120 FOR I=1 TO W
130 READ# 1 ; P(I,1),P(I,2),P(I,
    3),P(I,4)
140 DISP USING 400 ; P(I,4),P(I,
    1),P(I,2),P(I,3)
150 NEXT I
160 GOTO 360
170 FOR I=1 TO W
180 DISP "S1(";I;")S2(";I;")S3("
    ;I;")TIME(";I;")(SECS)"
190 INPUT P(I,1),P(I,2),P(I,3),P
    (I,4)
200 NEXT I
210 DISP "DONE"
220 DISP "STORE DATA ON TAPE?"
230 INPUT R$[1,32]
240 IF UPC$(R$[1,1])="N" THEN 3E
    0
250 IF UPC$(R$[1,1])#"Y" THEN 22
    0
260 DISP "FILE NAME"
270 INPUT R$
280 CREATE R$,4,200
290 ASSIGN# 1 TO R$
300 FOR I=1 TO W
310 PRINT# 1 ; P(I,1),P(I,2),P(I
    ,3),P(I,4)
320 NEXT I
330 ASSIGN# 1 TO *
340 GOTO 350
350 DISP "DONE"
360 DISP "PRINT DATA:Y/N"
370 INPUT R$[1,32]
380 IF UPC$(R$[1,1])="N" THEN 4E
    0
390 IF UPC$(R$[1,1])#"Y" THEN 76
    0
400 IMAGE DD.DDD,1X,DDD.DD,1X,DD
    D.DD,1X,DD.DDD
410 PRINT "T(SEC) SITE1 SITE2 SI
    TE3"
420 FOR I=1 TO W
430 PRINT USING 400 ; P(I,4),P(I
    ,1),P(I,2),P(I,3)
440 NEXT I
450 CLEAR
```

```
460 DISP "RELAXATION RATES OF 1
    ,2 AND 3"
470 INPUT R1,R2,R3
480 PRINT "R1=";R1;"R2=";R2;"R3=
    ";R3
490 DISP "EQUIL.VALUES OF 1,2 AN
    D 3"
500 INPUT M1,M2,M3
510 PRINT "M1=";M1;"M2=";M2;"M3=
    ";M3
520 DISP "INITIAL VALUES OF 1,2
    AND 3"
530 INPUT I1,I2,I3
540 PRINT "I1=";I1;"I2=";I2;"I3=
    ";I3
550 DISP "RATE CONSTANTS IN UNIT
    S OF SEC-1 AB THEN BC THEN A
    C"
560 INPUT K1,K2,K3
570 PRINT "K1=";K1;"K2=";K2;"K3=
    ";K3
580 DISP "TOTAL TIME IN SECS"
590 INPUT T
600 PRINT "TOTAL TIME=";T
610 DISP "NO.OF INCREMENTS"
620 INPUT N
630 PRINT "NO.OF INCREMENTS=";N
640 D1=T/N
650 GCLEAR
660 PENUP
670 SCALE -T/20,T+T/20,I1,M1+.1*
    M1
680 XAXIS 0,1,0,T
690 YAXIS 0,M1/10,0,M1
700 GOSUB 2190
710 GOSUB 2010
720 PENUP
730 MOVE 0,I1
740 A=I1
750 B=I2
760 C=I3
770 FOR X=2.5 TO N STEP 2.5
780 A=A+D1*(R1*(M1-A)-K1*A+K1*B*
    M1/M2-K3*A+K3*C*M1/M3)
790 B=B+D1*(R2*(M2-B)-K1*B*M1/M2
    +K1*A+K2*C*M2/M3-K2*B)
800 C=C+D1*(R3*(M3-C)-K2*C*M2/M3
    +K2*B+K3*A-K3*C*M1/M3)
810 A1=A
820 B1=B
830 C1=C
840 A1=A1+D1*(R1*(M1-A1)-K1*A1+K
    1*B1*M1/M2-K3*A1+K3*C1*M1/M3
    )
850 B1=B1+D1*(R2*(M2-B1)-K1*B1*M
    1/M2+K1*A1+K2*C1*M2/M3-K2*B1
    )
860 C1=C1+D1*(R3*(M3-C1)-K2*C1*M
    2/M3+K2*B1+K3*A1-K3*C1*M1/M3
    )
```

```
870  A2=A1
880  B2=B1
890  C2=C1
900  A2=A2+D1*(R1*(M1-A2)-K1*A2+K
     1*B2*M1/M2-K3*A2+K3*C2*M1/M2
     )
910  B2=B2+D1*(R2*(M2-B2)-K1*B2*M
     1/M2+K1*A2+K2*C2*M2/M3-K2*B2
     )
920  C2=C2+D1*(R3*(M3-C2)-K2*C2*M
     2/M3+K2*B2+K3*A2-K3*C2*M1/M2
     )
930  A3=A2
940  B3=B2
950  C3=C2
960  A3=A3+D1*(R1*(M1-A3)-K1*A3+K
     1*B3*M1/M2-K3*A3+K3*C3*M1/M2
     )
970  B3=B3+D1*(R2*(M2-B3)-K1*B3*M
     1/M2+K1*A3+K2*C3*M2/M3-K2*B3
     )
980  C3=C3+D1*(R3*(M3-C3)-K2*C3*M
     2/M3+K2*B3+K3*A3-K3*C3*M1/M3
     )
990  A=(A+2*A1+2*A2+A3)/6
1000 B=(B+2*B1+2*B2+B3)/6
1010 C=(C+2*C1+2*C2+C3)/6
1020 DRAW N/N*T,A
1030 NEXT N
1040 BEEP
1050 PAUSE
1070 DISP "COPY? Y/N"
1080 INPUT R$[1,32]
1090 IF UPC$(R$[1,1])="N" THEN 1
     140
1100 IF UPC$(R$[1,1])#"Y" THEN 1
     070
1110 PRINT "VARIATION OF A WITH
     TIME"
1120 GRAPH
1130 COPY
1140 GCLEAR
1150 SCALE -T/20,T+T/10,-M2/10,M
     2
1160 XAXIS 0,1,0,T
1170 YAXIS 0,M2/10,0,M2
1180 GOSUB 2050
1190 GOSUB 2070
1200 PENUP
1210 MOVE 0,I2
1220 A=I1
1230 B=I2
1240 C=I3
1250 FOR N=2.5 TO N STEP 2.5
1260 A=A+D1*(R1*(M1-A)-K1*A+K1*B
     *M1/M2-K3*A+K3*C*M1/M2)
1270 B=B+D1*(R2*(M2-B)-K1*B*M1/M
     2+K1*A+K2*C*M2/M3-K2*B)
1280 C=C+D1*(R3*(M3-C)-K2*C*M1/M
     3+K2*B+K3*A-K3*C*M1/M3)
```

```
1290 A1=A
1300 B1=B
1310 C1=C
1320 A1=A1+D1*(R1*(M1-A1)-K1*A1+
     K1*B1*M1/M2-K3*A1+K3*C1*M1/
     M3)
1330 B1=B1+D1*(R2*(M2-B1)-K1*B1*
     M1/M2+K1*A1+K2*C1*M2/M3-K2*
     B1)
1340 C1=C1+D1*(R3*(M3-C1)-K2*C1*
     M2/M3+K2*B1+K3*A1-K3*C1*M1/
     M3)
1350 A2=A1
1360 B2=B1
1370 C2=C1
1380 A2=A2+D1*(R1*(M1-A2)-K1*A2+
     K1*B2*M1/M2-K3*A2+K3*C2*M1/
     M3)
1390 B2=B2+D1*(R2*(M2-B2)-K1*B2*
     M1/M2+K1*A2+K2*C2*M2/M3-K2*
     B2).
1400 C2=C2+D1*(R3*(M3-C2)-K2*C2*
     M2/M3+K2*B2+K3*A2-K3*C2*M1/
     M3)
1410 A3=A2
1420 B3=B2
1430 C3=C2
1440 A3=A3+D1*(R1*(M1-A3)-K1*A3+
     K1*B3*M1.M2-K3*A3+K3*C3*M1/
     M3)
1450 B3=B3+D1*(R2*(M2-B3)-K1*B3*
     M1/M2+K1*A3+K2*C3*M2/M3-K2*
     B3)
1460 C3=C3+D1*(R3*(M3-C3)-K2*C3*
     M2/M3+K2*B3+K3*A3-K3*C3*M1/
     M3)
1470 A=(A+2*A1+2*A2+A3)/6
1480 B=(B+2*B1+2*B2+B3)/6
1490 C=(C+2*C1+2*C2+C3)/6
1500 DRAW X/N*T,B
1510 NEXT X
1511 DISP "COPY? Y/N"
1512 INPUT R$[1,32]
1513 IF UPC$(R$[1,1])="N" THEN 1
     518
1514 IF UPC$(R$[1,1])<>"Y" THEN 1
     512
1515 PRINT "VARIATION OF B WITH
     TIME"
1516 GRAPH
1517 COPY
1518 GCLEAR
1520 SCALE -T/20,T+T/10,-M3/10,M
     3
1522 XAXIS 0,1,0,T
1524 YAXIS 0,M3/10,0,M3
1526 GOSUB 2301
1528 GOSUB 2130
1530 PENUP
1550 MOVE 0,13
```

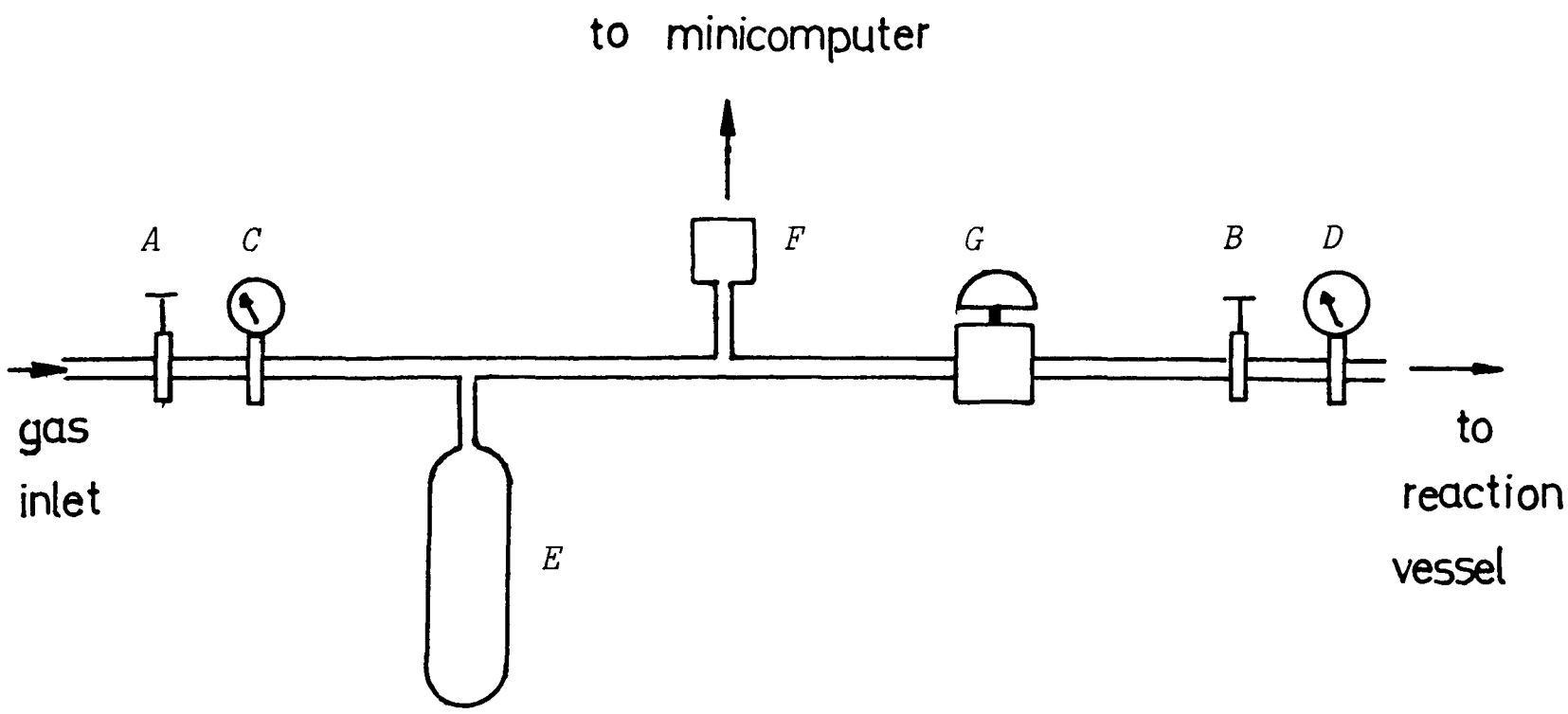
APPENDIX B

APPENDIX B

Automatic Gas-uptake measurement device

(i) Equipment

In order to facilitate kinetic measurements, an automatic gas-up-take measurement device was assembled, schematically shown below.



The main components are

(a) Gas taps *(A* and *B)*, obtained from Hoke Ltd.,

(b) Pressure gauges *(C* and *D)* (0-25 psi) and pressure reservoir *(E)*, (500 ml capacity), from Air Products Ltd.,

(c) Pressure-transducer *(F)* (0-30 psi), operating with a nine volt stabilized electrical supply, from Penny and Giles Ltd.,

(d) Pressure-limiting valve *(G)*, model L-15 from Hale-Hamilton Ltd.,

(e) One quarter inch O.D copper-tubing and gas-tight connectors (Hoke Ltd.).

The device is operated as outlined below. With taps *A* and *B* open, the system is purged with hydrogen and carbon monoxide (1:1 mixture) *via* the reaction vessel. Tap *B* is then closed, the system pressurized to *ca.* 25 psi and Tap *A* closed. Tap *B* is then reopened and stirring in the reaction vessel commenced. Pressure in the reaction is limited to atmospheric plus 2 psi (adjustable) by valve *G*. Thus the gas consumed in the course of the reaction is compensated for by a corresponding drop in pressure between tap *A* and valve *G*. Monitoring of the residual pressure between these points by pressure-transducer *F* allows the uptake of gas to be calculated. Automatic data collection is achieved by linking the pressure-transducer to a mini-computer (Hewlett-Packard model HP-85) *via* a digital to analogue interface (Microlink). Computer operating programs which govern data acquisition, graph-plotting and datal storage-retrieval were compiled by the author and are recorded subsequently.

Initial studies using the apparatus with the quantities of substrate, catalyst and solvent described for other low-pressure hydroformylations in Chapter II, Section 4 showed that gas uptake could be measured, but the digital resolution (1 point per 4 ml of gas uptake) was not sufficient for accurate analytical measurements. At the time of writing, a new

smaller volume pressure reservoir C is awaited; this will enable gas volume changes of 1 ml or less to be measured accurately.

(ii) Operating program for automatic data collection employing a Hewlett-Packard (HP 85) minicomputer

```
 10 DIM A(500,2)
 11 Y=1 @ N=2
 15 V1=7
 20 DISP "SECONDARY ADDRESS"
 30 INPUT V2
 40 DISP "TIME INTERVAL (SECS)" _
 50 INPUT Z
 60 G=Z*1000
 70 DISP "HOW MANY READINGS (MAX
    IMUM 500)"
 80 INPUT X
 90 IF X>500 THEN 70
100 FOR S=0 TO X
110 SEND 7 ; UNL TALK V1 SCG V2
    MLA
120 ENTER 7 USING "#,B" ; W
121 WAIT G
125 T=S*Z
130 DISP "TIME=";T;"SECS   READI
    NG=";W
131 A(S,1)=W
132 A(S,2)=T
140 NEXT S
144 GOTO 180
145 DISP "DO YOU WANT A PLOT Y/N
    "
146 INPUT L
147 ON L GOTO 900,150
150 DISP "STORE DATA ON TAPE Y/N
    "
160 INPUT L
170 ON L GOTO 1500,2000
180 DISP "PRINT DATA Y/N"
190 INPUT L
200 ON L GOTO 210,145
210 DISP @ PRINT "TIME(MINS)
             READING"
220 FOR S=0 TO X
230 DISP @ PRINT "      ";A(S,2);
    "                 ";A(S,1)
240 NEXT S
250 GOTO 145
900 CLEAR
910 SCALE -T/5,T+T/5,-20,260
911 T=Z*X
912 IF T<=10 THEN 915 ELSE 913
913 IF T>10 THEN 917 ELSE 914
914 IF T>=100 THEN 917
915 D=1
916 GOTO 920
917 D=10
918 GOTO 920
919 D=100
920 XAXIS 0,D,0,T
930 YAXIS 0,10,0,260
940 FOR S=0 TO X
950 PLOT A(S,2),A(S,1)
960 NEXT S
990 FOR F=0 TO T STEP D
995 MOVE F -20
```

```
1000 LABEL VAL$(F)
1010 NEXT F
1030 FOR J=0 TO 250 STEP 50
1040 MOVE -T/6,J
1050 LABEL VAL$(J)
1060 NEXT J
1065 WAIT 5000
1070 DISP "DO YOU WANT A COPY Y/
     N"
1080 INPUT L
1090 ON L GOTO 1200,150
1200 GRAPH @ COPY
1215 GOTO 150
1500 DISP "WHAT IS FILE NAME"
1510 INPUT L$
1520 CREATE L$,S,X*8
1530 ASSIGN# 1 TO L$
1540 FOR S=0 TO X
1550 PRINT# 1,S+1 ; A(S,1),A(S,2
     )
1560 NEXT S
1570 ASSIGN# 1 TO *
1580 DISP "DONE"
1590 GOTO 2000
2000 DISP "END"
2010 END
```

(iii) Data retrieval from tape-cassette

```
  10 DIM A(500,2)
  20 DISP "FILE NAME"
  30 INPUT L$
  40 ASSIGN# 1 TO L$
  50 DISP "NO  OF READINGS"
  60 INPUT L
  70 FOR S=0 TO L
  80 READ# 1,S+1 ; A(S,1),A(S,2)
  90 DISP "READING=";A(S,1);"TIME
     =",A(S,2);"SECS"
  95 NEXT S
 100 END
```