THE CARBONYLATION OF ALLYLIC HALIDES

Marc J. Payne

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at the
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The Carbonylation of Allylic Halides

A thesis presented for the degree of
Doctor of Philosophy
to the
University of St. Andrews
on the 21st October 1996
by
Marc J. Payne B. Sc. (Hons)

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To Fiona,
Mam and Dad
and
Mamgi and Grandad

"So little done, so much to do."

C.J. Rhodes (1853-1902)

CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

EXPERIMENTAL

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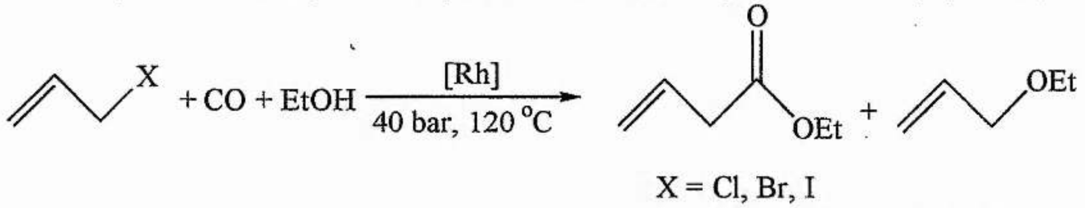
Finally I would like to thank my Mum and Dad for all the encouragement, financial assistance and help over the past seven years whilst I've been at university.

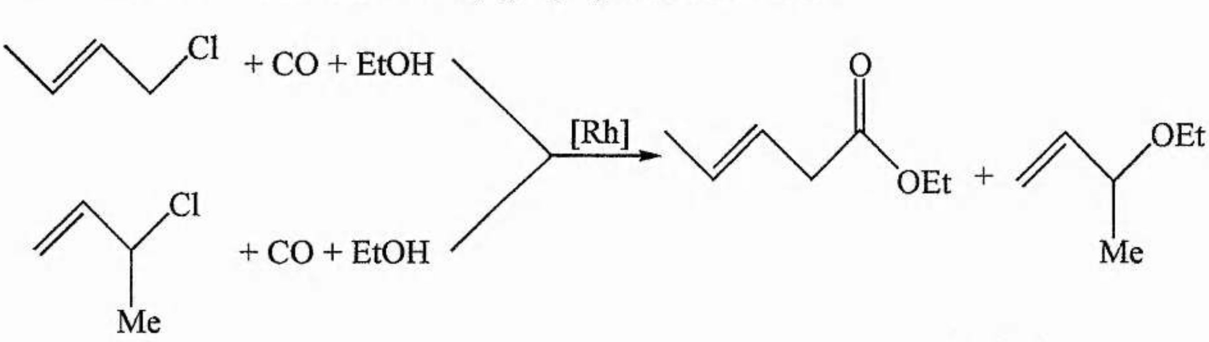
ABSTRACT

$[RhCl(CO)(PEt_3)_2]$ or a compound prepared *in situ* from $[Rh_2(OAc)_4]$ and PEt_3 have been shown to be active catalysts for the carbonylation of allylic halides under relatively mild conditions (Equation 1).



Equation 1

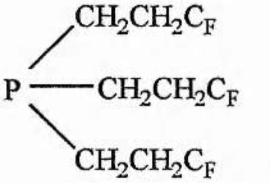
This reaction is of considerable significance since it is a rare example of a system in which C-Cl bonds can be carbonylated using a rhodium based system. The reaction occurs in the absence of added base and there is little isomerisation of the double bond when forming the ester. Using either 3-chlorobut-1-ene or 1-chlorobut-2-ene, the products obtained are identical (Equation 2). The oxidative addition of 1-chlorobut-2-ene occurs *via* an S_N2 mechanism whereas an S_N2' mechanism operates for the 3-chlorobut-1-ene because of the steric effects of the methyl group adjacent to the chlorine.



Equation 2

Extensive mechanistic studies have been carried out and many of the intermediates have been characterised using multinuclear variable temperature, high pressure NMR and high pressure IR as well as isolation of the intermediates. The oxidative addition and migratory insertion complexes have both been characterised using the above methods enabling the mechanism of the carbonylation reaction to be elucidated.

Supercritical carbon dioxide has been used to replace ethanol as the solvent to increase the concentration of carbon monoxide in the solution in an attempt to achieve a greater ester:ether ratio. However, catalyst solubility was a problem in these reactions. In an attempt to solve this problem phosphine ligands containing organo-fluorine groups were investigated.



$$P(CH_2CH_2C_F)_3$$

Where $C_F = -(CF_2)_5CF_3$

With the fluorinated groups present on the phosphine ligands the rhodium complex was soluble in the supercritical carbon dioxide. The ethylene spacer between the phosphorus atom and the fluorinated chain ensured that the fluorinated phosphines had a similar basicity to that of triethylphosphine. However, only low yields were obtained from the catalytic reactions possibly due the failure of the supercritical carbon dioxide to stabilise the ionic intermediates of the oxidative addition reaction.

CHAPTER 1

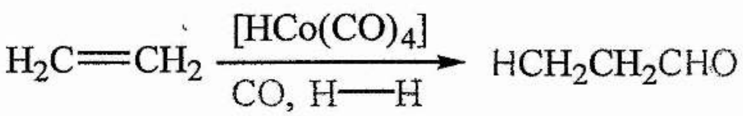
1. INTRODUCTION

Carbon monoxide is fast becoming one of the most versatile molecules in organic synthesis. A few years ago it was only considered as a petrochemical precursor. It was, and still is, used for methanol synthesis, Fischer-Tropsch synthetic gasoline production, acetic acid and oxo chemistry. However, carbon monoxide is today being used for fine chemical manufacture and can be considered as something other than just a raw-material for petrochemicals.

By choosing the correct conditions, carbon monoxide can react with a wide range of substrates to give many organic functional groups. However, by itself carbon monoxide is fairly unreactive and will not react without the assistance of a catalyst to activate the molecule. These catalysts are usually transition metal based and allow carbon monoxide to be brought into the reaction, often under mild conditions, by complexing with and thus activating it. With careful thought these catalysts can be 'engineered' to give optimum selectivity, rate and yield by careful selection of the metal and the ligands around it.

Carbonylation can be defined as "the reaction of an organic or organometallic intermediate compound with carbon monoxide."[1]

The first homogeneous transition metal catalysed carbonylation reaction was discovered accidently by Otto Roelen in 1938 during his work on ethene production from synthesis gas using a Th/Co oxide catalyst (Fischer-Tropsch process).[2] [3] He found that addition of carbon monoxide and hydrogen to ethene led to the formation of propanal in high yield (figure 1.1).



$$H_2C{=}CH_2 \xrightarrow[CO,\ H{-}H]{[HCo(CO)_4]} HCH_2CH_2CHO$$

(fig. 1.1)

The reaction was named oxonation (renamed later as **hydroformylation**) as hydrogen (blue) was added to one end of the double bond and a formyl group (red) was added to the other. Roelen suggested that this new process might be a homogeneous reaction catalysed by cobalt tetracarbonyl hydride [$HCo(CO)_4$], which had only recently been discovered. From that discovery until the present day carbonylation chemistry has been almost totally dominated by homogeneously catalysed processes.

For 25 years after this discovery there was not much advancement in the field of homogeneously catalysed reactions. The temperatures and pressures were high and the catalysts were very toxic, volatile and unstable ([$Ni(CO)_4$], [$Fe(CO)_5$] or [$HCo(CO)_4$]) giving a mixture of products requiring separation rather than just one or two products.

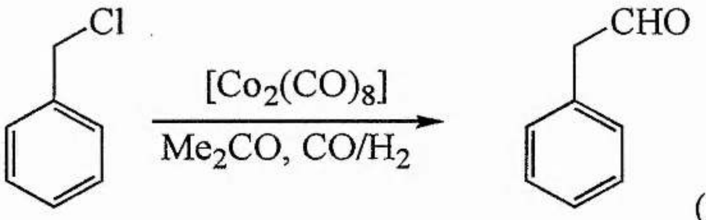
The 1960's, however, produced the discovery of palladium or rhodium based organophosphine complexes which are stable and extremely active catalysts. These catalysts work at much lower temperatures and pressures than the older catalytic systems. Only very small quantities of the stable catalyst precursors, which are converted to the active catalysts *in situ*, needed to be added to the system for the reaction to proceed quickly and efficiently. The reaction conditions, work-up procedures and functional group tolerances have all been investigated for these new catalysts. There has also been much work on the application of new techniques such as phase transfer applied to existing catalytic systems based on nickel, cobalt and iron.[4] More recently the use of supercritical solvents, such as CO_2 or ethene, to replace existing solvent systems or act as co-solvents has been utilised for carbonylation reactions.[5] Thus catalytic carbonylation chemistry, once the realm of industrial chemists, is now being used extensively by the synthetic organic chemists as part of their multistage syntheses where they offer better yields, less extreme reaction conditions and easier work-ups than can be afforded by the alternative stoichiometric organic reactions.

There are now many examples of carbonylation reactions involving a huge number of functional groups, which are assisted by homogeneous transition metal catalysts. The following review will be concerned only with the carbonylation of halocarbons, specifically allylic and benzylic halides.

1.1 Carbonylation of Halocarbons to Yield Aldehydes

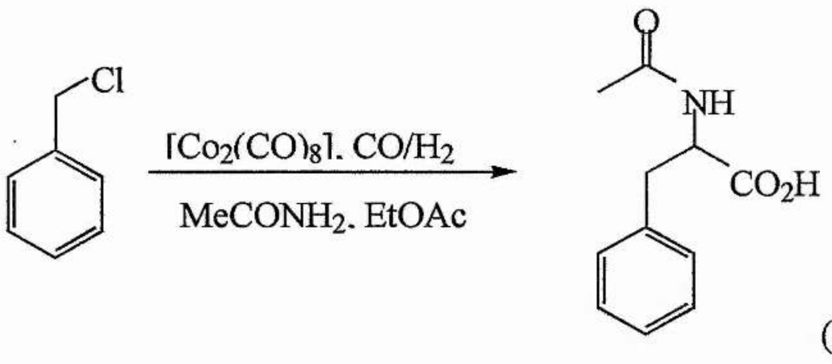
The carbonylation of allylic or benzylic halides to yield aldehydes has not been widely studied. The areas of research have tended to concentrate more on hydroformylation of alkenes and of simpler halocarbons like alkyl and aryl halides.

A Hungarian patent by L. Marko *et al.* from 1963 stated that 2-phenylethanal could be synthesised from benzyl chloride and synthesis gas using dicobalt octacarbonyl as the catalyst precursor (figure 1.2).[6]



(fig. 1.2)

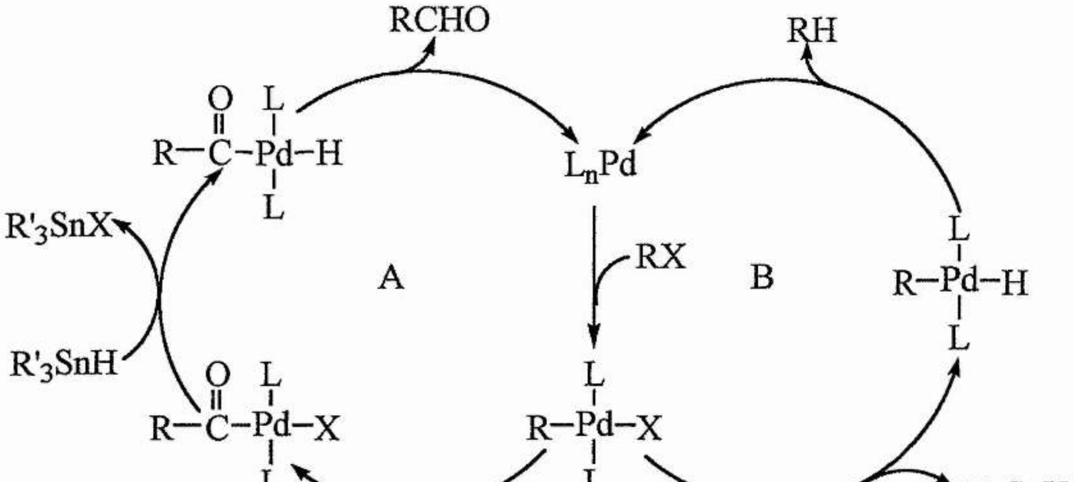
The reaction took place at 120 °C under 140 bar CO/H_2 for 4 hours producing $PhCH_2CHO$ in 41% yield. It was not stated what the other 59% of the products from the reaction were. DMF improved the rate of the reactions (52.2% after 20 minutes) but using acetamide, an N-acyl-α-amino acid was produced in 56.8% yield in 20 minutes at 200 bar and 100 °C (figure 1.3). [7]



(fig. 1.3)

Under much less forcing conditions, benzyl bromide was converted into 2-phenylethanal in 36% yield using $[Pd(PPh_3)_4]$ and poly(methylhydrosiloxane) (PHMS) as the hydrogen donor. The reaction was carried out under 3 bar CO at 80 °C with tribenzyl amine as the base.[8]

Another reaction of this type used for the carbonylation of allylic and benzylic halides, amongst other halocarbons, uses [Pd(PPh$_3$)$_4$] as the catalyst but the PHMS is replaced as the hydrogen donor by tributyl tin hydride (cycle A).[9] The reaction conditions were 50 °C, 1-3 bar CO and 2.5-3.5 hour reaction times. The use of tributyl tin hydride meant that no base was required as no hydrogen halide was produced in the reaction. However, the tributyl tin hydride needed to be added slowly *via* a syringe pump to avoid direct reduction of the halides to give the corresponding hydrocarbons (cycle B) (figure 1.4). The allylic chlorides and bromides tended to undergo this reaction readily with the chlorides generally giving better selectivities than the bromides.

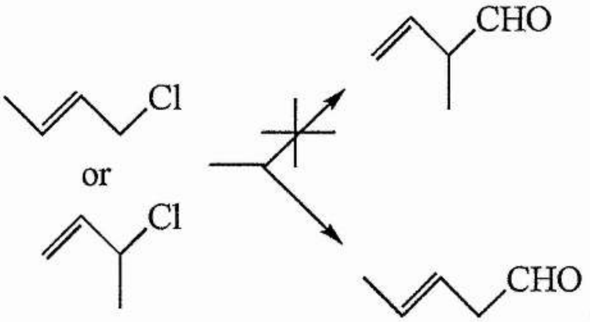


R= allylic, benzylic or other L= PPh$_3$ or dba

X= Cl, Br or I

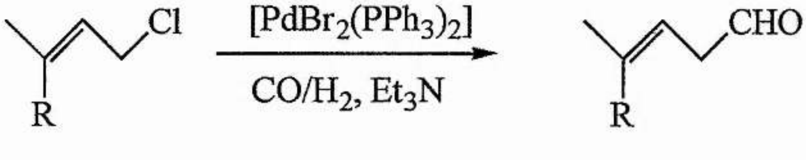
(fig. 1.4)

Within an unsymmetrical allylic system the formylation reaction occurred regioselectively at the less hindered position, thus retaining the geometry of the double bond. The formylation of 3-chlorobut-1-ene and 1-chlorobut-2-ene demonstrated this regioselectivity as no 2-methyl but-3-enal was observed (figure 1.5).



(fig. 1.5)

β,γ-unsaturated aldehydes can also be directly prepared from the corresponding allylic halides using dibromobis(triphenylphosphine) palladium (II) as the catalyst for 24 hours at 80 °C under 80 bar syn-gas (figure 1.6).[10]



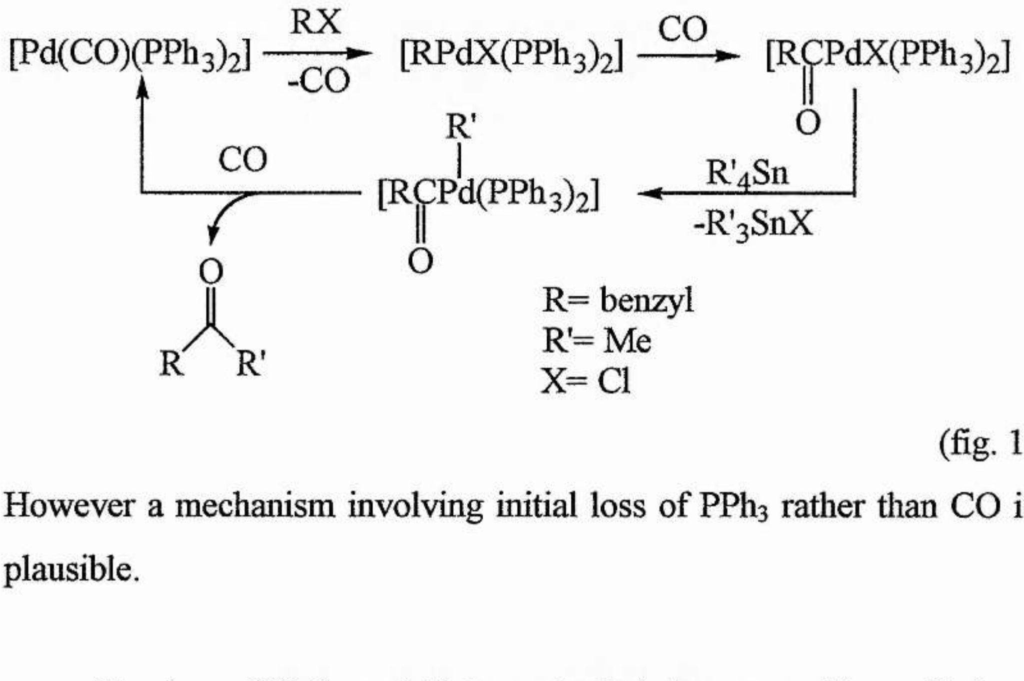
X=Cl or Br
R= H, Me or $(H_2C)_2HC{=}CMe_2$

(fig. 1.6)

1.2 Carbonylation of Halocarbons to Yield Ketones

The carbonylation reactions of allylic and benzylic halides to give ketones are very similar to those that produce aldehydes, the main difference being that the hydride or proton sources are replaced by carbanions or carbocations to give symmetrical, unsymmetrical or cyclic ketones *via* the formation of two C-C bonds under catalytic conditions.

The first catalytic carbonylation of organic halides to give unsymmetrical ketones was reported by M. Tanaka.[11] Benzyl chloride could be carbonylated using [PhPdI(PPh_3)$_2$] as the catalyst precursor with CO at 30 bar, Me_4Sn and HMPA at 120 °C to give 1-phenylpropan-2-one in 86% yield. The reaction was thought to proceed by the mechanism shown in figure 1.7.



(fig. 1.7)

However a mechanism involving initial loss of PPh_3 rather than CO is also plausible.

Tanaka and Kobayashi later extended the range of benzylic bromides that could be carbonylated to include α-methyl benzyl bromides.[12] The catalytic systems used were [$PdCl_2$(PPh_3)$_2$] or [$PdCl_2$($AsPh_3$)$_2$] with Me_4Sn and CO at a lower pressure of 20 bar in HMPA. The [$PdCl_2$($AsPh_3$)$_2$] system gave the best selectivity towards the methyl ketones despite having a lower catalytic activity. The side products for the reactions were styrenes obtained *via* β-hydride elimination.

Aryl benzyl ketones can be selectively prepared by reaction of aryl iodides and benzyl chlorides in the presence of a stoichiometric amount of zinc-copper couple and a catalytic amount of tetrakis(triphenylphosphine) palladium (0) under an atmospheric pressure of CO (figure 1.8).[13]

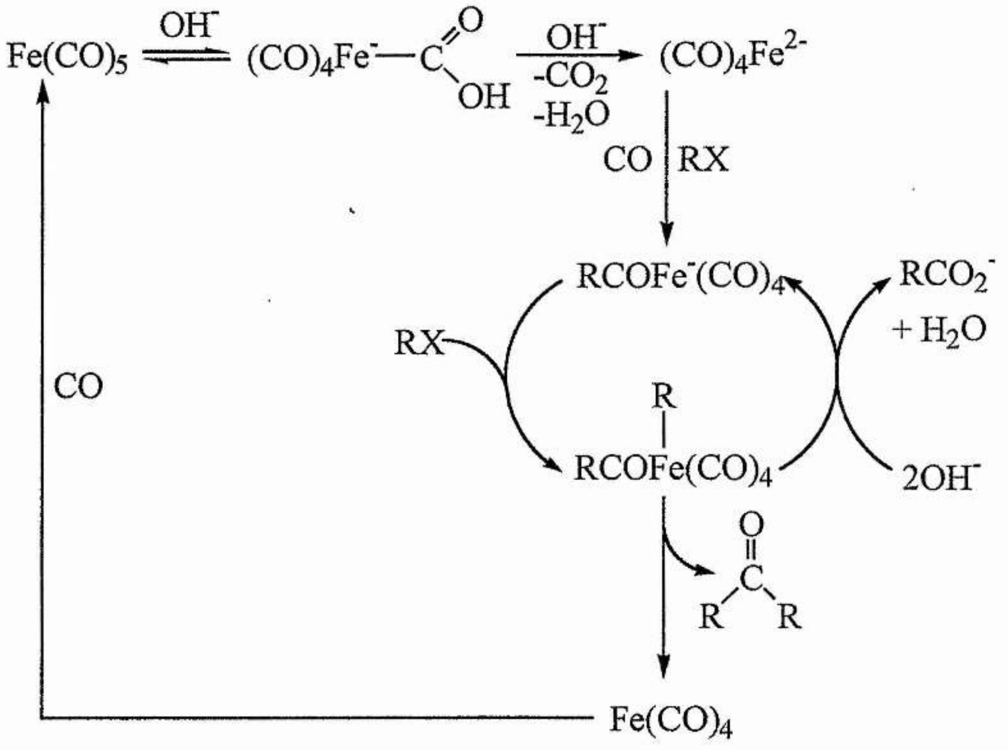
$$\mathrm{ArI + Ar'CH_2Cl \xrightarrow[\text{Zn-Cu, THF}]{[Pd(PPh_3)_4],\ CO} ArCOCH_2Ar' + ArCH_2Ar' + Ar'CH_2CH_2Ar'}$$

Ar= C_6H_5 or 4-MeOC_6H_4
Ar'= C_6H_5 or 4-ClC_6H_4

(fig. 1.8)

The mechanism of the reaction was thought to be similar to the one shown in figure 1.7 but the tetramethyl tin had been replaced by dibenzylzinc, produced *in situ* from the zinc-copper couple and benzyl chloride. Aryl iodides with electron donating substituents gave better yields of the unsymmetrical ketones. Under the same conditions 3-bromoprop-1-ene did not give any of the unsymmeterical ketone but gave a small amount of the cross coupling product, allyl benzene.

In a phase-transfer carbonylation utilising pentacarbonyliron as the catalyst, benzyl bromide was transformed into 1,3-diphenylpropan-2-one or phenylacetic acid.[14, 15] Selectivity towards formation of the ketone or the acid was dependent upon the aqueous concentration of the hydroxide anion, stirring speed, temperature and CO pressure. A simplified version of the mechanism is shown in figure 1.9.



$R = C_6H_5CH_2$
$X = Br$

(fig. 1.9)

In earlier work by Collman *et al.* and Cooke Jr. *et al.* it was shown that the initial alkylation of the tetracarbonyl ferrate (II) could be carried out by primary alkyl bromides and iodides (also primary and secondary alkyl tosylates).[16, 17] However the reduced nucleophilicity of the monoanionic intermediate meant that only highly reactive alkylating agents (e.g. benzyl halides) would be effective in the second step. Thus it could be possible to produce a mixture of unsymmetrical as well as symmetrical ketones *via* the cycle proposed by des Abbayes *et al.* e.g. by placing a primary alkyl or aryl halide into the reaction.

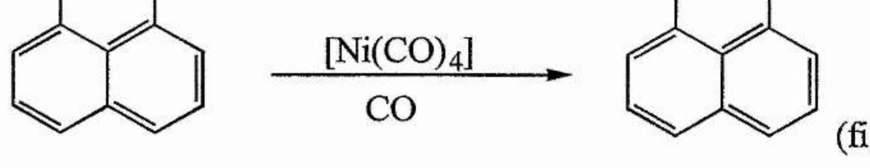
des Abbayes *et al.* showed that production of the ketone was favoured by: i) low aqueous concentration of hydroxide

- ii) an inert atmosphere (although reaction was then not catalytic)
- iii) a low stirring speed
- iv) an increase in temperature.

Conversely, formation of the acid was favoured by:

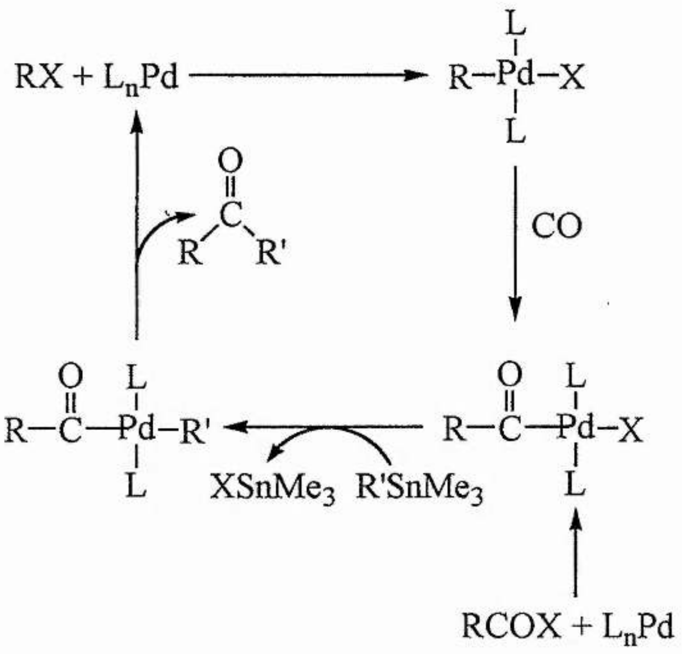
- i) a low $Fe(CO)_5$ / RX ratio
- ii) presence of carbon monoxide
- iii) an excess of hydroxide in the aqueous phase
- iv) a high stirring speed.

Carbonylation of 1,8-bis(bromomethyl)naphthalene, a dibenzyl naphthalene, with $[Ni(CO)_4]$ at 50-60 °C in acetonitrile for 3 hours yielded 2,3-dihydrophenalen-2-one in 20-40% yield (figure 1.10).[18]

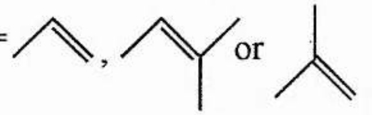


(fig. 1.10)

Unsymmetrical diallyl ketones can be synthesised *via* coupling of allylic chlorides and bromides with allyltin reagents under 3-6 bar CO using a palladium catalyst (figure 1.11).[19] The process is similar to the palladium catalysed coupling of acid chlorides and allyltin reagents to form unsymmetrical diallyl ketones.[20]



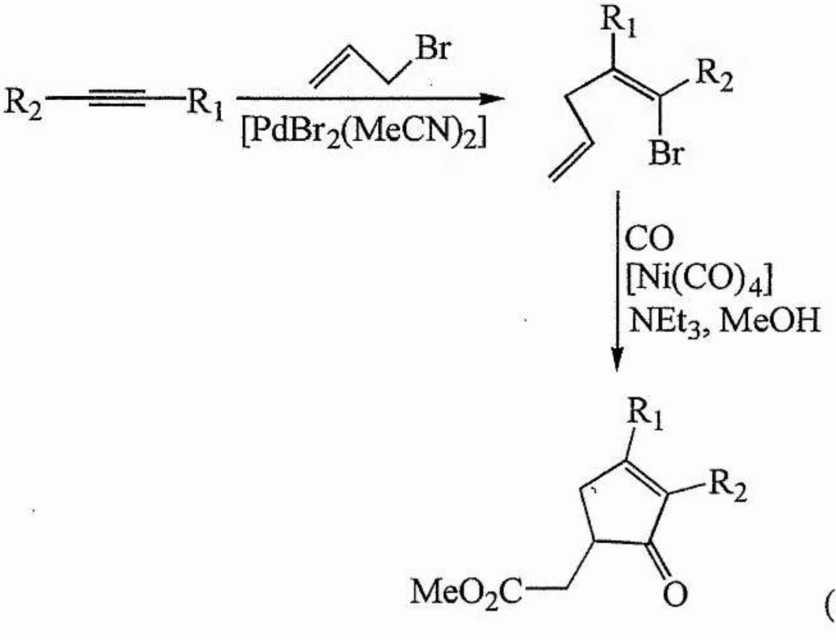
X= Cl or Br
R= various straight chain and cyclic allylic groups

R'=  L= PPh_3

(fig. 1.11)

It was found that the optimum palladium to PPh_3 ratio was 1:2 which gave up to 100% conversion of the allyltrimethyltin and up to 62% yield of the desired unsymmetrical diallylic ketone. The major side product in the reactions involving allyltrimethyltin was from carbonylative homocoupling to produce symmetrical diallylketone. In some reactions the yield of the homocoupled product approached 30% with consumption of as much as 60% of the tin reagent by this pathway, thus severely limiting the yield of the desired product. It was also found that the rates of reaction were faster for the allylic chlorides than the bromides. This was another example of the insertion of CO into the allyl palladium complex being regioselective, taking place at the least hindered carbon, with 1-chloro-but-2ene and 3-chlorobut-1-ene giving the same product.

Cyclopent-2-enone is an important skeleton in natural products thus homogeneously catalysed carbonylation reactions involving the synthesis of the five-membered have been incorporated into a series of natural product preparations. The vast majority of these involve the use of acetylenic compounds. One such two stage preparation by Moreto *et al.* involved the stereoselective *syn* addition of 3-bromoprop-1-ene to alkynes catalysed by palladium(II) bromide to give 1-bromo-1,4-dienes which were further converted to cyclopentenones through a nickel tetracarbonyl promoted carbonylation-cyclisation process (figure 1.12).[21] The two stage process was used because terminal acetylenes did not give cyclopentenones when only $[Ni(CO)_4]$ was used as the catalyst. Allylacrylic esters were the only isolable products along with products of oligomerisation. When symmetrically substituted acetylenes were used, or those with similar electronic characteristics in R_1 and R_2, in the one stage process, cyclic enones were only obtained in low yields.

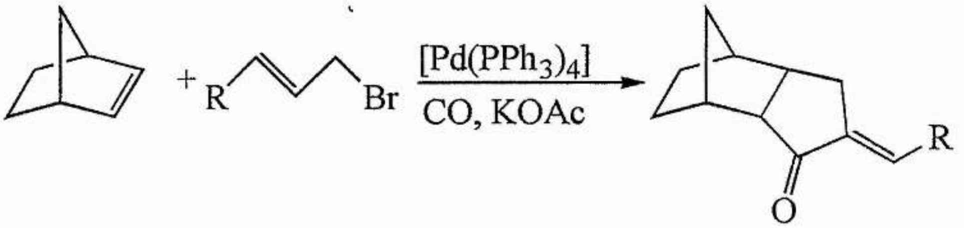


(fig. 1.12)

The *syn* addition of 3-bromoprop-1-ene to the acetylene occurred with 93% yield at 0 °C in acetonitrile. The [Ni(CO)$_4$] catalysed carbonylation-cyclisation was optimised to give 88% yield when carried out in acetonitrile with 4 equivalents of methanol and triethylamine at 36 °C for 5 hours. The production of the cyclopentenone was very dependent upon the reaction conditions and was especially sensitive to the type of base and the number of equivalents of methanol added. Earlier work by Moreto and co-workers had shown that the formation of cyclopentenones was very solvent dependent when monosubstituted acetylenes were used but was less dependent on the solvent when disubstituted acetylenes were used.[22] With just a slight variation of the reaction conditions large amounts of the uncyclised side product could be obtained *via* direct carbonylation of the vinylic bromide.

Moreto and co-workers have also investigated the effects of functional substitution on the allylic halide.[23] They found that electron withdrawing and unsaturated substituents had different effects depending upon their location. If they were placed centrally on the allyl moiety then carbonylative cycloaddition occurred to yield cyclohexenones (or aromatic) derivatives. Cyclopentenones were obtained from either centrally or terminally substituted silylallyl halides. Substitution at both ends of the allyl moiety led to the formation of 4,5-disubstituted cyclopentenones.

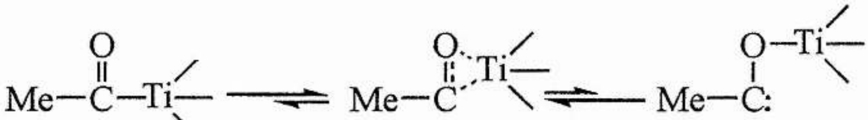
Chiusoli *et al.* produced fused ring methylenecyclopentenones *via* catalytic carbonylation of allylic halides in the presence of norbornene or norbornadiene using tetrakis(triphenylphosphine) palladium(0) as the catalyst (figure 1.13).[24]



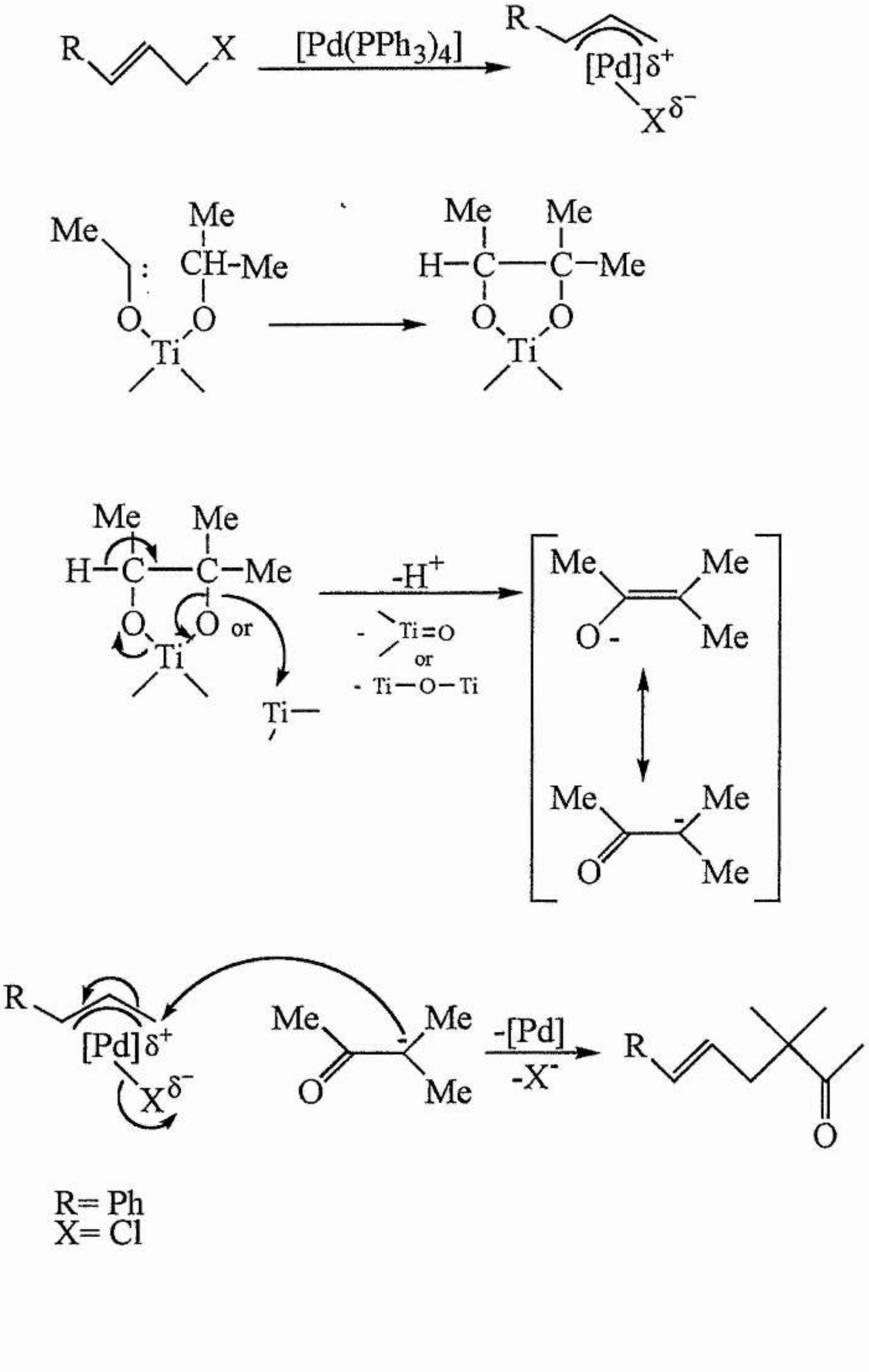
(fig. 1.13)

Y. Tsuji *et al.* have devised a variety of alkyltitanium compounds (triisopropoxymethyltitanium and diisopropoxydimethyltitanium) that have proved to be potent alkylating agents.[25] Their potency towards carbonylation was thought to be due to the fact that titanium has vacant d-orbitals and a stronger interaction with carbon monoxide than alkyllithium and Grignard reagents. The compounds could thus be carbonylated before reacting with aldehydes or allyl derivatives / palladium catalyst system to give unsaturated, unsymmeterical ketones incorporating the isopropyl group, in fair to good yields. A speculative mechanism for this reaction is given in figure 1.15. The methyltitanium compounds underwent coordination and insertion of CO into the carbon titanium bond with subsequent rearrangement to an oxycarbenoid species because of the oxophilicity of the titanium (as in figure 1.14). An enolate was formed, after rearrangement of the oxycarbenoid, which reacted with the palladium system to form the unsymmetrical ketone.

Floriani *et al.* carried out carbonylation of the methyl-titanium bond using π-$(C_5H_5)_2TiX-CH_3$ to give the corresponding acetyl complex π-$(C_5H_5)_2TiX-(COCH_3)$. X-ray analysis showed that the structure was regarded as the η^2–acyl, which is very common for early transition metal complexes (figure 1.14).[26] Another two papers stated that it was well known for some acyl complexes of early transition metals and actinides, that the contribution of the oxycarbenoid had greater importance.[27, 28]

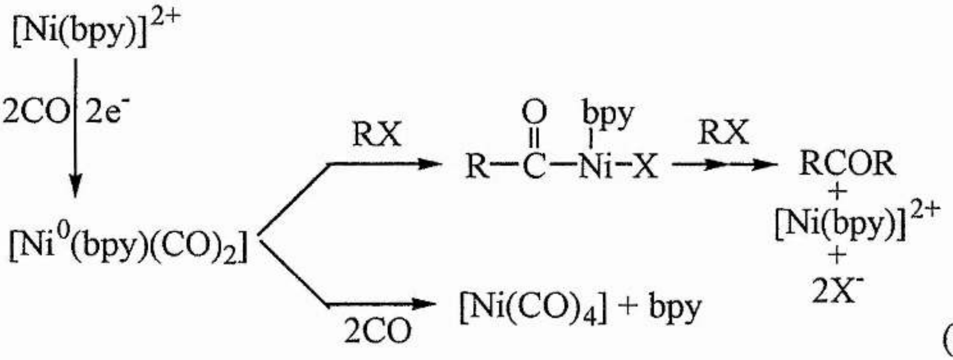


(fig. 1.14)



(fig. 1.15)

Allylic and benzylic chlorides and bromides can be electrolytically carbonylated to ketones in a solution of DMF containing 2,2'-bipyridine under an atmospheric pressure of CO.[29] The catalytic species reported in the paper seemed to have been serendipitously derived from the dissolution of various stainless steel anodes in a reaction vessel to produce homogeneous catalytic species. These metals included iron, nickel and chromium. The best yields were derived from a Fe(64%)/Ni(36%) anode, giving 90% $(PhCH_2)_2CO$ from benzyl chloride with 10% bibenzyl as the by-product. The best yields and selectivities were obtained when allylic or benzylic chlorides were used. The proposed mechanism for the reaction is given in figure 1.16 showing that the sacrificial anode was of crucial importance in providing both the precursors to the active catalytic species and the reducing potential.



(fig. 1.16)

1.3 Carbonylation of Halocarbons to Yield Carboxylic Acids

Carboxylic acids (and their derivatives) are an important group of compounds that can be readily synthesised *via* homogeneous catalytic carbonylation. Compared with a non-catalytic synthesis of carboxylic acids, which proceeds only under strongly acidic or basic conditions, the carbonylation reactions involving transition metal catalysts occur under almost neutral conditions.

Probably the best known and most widely studied example of carboxylic acid production is the Monsanto Process which is now operated by B.P. Chemicals Limited.[30] Over half the world production of acetic acid is produced *via* the methyl iodide promoted carbonylation of methanol using $[Rh(CO)_2I_2]^-$ anion as the catalyst. Acetic anhydride can be produced *via* a similar MeI promoted reaction carried out with methyl acetate as the substrate in the absence of water. However, B.P. Chemicals Ltd. Have recently installed a new iridium based catalytic system called Cativa.[31] The process uses iridium acetate as the catalyst precursor but the co-catalysts have not been revealed. As this is such a large field in itself (with probably more research being devoted towards the production of acetic acid than any other carboxylic acid or carboxylic acid derivative) acetic acid production will not be covered in this review.

The carbonylation of allylic and benzylic halides to produce β,γ-unsaturated acids or arylacetic acids usually occurs in the presence of water or base. In this review the three main carbonylation systems used to produce carboxylic acids will be discussed. These are:

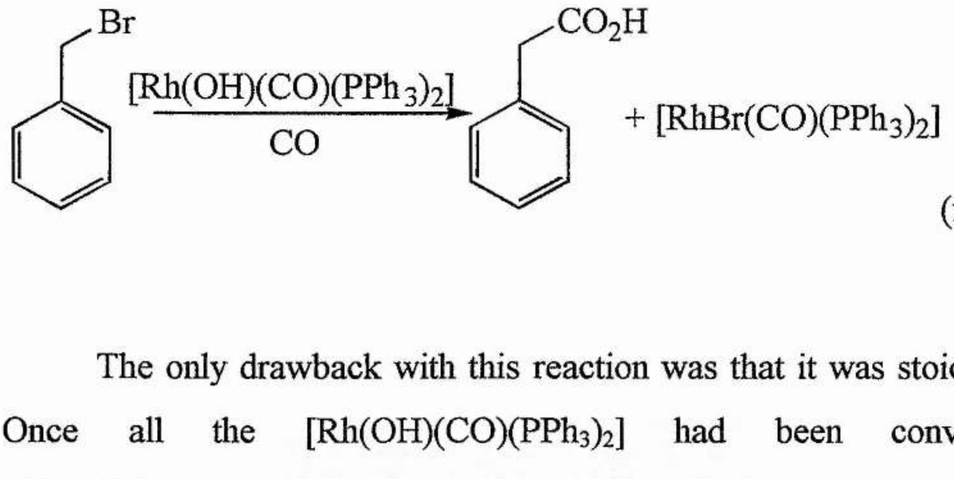
- Simple one phase systems where the water or base are miscible with the solvent.
- Biphasic systems where the catalyst remains in one phase and the substrates or products or both are in separate phases. This effectively heterogenises the homogeneous catalyst. Most of these systems involve the use of a phase transfer reagent (phase-transfer catalysis).
- Polymer supported systems where the metal centres are grafted onto specialised polymers *via* pendant ligands on the polymer backbone. Again these systems combine the ease of catalyst-product separation of a

heterogeneous system with the specificity of a homogeneous system. These systems are now being used to produce carboxylic acids.

Along with the above examples there are also a few interesting systems that rely on radicals and photostimulation (from sunlamps) to produce the carboxylic acids. These will also be discussed.

1.3.1 Single Phase Systems in the Carbonylation of Halocarbons to Yield Carboxylic Acids

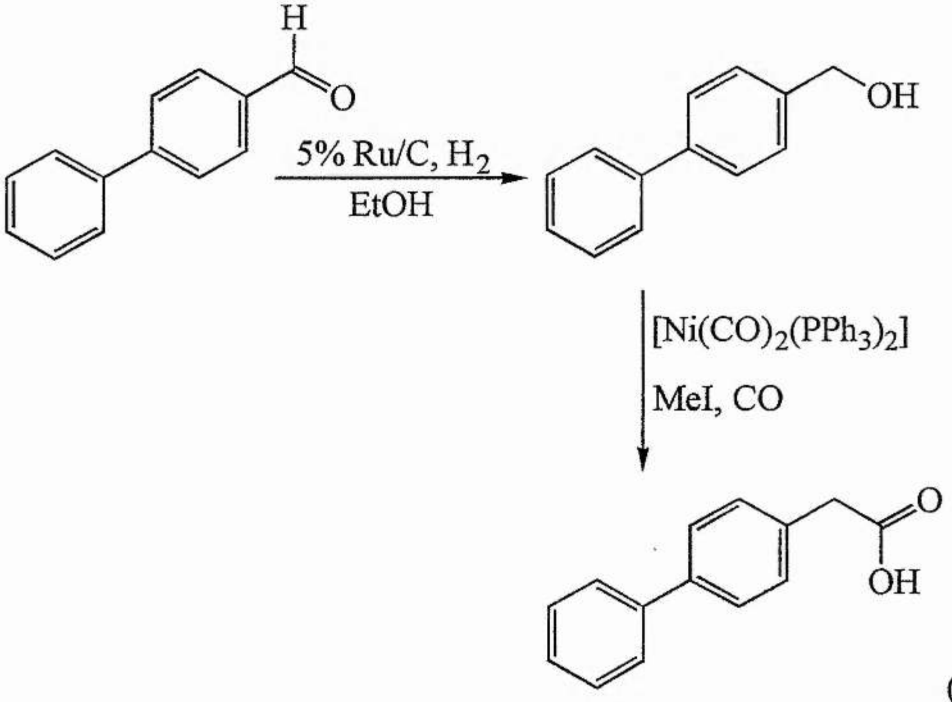
Benzyl bromide can be carbonylated directly to phenylacetic acid in 90% yield using [Rh(OH)(CO)(PPh$_3$)$_2$] in chloroform at 100 °C for 15 hours under CO (6 bar) (figure 1.17).[32]



(fig. 1.17)

The only drawback with this reaction was that it was stoichiometric. Once all the [Rh(OH)(CO)(PPh$_3$)$_2$] had been converted to [RhBr(CO)(PPh$_3$)$_2$] then the reaction could no longer produce phenylacetic acid. The catalyst was changed to [Rh(ClO$_4$)(CO)(PPh$_3$)$_2$] in the presence of water to get around this expensive problem. The reaction became catalytic with a turn over of 9 by changing the catalyst.

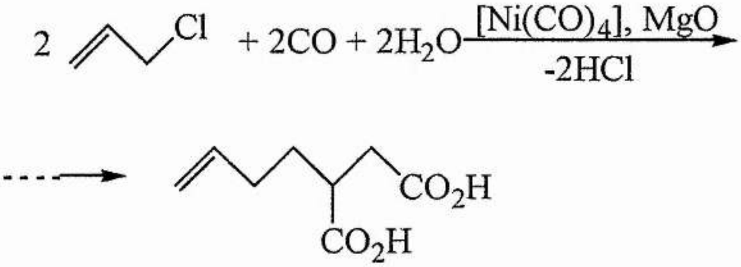
In a high yielding reaction 4-biphenylcarboxaldehyde can be converted to 4-biphenylacetic acid *via* a 4-biphenylmethanol intermediate.[33] The first stage was a hydrogenolysis reaction and occured over 5% Ru/C in aqueous ethanol to give 4-biphenylmethanol in 99.4% selectivity and 98.8% conversion. The second step used $[Ni(CO)_2(PPh_3)_2]$ with MeI as co-catalyst at 50 bar CO to carbonylate the 4-biphenylmethanol in 91.5% selectivity at 99.8% conversion (figure 1.18). The mechanism of the reaction probably involved conversion of the 4-biphenylmethanol to 4-biphenylmethylene iodide and subsequent oxidative addition of the latter to the Ni metal centre.



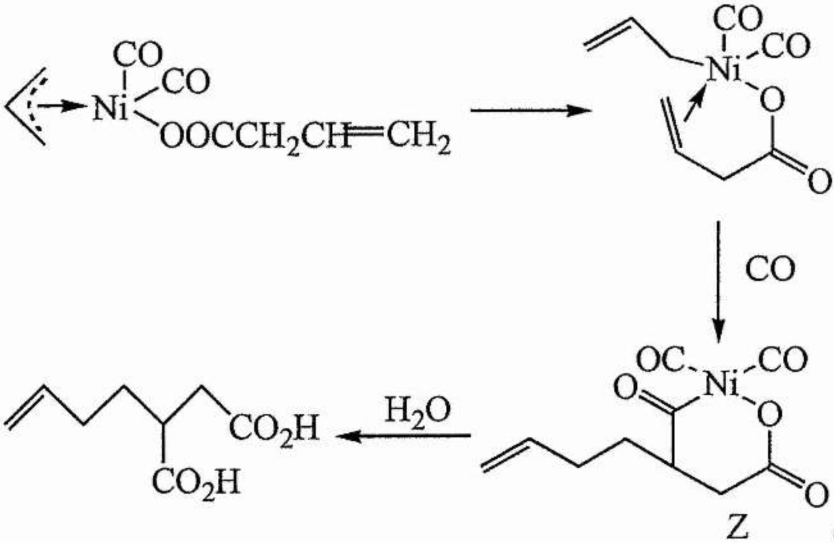
(fig. 1.18)

3-chloroprop-1-ene can be carbonylated in benzene at 50 °C and 200 bar to produce 3-butenoic acid in the presence of π-allylpalladium chloride.[34] Initially 3-butenoyl chloride was formed but this was converted into 3-butenoic acid (isolated yield 65%) by addition of water. 3-pentenoic acid was prepared in a similar manner in 85% yield.

But-3-enylsuccinic acid (60% yield) can be prepared by carbonylation of 3-chloroprop-1-ene in the presence of MgO as a base as shown in figure 1.19.[35] It was thought that but-3-enoic acid was the first product and that it was further carbonylated. Indeed if MgO was left out of the reaction the simple carbonylation product, 3-butenoic acid, was the main product. It was thought the mechanism involved a pentacoordinated π-allyldicarbonylnickel intermediate (figure 1.20).



(fig. 1.19)

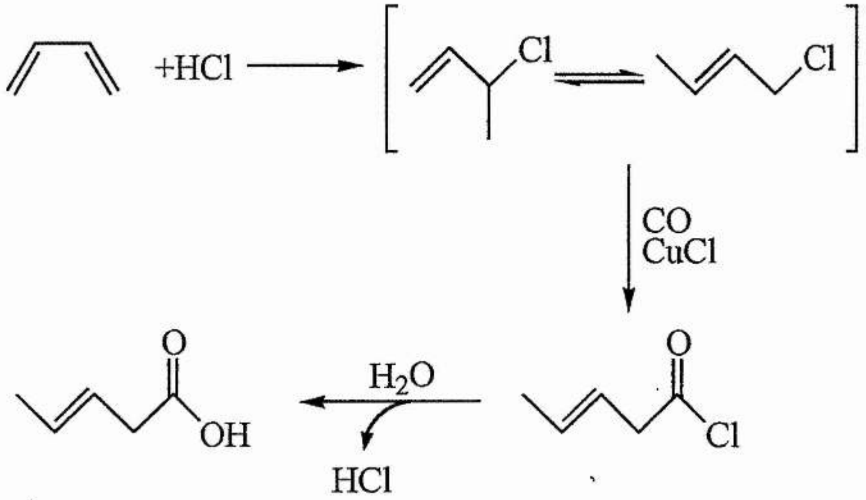


Z (fig. 1.20)

π–σ-allyl conversion created a vacant coordination site available for the double bond of the 3-butenyl group. Allyl migration, followed by CO insertion led to intermediate Z, from which the product was obtained by hydrolysis.

3-chloroprop-1-ene can be carbonylated to give a mixture of 2-methylprop-2-enoic acid (15%), but-2-enoic acid (7.6%) and 2-methylpropanoic acid (1.9%).[36] The reaction was carried out in ethanoic acid for 4 hours at 120 °C under 55 bar CO using $PdCl_2$ as the catalytic precursor. Optionally PPh_3 or a zeolite can be added to the solution. The formation of but-2-enoic acid can be readily rationalised by the insertion of CO into the terminal Pd-C bond of a π-allyl intermediate but, the formation of the 2-methylprop-2-enoic acid and the 2-methylpropanoic acid must involve insertion of carbon monoxide between the central carbon atom of the allyl group and the palladium.

3-pentenoic acid can be prepared catalytically by reaction of 3-pentenoyl chloride with water and 1,3-butadiene with HCl (figure 1.21).[37]

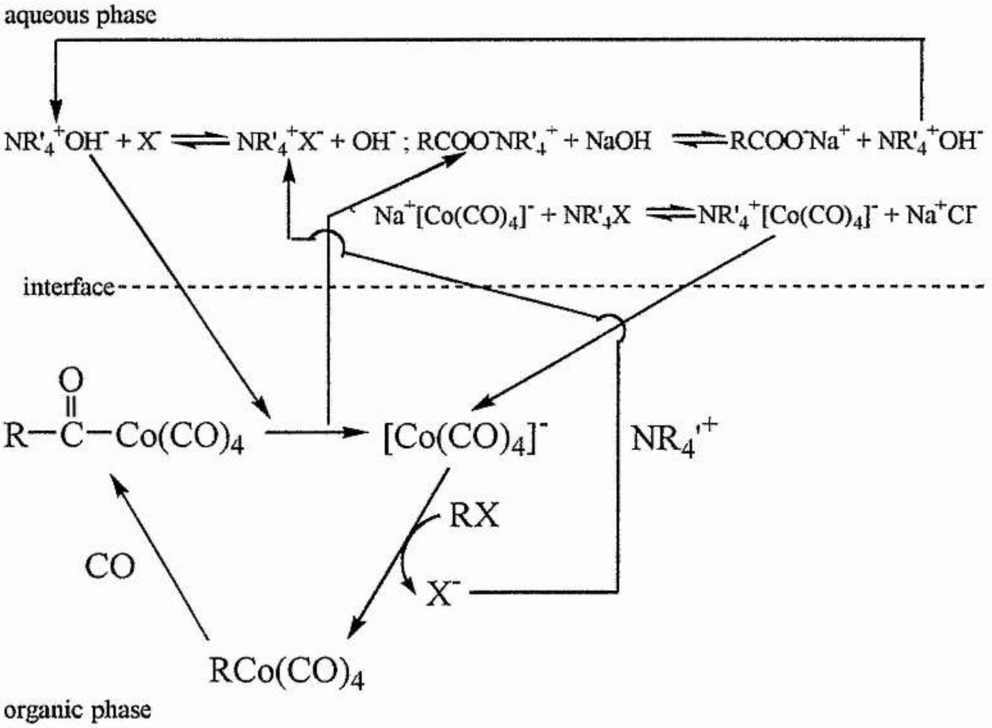


(fig. 1.21)

The reaction was a two stage process. 1-chloro-2-butene and 3-chloro-1-butene were prepared by the reaction of 1,3-butadiene with HCl. The HCl was produced by the reaction of 3-pentenoyl chloride with water to produce the carboxylic acid. The resulting chlorobutene was carbonylated to give 3-pentenoyl chloride at 120 °C under 21 bar CO in a solution of concentrated HCl and CuCl. The autoclave was initially loaded with a small amount of 3-pentenoyl chloride synthesised *via* the palladium catalysed carbonylation of chlorobutene.

1.3.2 Biphasic Systems in the Carbonylation of Halocarbons to Yield Carboxylic Acids

Phenylacetic acid and its sodium salt can be prepared by carbonylating benzyl chloride or bromide in the presence of $Na[Co(CO)_4]$ in 87% yield (for the chloride).[38, 39] The reaction took place under 1 bar CO at 55 °C for over 3 hours. The aqueous phase consisted of 40% NaOH and $[Me_3NBz]X$ (X=Cl or Br) as phase transfer catalyst. $R_4N[Co(CO)_4]$ (or $[Co_2(CO)_8]$) as catalytic precursors were in the organic phase. The benzyl halide was dissolved in diphenyl ether (figure 1.22). In addition to acting as a phase transfer catalyst, $[Me_3NBz]X$ also assisted in the conversion of $[Co_2(CO)_8]$ to $[Co(CO)_4]^-$.



(fig. 1.22)

Benzyl halides can also be carbonylated to phenylacetic acid using $[Pd(PPh_3)_4]$ as the catalytic precursor and tetrabutylammonium chloride as the phase-transfer catalyst (figure 1.23).[40] The reaction took place at 95 °C under 5 bar CO to give 83% yield of phenylacetic acid. The mechanism of the reaction was very similar to the one given in figure 1.22. However the palladium catalyst remained in the organic phase.

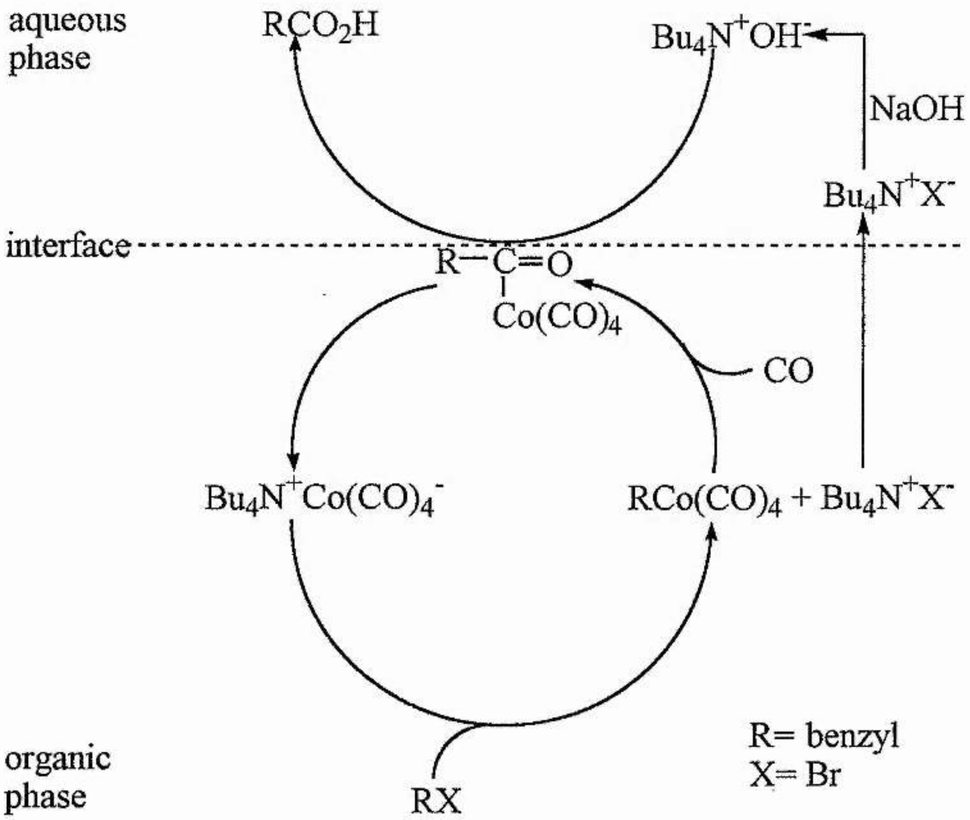
$$RX + CO + 2NaOH \xrightarrow[[Pd(PPh_3)_4],\ NR'_4X]{\text{NaOH aqueous/xylene}} RCOONa + NaX + H_2O$$

R= benzyl
X= Cl
R'= Bu

(fig. 1.23)

The xylene solution could be recycled many times without the loss of catalytic activity but the addition of a small quantity of PPh_3 was required to prevent palladium metal precipitating out of the solution. This was because the PPh_3 was slowly transformed into a phosphonium salt, probably by reaction with benzyl chloride to produce $PhCH_2PPh_3^+ Cl^-$.

des Abbayes *et al.* have shown that the rate determining step in the cobalt catalysed phase-transfer carbonylation of benzyl bromide was reductive elimination of the acetyl species which occured at the liquid-liquid interface (figure 1.24).[41, 42]



(fig. 1.24)

The key step involved cleavage of the acetyl cobalt species by the hydroxide anion to give the carboxylic acid (this would immediately react with NaOH to give a sodium phenylacetate which would remain in the aqueous phase) thus regenerating the catalytic ion pair. As this stage occurred at the interface of the two solutions it was highly dependent upon the stirring speed, since faster stirring increased the area of the interface between the two liquids.

Another product from the reaction was dibenzyl ketone, possibly from reaction of $RCOCo(CO)_4 + RCOCo(CO)_3$ followed by reductive elimination of the ketone and production of dicobalt octacarbonyl. Another possibility for the production of dibenzyl ketone could have been the attack of the acetyl-cobalt species by benzyl bromide. Toluene and diphenylethane were also produced in the reaction. The mechanisms for the formation of these compounds were unclear but it was suggested that radical species could have been involved. Another suggestion was that an unstable hydroxycarbonyl was formed *via* reaction of $Bu_4N^+OH^-$ and $C_6H_5CH_2Co(CO)_4$ (figure 1.25).

$$C_6H_5CH_2Co(CO)_4 \xrightarrow{Bu_4N^+OH^-} \left[\begin{array}{c} C_6H_5CH_2Co(CO)_3 \\ | \\ HO-C=O \end{array}\right]^- Bu_4N^+$$

(fig. 1.25)

Decomposition of the hydroxycarbonyl would have given products such as toluene and CO_2 and would recycle the catalyst. The diphenylethane could have been produced *via* a radical reaction between two molecules of $C_6H_5CH_2Co(CO)_4$ generating dicobaltoctacarbonyl in the process. These observations tied in well with the experimental data.

Benzyl halides can also be carbonylated using $[Co(PPh_3)_2Cl_2]$ as the catalyst and $Bu_4N^+Br^-$ as phase-transfer catalyst.[43] The yields and the proposed mechanism were much the same as the work carried out by des Abbayes and co-workers.

Benzyl halides can be carbonylated in a palladium catalysed reaction without the addition of a phase-transfer agent in an aqueous NaOH/*p*-xylene biphasic system.[44] Many ligands were tried in the reaction and were classified into three groups:

1. Ligands which did not stabilise Pd(0) under CO e.g. benzonitrile, sulphur containing ligands, tetrachloroethylene, quinones and dibenzylidenacetone.
2. Ligands which gave palladium (0) compounds of low solubility e.g. $BiPh_3$, $SbPh_3$, $P(\alpha\text{-}C_{10}H_7)_3$, $Sb(C_6F_5)_3$ and $P(OPh)_3$.
3. Ligands which gave soluble palladium(0) compounds e.g. PPh_3, $P(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}CH_3OC_6H_4)_3$.

Ligands in group 3 were found to have the highest activity whilst the ones in group 1 allowed palladium black to be formed. Benzyl halides were more reactive than phenyl halides whilst alkyl halides were unreactive. Benzyl chloride was therefore carbonylated to sodium phenylacetate in 93% yield using $[Pd(PPh_3)_4]$ as the catalytic precursor under <1 bar of CO at 50 °C. A slight excess of phosphine was used in the system due to the formation of quaternary phosphonium salts. Side reactions in this system were the unavoidable reactions of the benzyl halides with NaOH to give the corresponding alcohols and reaction of CO with NaOH to give sodium formate.

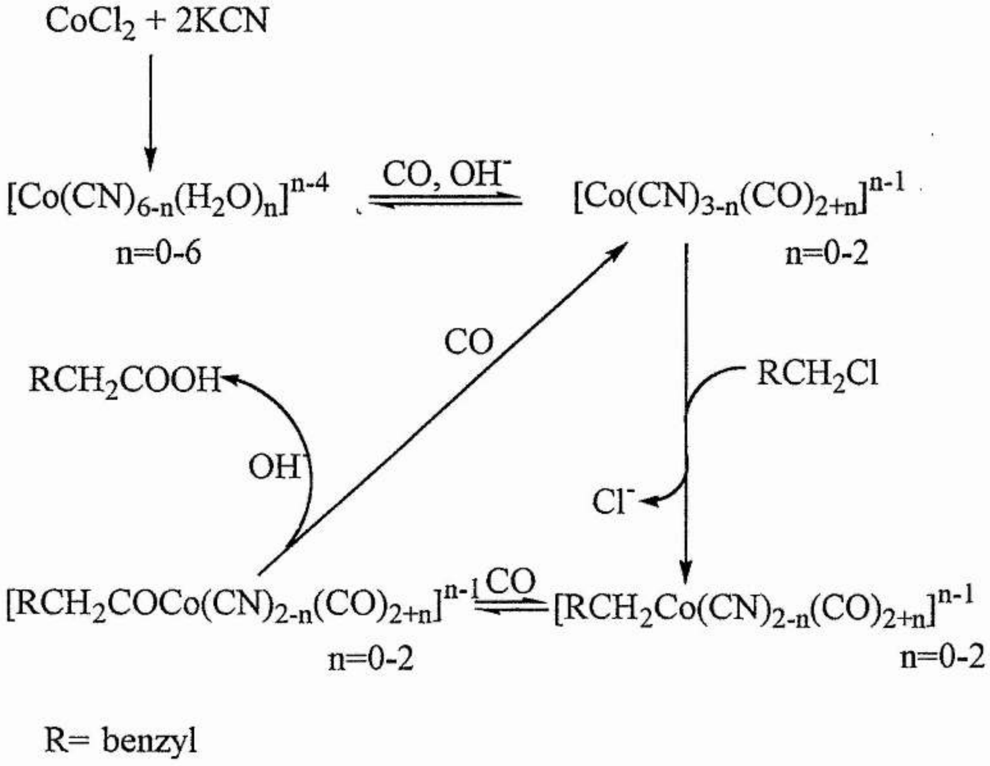
Benzyl halides can also be carbonylated using a catalytic amount of iron pentacarbonyl.[45] The mechanism for the reaction was very similar to the one given in figure 23 with iron replacing cobalt.[14] The reactions took place between 20 and 60 °C under either 1 or 60 bar CO using $Bu_4N^+HSO_4^-$ as the phase-transfer catalyst to give reasonable yields (31-75%) of phenylacetic acid after work-up. The reactions were slow, often requiring a day or more to go to completion. Increasing the reaction temperature had the effect of altering the product ratios in favour of by-products, mainly ketones formed *via* the mechanism given in figure 1.10. Production of the acid in the biphasic system was favoured principally by high stirring speeds.

Benzyl halides can be carbonylated to the corresponding phenylacetic acids using a catalytic system based on tetracarbonyl cobalt anion.[46] Benzyl bromide in THF was added and the solution heated to 50 °C for 3 hours whilst bubbling CO through it. The best yield was obtained with benzyl bromide (86% phenylacetic acid after work-up). When 2,2'-bis(bromomethyl)biphenyl was used as a substrate a cyclic ketone (the same as shown in figure 1.13) rather than a carboxylic acid was obtained.

Benzyl chloride can be carbonylated to phenylacetic acid in a two phase system under 1 bar CO at 50 °C using the water soluble palladium complex, $[PdCl_2(Ph_2P(m\text{-}C_6H_4SO_3Na))_2]$, giving 89-93% yields.[47] The palladium complex was very soluble in water though scarcely soluble in organic solvents. In order for carbonylation to proceed the Pd(II) complex had to be reduced to a Pd(0) species; an induction period was observed for the reaction. The Pd(0) complex was shown to be the trinuclear palladium complex, $[Pd_3(CO)_3(Ph_2P(m\text{-}C_6H_4SO_3Na))_4]$. In order to cut out the induction period the benzyl palladium complex, $[C_6H_5CH_2Pd(Ph_2P(m\text{-}C_6H_4SO_3Na))_2Cl]$ was synthesised and used as the catalyst. The product forming step for this process was thought to involve a carboxypalladium complex to give the carboxylic acid. As in previous work involving hydroxide ions there was considerable isomerisation of the β,γ-unsaturated acids to the thermodynamically favoured α,β-unsaturated acids. Surfactants (>100 x [catalyst]), increase the rate and yield of the reaction with $n\text{-}C_7H_{15}SO_3Na$ and $n\text{-}C_7H_{15}COONa$ producing the higher yields but surfactants with shorter chains were much less efficient.

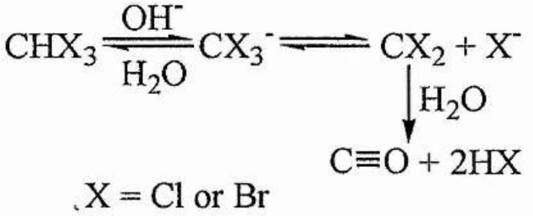
As the sulphonates are more acidic than phenylacetates then the phenylacetic acid is easily separated by careful acidification of the aqueous layer leaving the surfactant in the aqueous solution. The role of the surfactant in the mechanism of the reaction is still unclear but it was thought not to be ascribed to a simple surface activation. It was suspected that the water-soluble palladium complex was acting as a counter phase-transfer catalyst; it was thought the surfactant somehow activated the reaction environment of a counter phase-transfer catalysis by some sort of mutual interaction between it and the water-soluble catalyst.

A cobalt chloride-potassium cyanide system was found to catalyse carbonylation of benzyl chlorides into arylacetic acids under phase transfer conditions.[48] The reaction took place at 55 °C under 1 bar CO with either quaternary ammonium or phosphonium salts as co-catalysts. The catalytic solution had to be pre-treated under a CO atmosphere for an hour to generate the catalyst before the substrate was added, otherwise the main reaction was hydrogenolysis of the benzyl chlorides to give mainly toluene derivatives. The best yields were obtained when methyltrioctyl- or tetrabutylammonium salts were used as co-catalysts in a ratio of 2:1 with $CoCl_2$ and 5M NaOH as the aqueous phase. If the concentration of base was raised then the catalytic system was poisoned after a short time whilst lower concentrations caused the rate of carbonylation to drop. The presence of cyanide was essential for the carbonylation reaction. Again the best yields were obtained when a ratio of 2:1 CN^-:$CoCl_2$ was used. Higher ratios gave low yields of carbonylation products. The nature of the organic phase affected both the conversion and the yield. Polar solvents promoted faster reactions than non-polar ones but the polar ones were not as selective. A possible mechanism for the reaction was suggested as shown in figure 1.26.



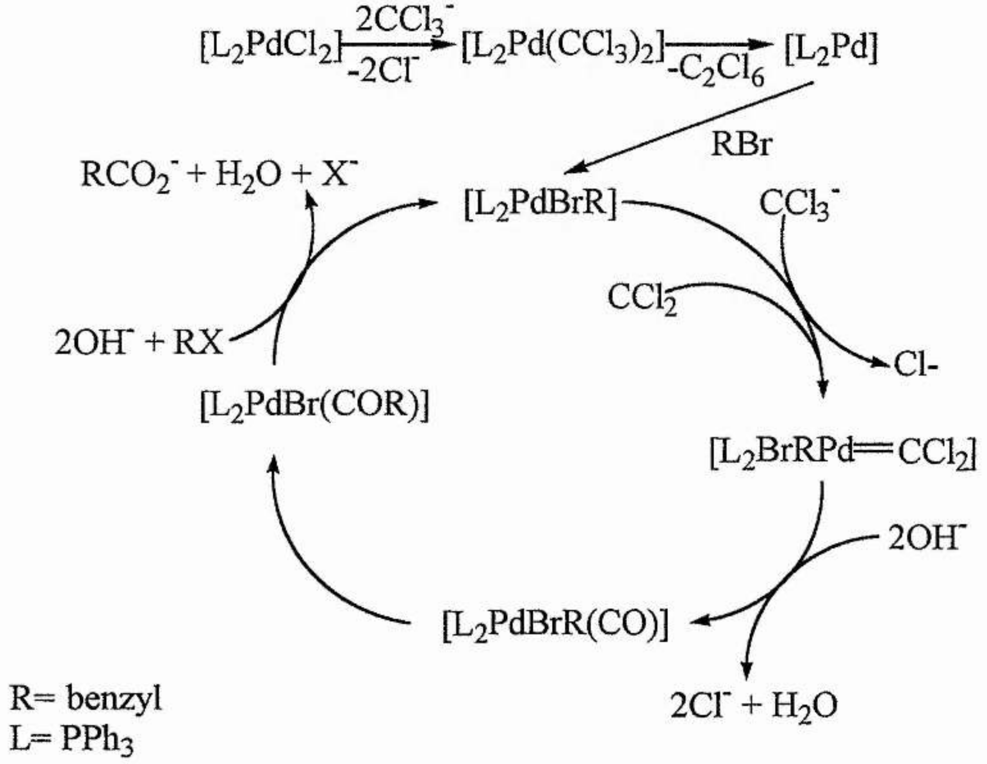
(fig. 1.26)

Benzyl halides can be catalytically carbonylated in the presence of e.g. $[PdCl_2(PPh_3)_2]$ by CO generated *in situ* from chloroform and aqueous alkali.[49] The reactions took place at ambient temperature under nitrogen affording phenylacetic acids in up to 70% yields with bromides, chlorides gave less than 12% yields. The reaction times however were in the order of 24 hours (some as long as 96 hours) and increasing the temperature had the effect of reducing the yield of the carboxylic acid though the reaction time was reduced by 4 hours. The CO was generated from chloroform *via* the following reaction with 50% NaOH (figure 1.27).



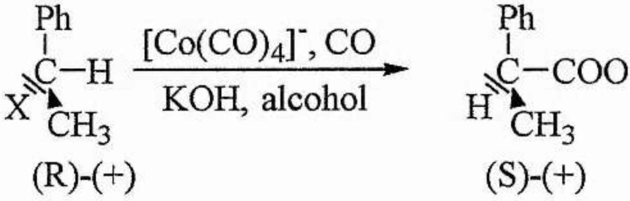
(fig. 1.27)

A possible mechanism for the reaction is given below in figure 1.28.

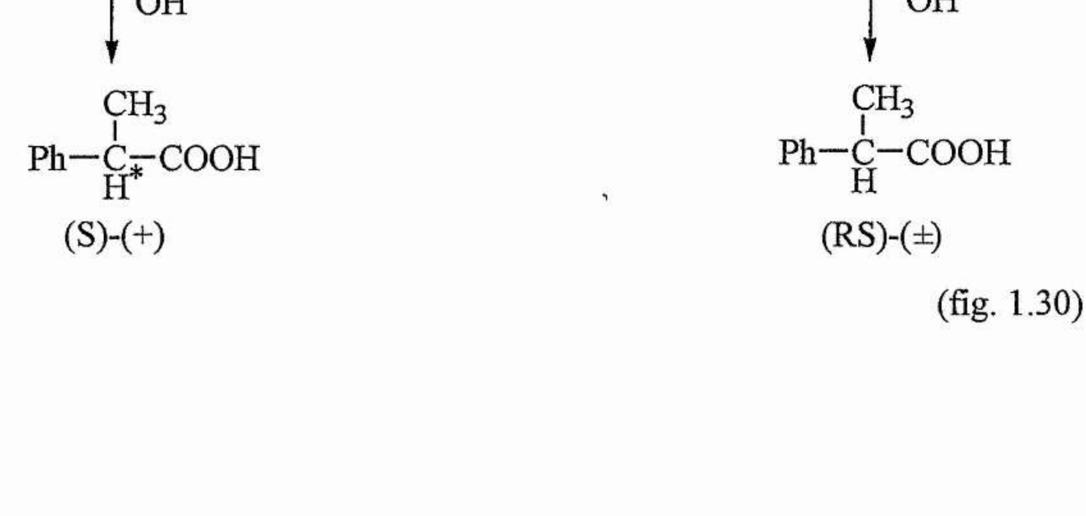


(fig. 1.28)

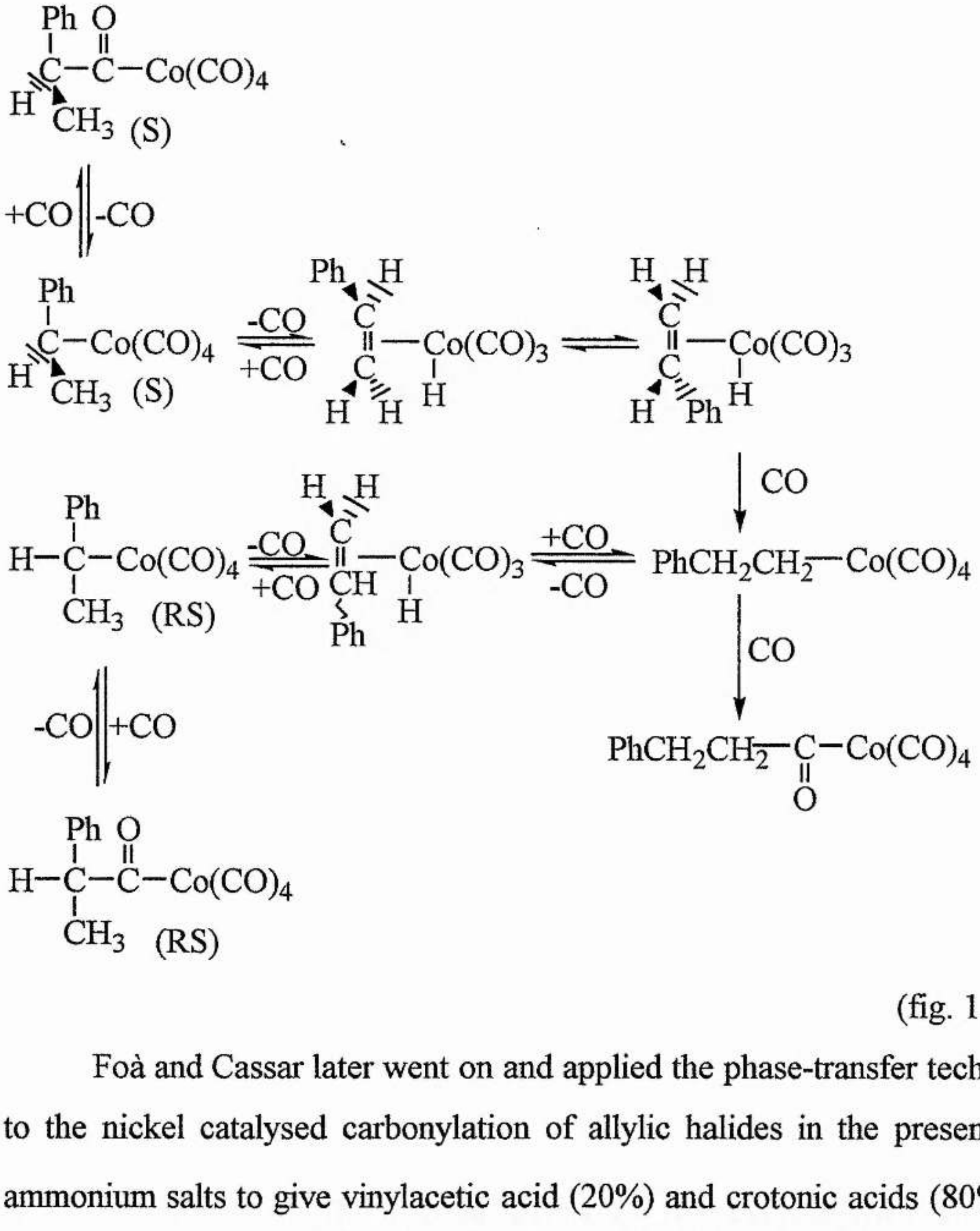
The carbonylation of optically active benzylic halides was studied by Foà *et al.* in order to obtain more information about the carbonylation of secondary benzyl halides[50] and the course of the reaction.[51] Under phase transfer conditions (50% KOH / various alcohols) with $C_6H_5N(CH_3)_3Br$ as co-catalyst under 1 bar CO at 35 °C using $[Co_2(CO)_8]$ as catalytic precursor a hydratropic acid, predominantly of the opposite configuration was obtained, although this was accompanied by extensive racemisation (figure 1.29). The inversion of configuration was in agreement with an S_N2 mechanism. This racemisation was accounted for by two mechanisms. The first one explained the racemisation in terms of keto-enol tautomerisation of the acyl complex (figure 1.30) and the second one explained it as an equilibrium between branched and linear alkyl complexes (figure 1.31). Evidence for both of the mechanisms was obtained by varying the polarity of the solvent with more polar solvents favouring the keto-enol tautomerisation mechanism.



(fig. 1.29)



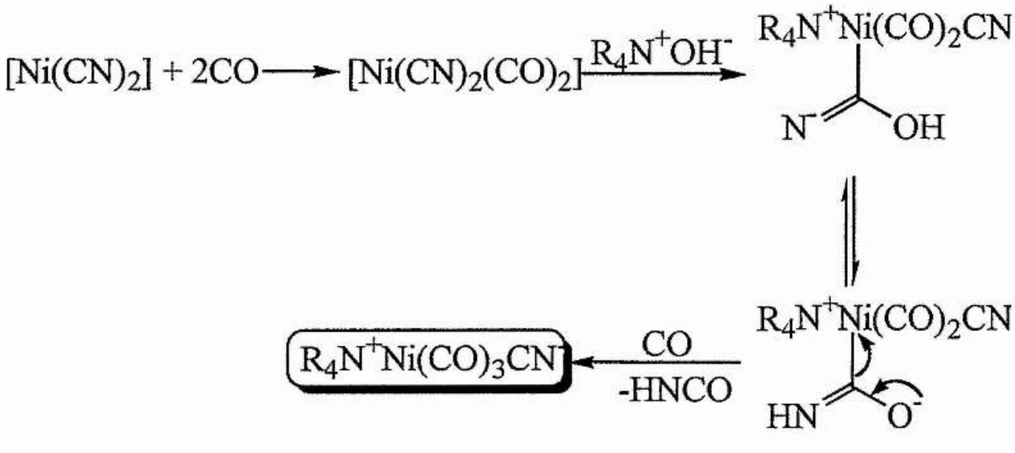
(fig. 1.30)



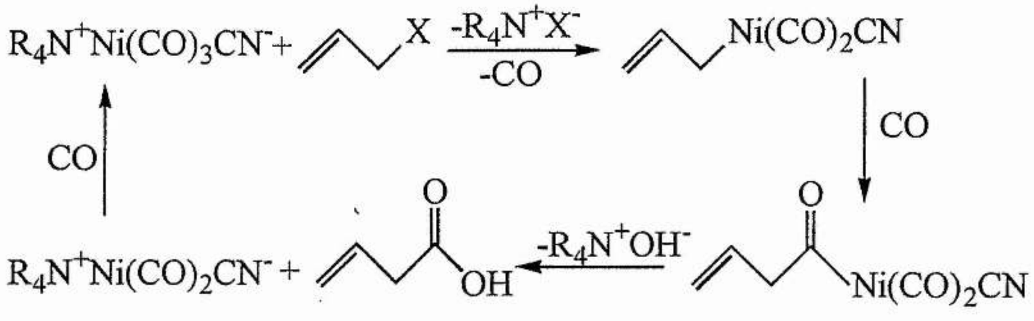
(fig. 1.31)

Foà and Cassar later went on and applied the phase-transfer technique to the nickel catalysed carbonylation of allylic halides in the presence of ammonium salts to give vinylacetic acid (20%) and crotonic acids (80%).[52] The catalytic precursor for this reaction was [Ni(CO)$_4$]. This was quickly transformed into nickelates ([Ni$_5$(CO)$_{12}$]$^{2-}$ and mainly [Ni$_6$(CO)$_{12}$]$^{2-}$) in the phase-transfer system which were shown to catalyse the carbonylation of 3-chloroprop-1-ene in separate reactions. Nickel catalysed cyclisation-carbonylation in the presence of allyl halides and acetylenes to produce cyclic ketones is a well known reaction; however very poor yields of ketones were obtained when acetylenes were introduced into the phase transfer system. A key feature of the catalyst present in the cyclisation reaction was that it was halogenated; Foà and Cassar hypothesised that this may have been a requirement for acetylene insertion. This accounted for the poor yields of cyclic ketones when acetylene was introduced into the phase transfer system.

In order to get around the problem of using the extremely toxic [$Ni(CO)_4$] as a carbonylation catalyst for allylic halides Joó and Alper used cyanonickel (II) catalysts under phase-transfer conditions to afford butenoic acids.[53] In the best system, [$Ni(CN)_2$] was pre-treated with CO at 60 °C to give the active catalyst (figure 1.32). The substrate was then added slowly to the phase transfer system which was cooled to room temperature (figure 1.33). The best co-catalyst was tetrabutylammonium hydrogen sulphate with 4-methylpentan-2-one being used as the organic solvent.



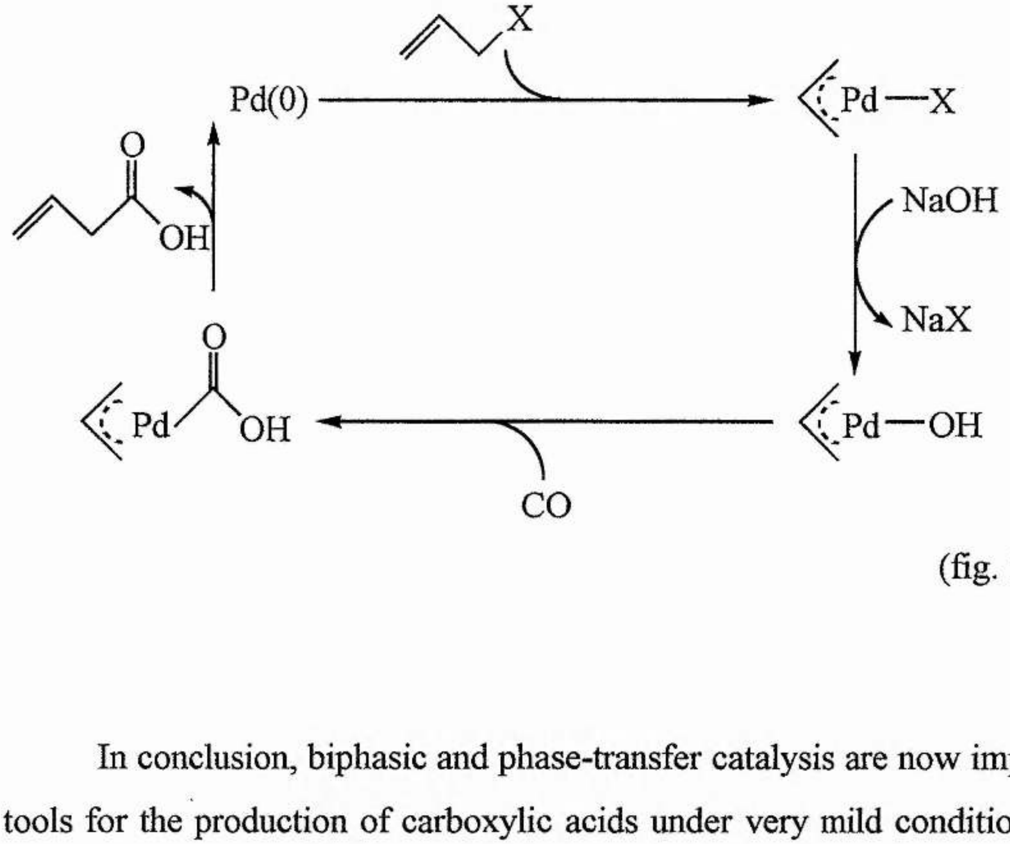
(fig. 1.32)



(fig. 1.33)

The ratio of conjugated to unconjugated acid produced was dependent upon the concentration of the base. As the concentration of the base decreased the amount of (E)-2-butenoic acid decreased and the amount of 3-butenoic acid increased. However the overall yield of acids decreased with decreasing base concentration. The carbonylation of 3-bromoprop-1-ene gave a yield of 98% (79% selectivity to (E)-2-butenoic acid) whilst 3-chloroprop-1-ene gave 88% (86% selectivity to (E)-2-butenoic acid). The base induced isomerisation of double bonds is a well known reaction.[54] Thus in this system the double bond is isomerised so that it is in conjugation with the carbonyl group (a thermodynamically favourable reaction).

Allylic chlorides can be carbonylated in a two phase reaction under 1 bar CO at room temperature using a palladium-phosphine based catalyst without the addition of a phase-transfer reagent to yield 3-butenoic acids.[55] The phosphine complexes, $PdCl_2L_2$ (I) (a, L= $Ph_2P(m\text{-}C_6H_4SO_3Na)$; b, L= PPh_3), and (II) Na_2PdCl_4 were used as catalysts. Ia and II were soluble in the aqueous phase whilst Ib was soluble in benzene. When II was used as the catalyst palladium black was formed,hence the phosphine systems were used. It was shown that the presence of the hydroxide ion was essential for the reaction to proceed. In this system, compared with the Joó/Alper system for benzyl halides, only 4-20% 2-butenoic acid was produced *via* base catalysed isomerisation of 3-butenoic acid. In order to try and suppress the isomerisation reaction the sodium hydroxide was added dropwise to the solution thus keeping the base at low concentrations. These reactions occurred without the use of a phase-transfer reagent; therefore it was likely that the reactions took place at the liquid-liquid interface. It was thought that the reaction proceeded through a carboxypalladium intermediate; the product forming step would have been the reductive elimination of the allyl and carboxy groups and not CO insertion into the allyl-Pd bond followed by hydrolysis (figure 1.34).



(fig. 1.34)

In conclusion, biphasic and phase-transfer catalysis are now important tools for the production of carboxylic acids under very mild conditions and as such are being used more and more in synthetic organic chemistry. Research into the use of phase-transfer catalysis began in the mid 1970's with the use of the extremely toxic nickel tetracarbonyl and other transition metal carbonyl species e.g. cobalt and iron. As more interest was shown in the field the inevitable development of more active and more stable catalysts occurred. It also meant that the use of the extremely toxic nickel tetracarbonyl could be phased out in favour of these better catalysts. The main drawback with these systems was the side-reaction of the allylic and benzylic halides with the hydroxide that needed to be present for the reaction to proceed. Also the occurrence of the base induced isomerisation of the β,γ-unsaturated acids to α,β-unsaturated acids was also an undesirable side-reaction.

1.3.3 Polymeric Systems in the Carbonylation of Halocarbons to Yield Carboxylic acids

Catalytic reactions are most readily studied in a liquid homogeneous phase. All the metal atoms in the catalytic solution are usually active and are usually specific to one or two functional groups. To study these reactions NMR and IR techniques can be used along with isolating reactive intermediates. However, catalyst recovery at the end of a reaction is more difficult in the homogeneous case than in the heterogeneous case. One technique of heterogenizing the homogeneous catalyst has just been discussed but interest is increasing in another technique, namely polymer supported metal complexes. The polymers in question have ligands (phosphines, pyrrolidones, etc.) grafted onto their backbones that enable them to bind metal complexes e.g. poly(styrene) supported Wilkinson's catalyst. The polymer mounted metal complexes can catalyse the same reactions with the same specificity as before but with the added advantage that the polymeric support enables quantitative recovery of the catalyst at the end of the reaction. Therefore the specificity and mild reaction conditions of a homogeneous catalyst can be combined with the ease of separation of a heterogeneous catalyst

Allyl halides can be carbonylated by the water soluble poly(N-vinyl-2-pyrrolidone) anchored palladium catalyst (PVP-Pd) to give β,γ-unsaturated acids under 1 bar of CO at room temperature.[56, 57] The system works in monophasic, biphasic and in phase-transfer conditions. The monophasic carbonylation was carried out in alcoholic solvents and gave the highest rates; however, this system suffered from two side reactions. One was reaction of the allyl halides with ethanol to produce allyl ethyl ether and the other was reaction of CO with NaOH to produce sodium formate. The best results were obtained with water as the solvent and $Me_4N^+Cl^-$ as the phase-transfer catalyst. The rate was not as high as for the phase-transfer system but the yield and selectivity of the products was better. 3-bromoprop-1-ene gave higher yields than 3-chloroprop-1-ene. The mechanism of the reaction was probably the same as for the non-polymer bound palladium catalysed carbonylation of allylic halides shown in figure 1.34. At the end of the reaction the catalyst was easily removed from the reaction mixture and could be used repeatedly. No study was carried out on leaching of the palladium from the polymer or aggregation of palladium on the polymer.

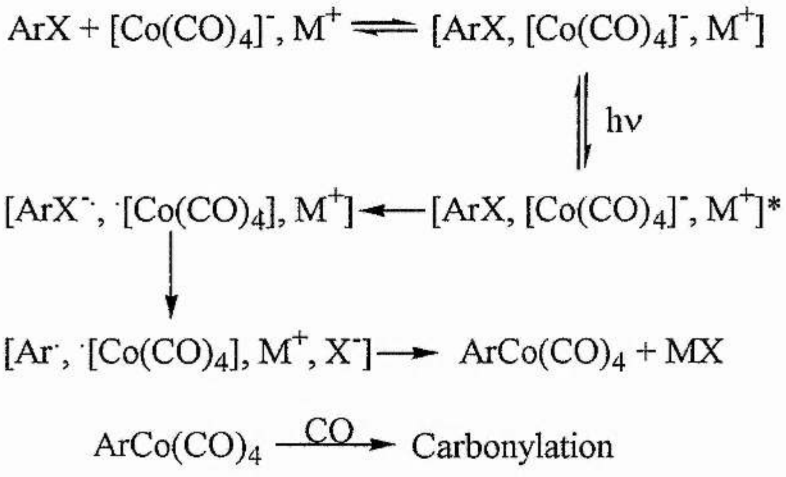
Liao and co-workers compared various polymers for use as agents for supporting the palladium.[58] They found that PVP-Pd gave the best yields and rate but polysulphone-diphenylphosphinyl-palladium (PSF-DPP-Pd) gave the best selectivity of β,γ-unsaturated acids to α,β-unsaturated acids. They also found that the PVP-Pd was more active than water-insoluble catalysts. The ligands also had an effect on the carbonylation reaction. Again DPP gave a good rate and selectivity but in comparison the *o*-carboxyphenylamino (CPA) group had a much higher selectivity though the rate of reaction was lower. Chelating ligands gave a lower rate of reaction. The lower activity of the catalysts with these ligands probably resulted from their strong coordination to palladium thus inhibiting the creation of the vacant sites and hence the oxidative addition of the allyl halide. The addition of a phase transfer reagent increased the rate of reaction by 2.5- 3.0 times when used with the PVP-Pd system and also increased the rate in other systems by a smaller extent. It was noted that the products of the reactions, sodium butenoates, could also act as phase-transfer reagents as they possessed surface active properties.

Polymer-anchored bimetallic catalysts have been used to carbonylate 3-chloroprop-1-ene to give butenoic acids.[59] The PVP-Pd system was modified by incorporating various other metal centres ($FeCl_3$, $NiCl_2$, $Co(OAc)_2$ and $RuCl_3$) to the polymer along with the palladium. The result of doing this was to reduce the rate of reaction, as compared to the PVP-Pd system, but to increase the selectivity towards the β,γ-butenoic acid. The best systems were PVP-Pd-$NiCl_2$ and the PVP-Pd-$Co(OAc)_2$ both giving >99% butenoic acids in 19:1 β,γ:α,β mole ratio. If the palladium was omitted from the system, hardly any catalytic activity was achieved. The mechanism of this synergic effect between the two metal centres remains to be clarified.

3-bromoprop-1-ene can be carbonylated to β,γ- and α,β- butenoic acids over phosphinated poly(oxy(2,6-dimethyl-1,4-phenylene)) supported palladium catalysts.[60] The reactions were carried out in either biphasic or phase-transfer conditions (NaOH/benzene system) under 1 bar CO at room temperature. As in other examples the activity of the catalyst with a phase-transfer reagent was greater than without. The P/Pd ratio also affected the activity of the catalyst. The reaction rate increased with an increase in reaction temperature.

1.3.4 Free Radicals in the Carbonylation of Halocarbons to give Carboxylic Acids

One novel use of a sunlamp is carbonylating benzyl or allyl triethylammonium halides to the corresponding acid under phase-transfer conditions.[61] The reactions took place at 65 °C under 1 bar CO in either 5M NaOH or 5M NaOH/benzene using $[Co_2(CO)_8]$ (which formed $[Co(CO)_4]^-$ *in situ*) as the catalytic precursor. The wavelengths of the radiation given out by the sunlamp were principally 300, 315, 365, 405 and 435 nm. Without the use of the sunlamp there was very little carbonylation of the allyl and benzyl triethylammonium halides. However, when the reactions were irradiated yields of no less than 70% were obtained depending on the halide chosen. The suspected mechanism of the reaction was thought to be as shown in figure 1.35. When allyltriethylammonium halides were used as substrates the products were the base isomerised 2-butenoic acids and not 3-butenoic acids.



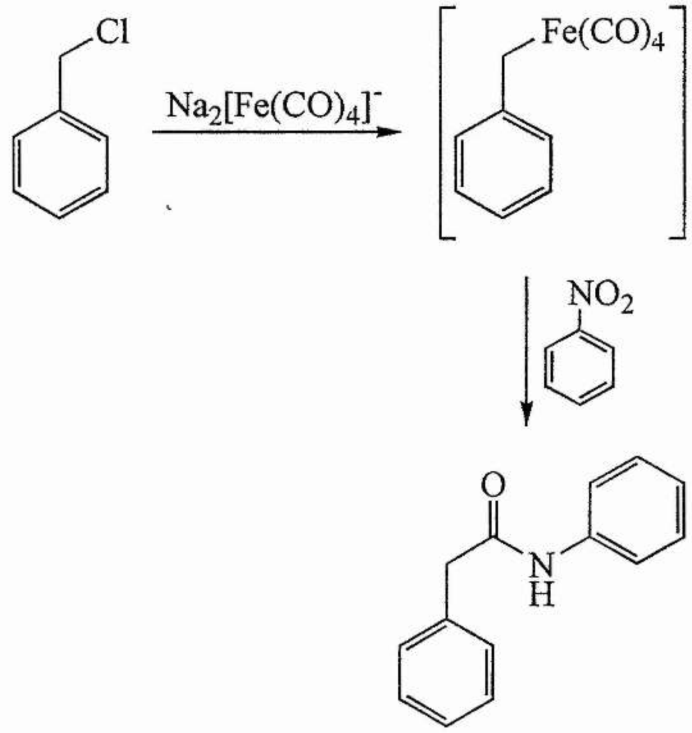
(fig. 1.35)

1.4.1 Carbonylation of Halocarbons to Yield Esters

Esters are probably the most widely investigated of all the carboxylic acid derivatives. They are easily purified from reaction mixtures and are reactive enough for further synthesis. In many cases the reactant alcohol can be used as the solvent in the reaction.

With the exception of allylic halides, work on the palladium catalysed carbonylation of organic halides has been quite scarce due to the severe reaction conditions required. However, it was found that when palladium-phosphine complexes were used, less severe reaction conditions were needed.[62] Thus benzyl chloride was carbonylated to methyl phenylacetate under 200 psi CO at 80 °C in the presence of various bases. The catalytic precursor for the reaction was $[PdCl_2(PPh_3)_2]$. The times for the reactions were quite long and varied from 24-40 hours. The Pd(II) complex was first reduced to either $[Pd(CO)(PPh_3)_3]$ or $[Pd_3(CO)_3(PPh_3)_4]$ before oxidative addition of benzyl chloride and insertion of CO. Alcoholysis of the acylpalladium(II) complex would afford the ester and regenerate the palladium(0) compound. The best yields of ester were achieved when 1,8-bis(dimethylamino)naphthalene was used as a base. This was a strong base with poor nucleophilicity, which did not react with benzyl chloride. Sodium acetate did react to produce benzyl acetate because of its higher nucleophilicity. The other side product from the reaction was benzyl methyl ether from reaction of benzyl chloride with methanol.

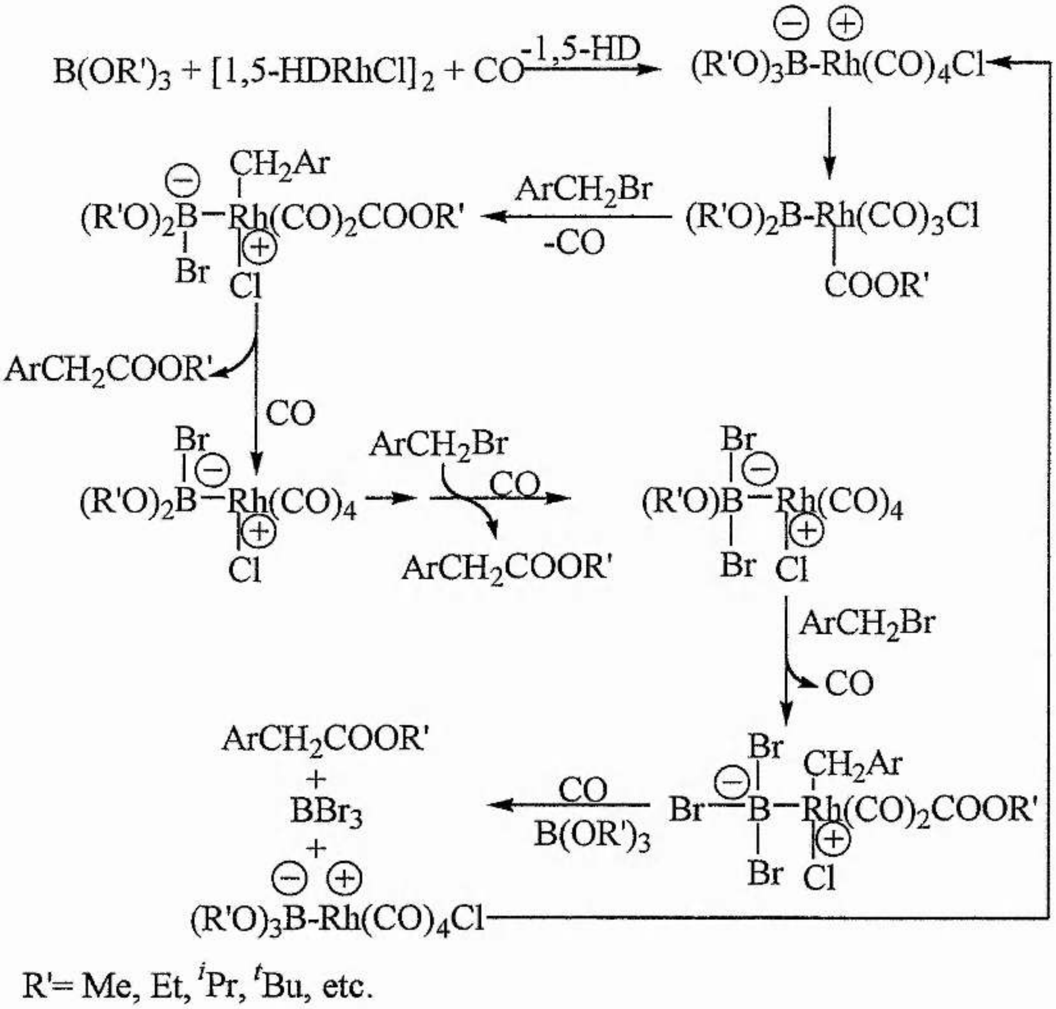
Alkyl derivatives of tetracarbonylferrates are powerful reducing agents for the reduction of nitro compounds giving amides.[63] The reactions were stoichiometric but led to the production of carbonylated products. Hence nitrobenzene reacted smoothly at room temperature with benzyltetracarbonylferrate to produce a phenylacetamide in 35% yield (figure 1.36).



(fig. 1.36)

If the nitrobenzene was replaced by iodine/ethanol then the product of the reaction was ethyl phenylacetate. It was thought that the first stage of this reaction was oxidative addition of iodine to alkyl ferrate(0) and that coordination of iodine caused the alkyl migration to one of the CO ligands to give an acyl iron(II) complex such as [$RCOFe(CO)_3I_2$] from which the acyl iodide could reductively eliminate. It was also thought that the reaction of nitrobenzene involved an oxidising step to iron(II) complexes.

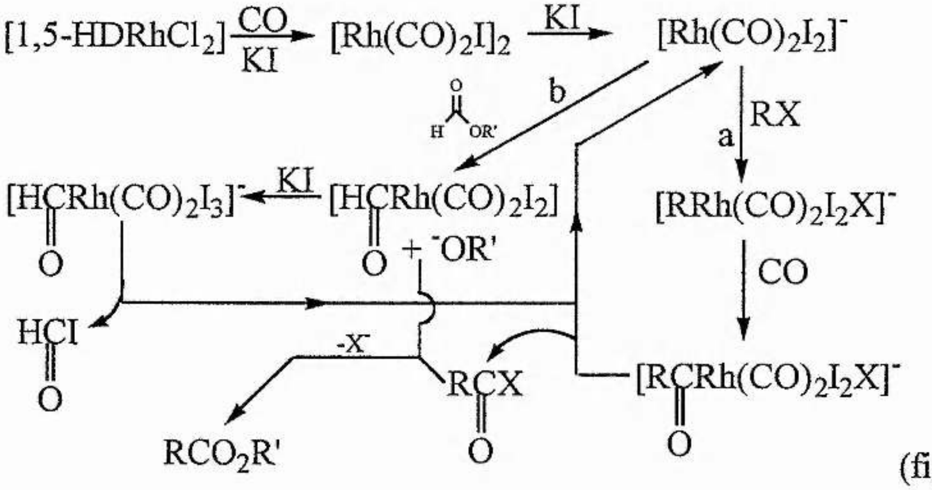
Benzyl bromides can react with trialkylborate esters and carbon monoxide in the presence of 1,5-hexadienerhodium dimer to esters in excellent yields.[64] The reactions took place at 75 °C under 1 bar CO for at least 12 hours using either the borate or heptane as the solvents. The reactions could also be carried out at room temperature but took three days to go to completion. A tentative mechanism was provided for the reaction which involved the use of three moles of benzyl bromide to 1 mole of trialkylborate ester (figure 1.37). The yields depended on which borate ester was used, with the best yields coming from tripropyl borate (up to 100%). This reaction was also successful with benzyl chloride, however, potassium iodide was needed as the co-catalyst presumably to generate $PhCH_2I$.



R'= Me, Et, ^{i}Pr, ^{t}Bu, etc.

(fig. 1.37)

In an attempt to improve the above reaction Alper *et al.* replaced the trialkylborate esters with formate esters as the source of the alkoxy function.[65] The reactions took place under approximately 6 bar CO with the alkyl formates acting as reagents and solvents at temperatures ranging from room temperature to 75 °C. The catalysts employed for the reaction were either $[1,5\text{-HDRhCl}]_2$ or the bimetallic system $[Pd(PPh_3)_4]$/ $[1,5\text{-HDRhCl}]_2$ depending on the substrates used. The carbonylation reaction did not proceed in the absence of carbon monoxide; therefore the formate ester carbonyl group was not the source of the carbonyl function in the product ester. The by-product of the reaction was thought to be the formyl halide although none was isolated from the reaction. A possible mechanism for the formation of both the ester and the formyl halide is given in figure 1.38.



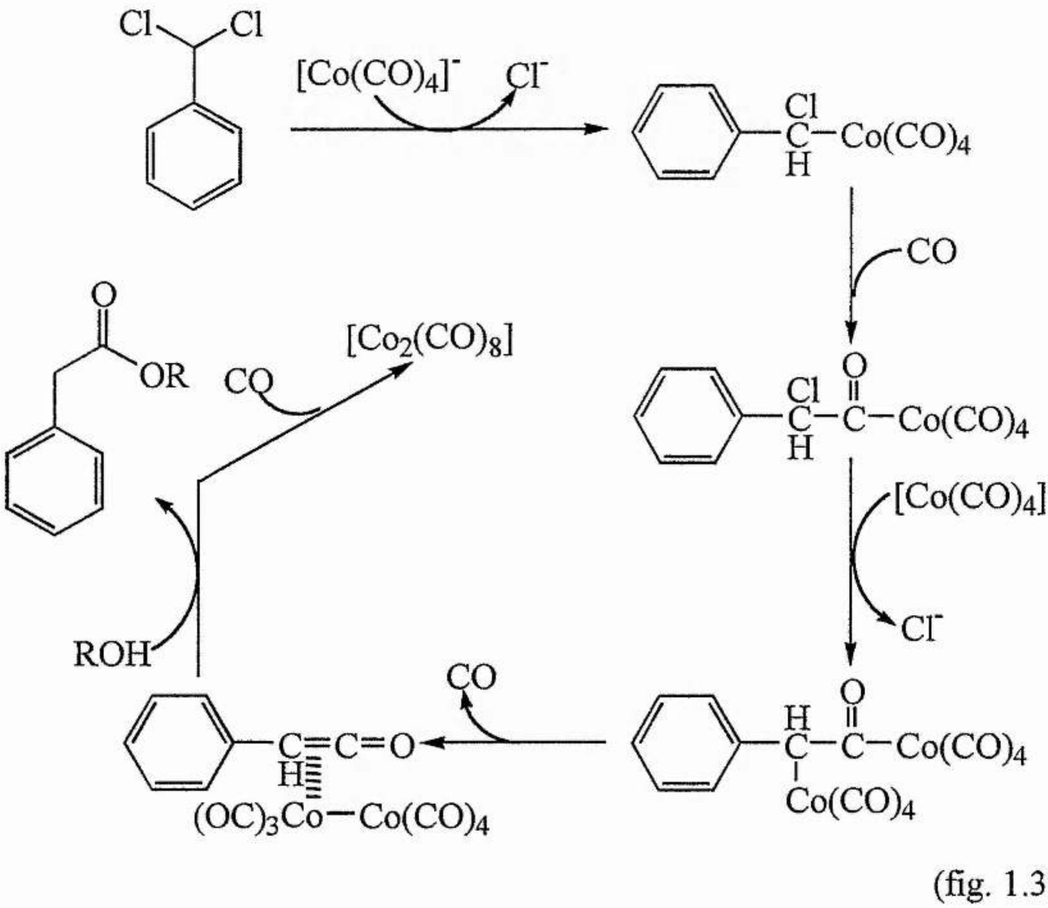
(fig. 1.38)

The active catalyst (which was the same as the Monsanto catalyst for methanol carbonylation[30]) could react with the benzylic halide, insert CO and reductively eliminate the acyl halide (route a) before reacting with the alkoxide ion generated from route b. There was good evidence for the processes occurring *via* route a. However, no evidence could be obtained for path b as the formate-halide could not be isolated. It was known however, that the carbonyl group in the ester came from CO and not the formate. The carbonylation reaction did not proceed in the absence of CO. This scheme also does not account for the bimetallic process.

Benzyl chloride can be catalytically carbonylated to ethyl phenylacetate (70% yield) in the presence of $[Pd(PPh_3)_2Cl_2]$, *n*-tetrabutylammonium iodide and sodium hydrogen carbonate under 2 bar CO.[66] The reaction was carried out in ethanol and was claimed to be an example of solid-liquid phase-transfer catalysis because the sodium hydrogen carbonate was insoluble in the ethanol and that the $^{t}Bu_4N^+I^-$ assisted in solubilising the $NaHCO_3$. However, $NaHCO_3$ is slightly soluble in ethanol[67]; it could be assumed that this reaction would proceed in the absence of $^{t}Bu_4N^+I^-$ albeit at a slower rate.

Benzylic halides and 3-chloroprop-1-ene can be similarly carbonylated under atmospheric pressure of CO using $[Co_2(CO)_8]$ as the catalytic precursor at 25 °C.[68] The reactions were carried out in benzene using tetrabutylammonium iodide as the phase transfer agent and sodium ethoxide as the base/nucleophile. The phase-transfer reagent was an essential part of the process as no carbonylation took place in its absence.

Phenyldichloromethane (benzal chloride) can be carbonylated to alkylphenyl acetates using $[Co_2(CO)_8]$ as the catalytic precursor in ethanol under 30 bar CO at 60-80 °C.[69, 70] The yields were dependent on the type of base used for the (K_2CO_3 gives the highest yields) and the pressure of CO used. If the pressure used was less than 30 bar then the yields dropped significantly. The proposed mechanism for the reaction is given in figure 1.39. A very reactive ketene intermediate was proposed that would have reacted instantly with the alcoholic solvent to give the product. Evidence for the presence of this intermediate was not given but the occurrence of a phenyl substituted diketene in the reaction products would have supported such a mechanism; however this would be unlikely to occur in an alcoholic solvent (a reaction could be carried out in an inert solvent to try and isolate a diketene). A labelling study using deuterated ethanol would be more effective in determining if a ketene intermediate was involved. If the temperature was raised to 100 °C then the yields of ester dropped and that of benzaldehyde, the by-product, increased dramatically.



(fig. 1.39)

Shim *et al.* also carbonylated phenyldichloromethane to alkyl phenylacetates using a system based on [Fe(CO)$_5$].[71] The reactions took place in the presence of a base at 40 °C under 1 bar CO for 20 hours in ethanol. Unlike the cobalt catalysed reaction the best base for this system was KOH. The yields for the iron based system were not as high as the ones reported for the cobalt system with the best yield being 40%. Nothing was said about the overall conversion or the presence of any by-products.

Benzyl halides can be carbonylated using either $[Co_2(CO)_8]$ or $[Pd(PPh_3)_2Cl_2]$ in *N, N, N', N'*-tetramethylurea (TMU) under 50 bar CO at 100 °C in the absence of base.[72] Ethanol was added to the mixture in a ten-times excess in order to obtain the ethyl phenylacetate as the final product in 47-84% yield. The by-product of the reaction was ethyl benzyl ether from the reaction of benzyl chloride with ethanol. The HCl produced in the reaction probably formed a salt with the TMU thus preventing its build up and possible deactivation of the catalyst. The opening sentence of this paper reads "How to replace the halogen atom of an alkyl halide with another functional group by means of a transition metal catalyst reaction remains an unsolved problem." How the authors came to this conclusion was a bit of a mystery because since the 1940's transition metal based catalytic systems have been replacing the halogen on alkyl halides in high yielding reactions!

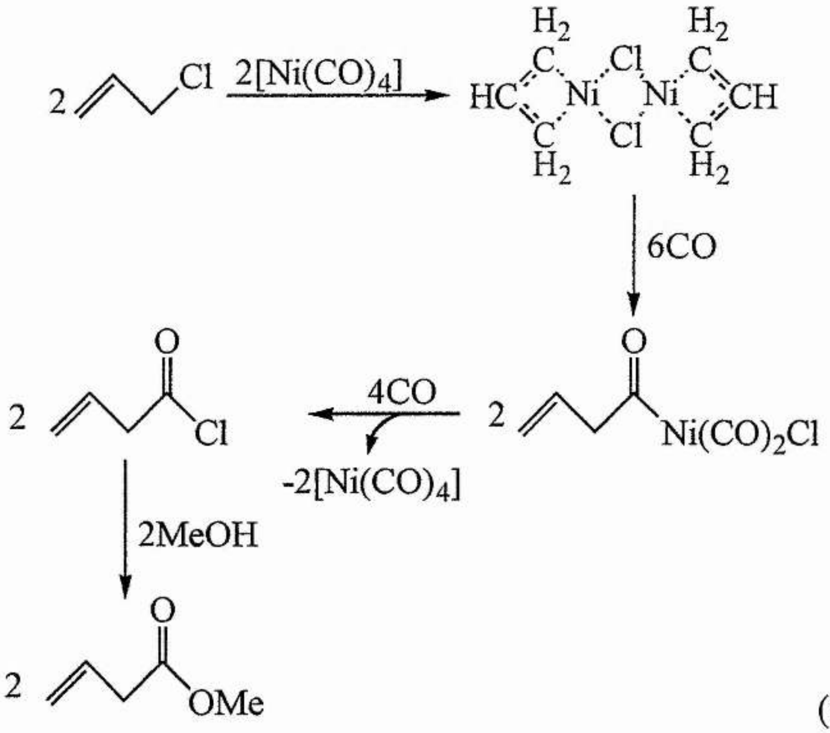
Acid fluorides are compounds that are not very frequently used. It may be because their synthesis requires difficult to handle fluorinating agents or the starting materials are very limited. However, a relatively simple method of producing phenylacetoyl fluoride, amongst other acid fluorides, has quite recently been published by Okano *et al.*.[73] The reactions took place at 100 °C under 1 bar CO in DMF (best of the solvents tried) for 8 hours in the presence of spray dried KF using $[Pd(PPh_3)Br_2]$ as the catalytic precursor. The system was very sensitive to changes in phosphine and temperature. The best systems involved the use of PPh_3 and $P(p\text{-}C_6H_4Cl)_3$ at temperatures around 100 °C. Temperatures below 100 °C resulted in a decreased yield. This suggested that the action of dissolved KF was more important than that of the surface of the solid. It was interesting to note that the addition of a small amount of water to the system increased the rate of absorption of CO though, not surprisingly, the selectivity to the acid fluoride decreased drastically in favour of phenylacetic acid (HF would have been the other product in this reaction).

Benzylic halides can be carbonylated to methyl phenylacetate in the vapour phase over charcoal supported $RhCl_3$/KI under a stream of CO at 150 °C in low to moderate yields.[74] The activity decreased in the order I>Br>Cl. The main products from the reactions were not esters but ethers (or alcohols if water replaced methanol). Small but not insubstantial amounts of toluene were also produced in the reactions.

3-chloroprop-1-ene and 3-bromoprop-1-ene can be carbonylated in the presence of π-allylnickel halide dimer in methanol solution to give methyl but-3-enoate.[75-77]

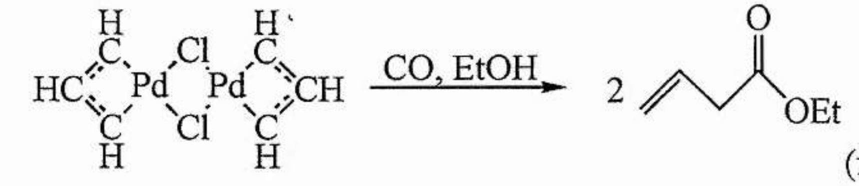
The first account of the carbonylation of 3-bromoprop-1-ene to give esters was by Fischer *et al.* in 1962. The reaction was carried out in methanol at 100 °C under 50 bar CO using $[Ni(CO)_4]$ as the catalytic precursor to give, what was claimed as a 70% yield of methyl methacrylate and 0.25% methyl crotonate. An intermediate in the reaction was thought to be π-allylnickel bromide dimer. Subsequently, Chiusoli *et al.* showed that methyl methacrylate was not formed in the reaction and that the product was in fact methyl but-3-enoate, the expected β,γ-unsaturated ester.

Heck *et al.* found that the system operated as efficiently at lower temperatures and pressures (0 °C, 1 bar of CO). It was found that the π-allylnickel bromide dimer was a very efficient catalyst for the production of β,γ-unsaturated esters. The reaction was thought to proceed as shown in figure 1.40.



(fig. 1.40)

Palladium can react with allylic chlorides to produce palladium complexes of similar structure to the nickel complexes shown above.[78] The π-allyl palladium chloride dimer can easily be synthesised and isolated from a reaction of 3-chloroprop-1-ene with $PdCl_2$. Tsuji *et al.* showed that this complex could react with CO in the presence of ethanol to produce the β,γ-unsaturated ester, ethyl but-3-enoate (figure 1.41).

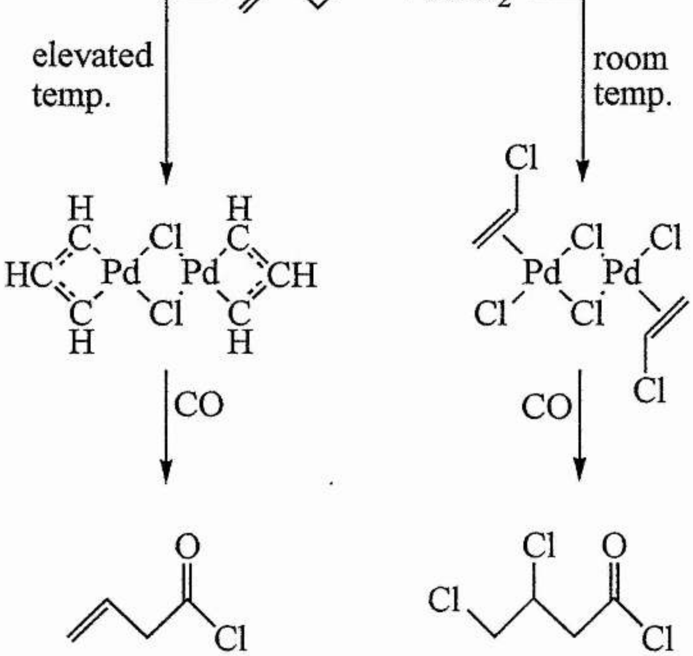


(fig. 1.41)

Tsuji and co-workers then applied the above palladium system to the catalytic carbonylation of 3-chloroprop-1-ene to give ethyl but-3-enoate, amongst other esters, depending on the conditions used for the reaction.[79] The reactions were carried out in either ethanol, benzene or THF using $PdCl_2$ as the catalytic precursor under 100 bar CO. Reaction times varied from 20-40 hours and temperatures from 80-130 °C. Ethyl but-3-enoate was formed in 47% yield when 3-chloroprop-1-ene was carbonylated at 120 °C for 40 hours. The product from the side reaction was ethyl but-2-enoate (5%) which undoubtedly resulted from the isomerisation of ethyl but-3-enoate. When the temperature was raised to 130 °C the yield of ethyl but-3-enoate dropped to 9% whilst that of the isomer remained at 5%. The main product from this reaction was ethyl 2-methylpropanoate (13%). Apparently, this was formed from propene produced by hydrogenolysis of 3-chloroprop-1-ene under the reducing action of the palladium-ethanol system. In order to try to eliminate the by-products the reaction was carried out in a benzene/THF solvent system. 3-butenoyl chloride was initially formed but this reacted immediately with THF, *via* a ring opening reaction, giving 4-chloro-1-butyl-3-butenoate thus eliminating the production of HCl (figure 1.42).

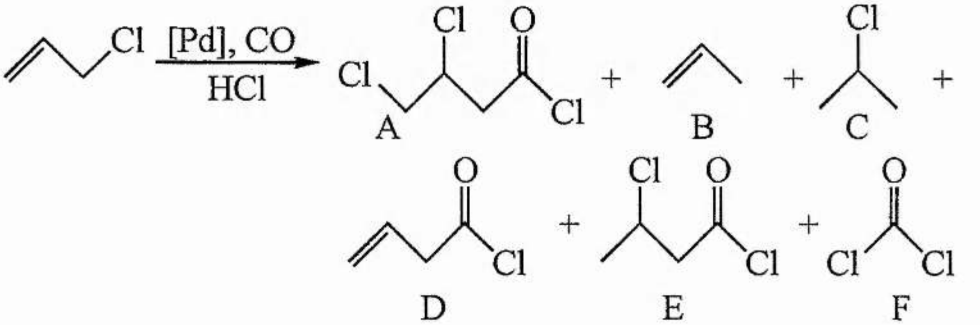
(fig. 1.42)

The reaction of 3-chloroprop-1-ene in benzene at elevated temperatures gave 3-butenoyl chloride, however, when the reaction was carried out at room temperature the only product was 3,4-dichlorobutanoyl chloride. The reaction at room temperature required a stoichiometric amount of palladium chloride. The differences were accounted for by the mechanism shown in figure 1.43. The structures of the intermediate palladium complexes were different because, at room temperature, 3-chloroprop-1-ene reacted as a simple alkene not as an allylic compound forming the alkene-palladium chloride complex.[80, 81] This reacted with CO and reductively eliminated the 3,4-dichloroacyl chloride.



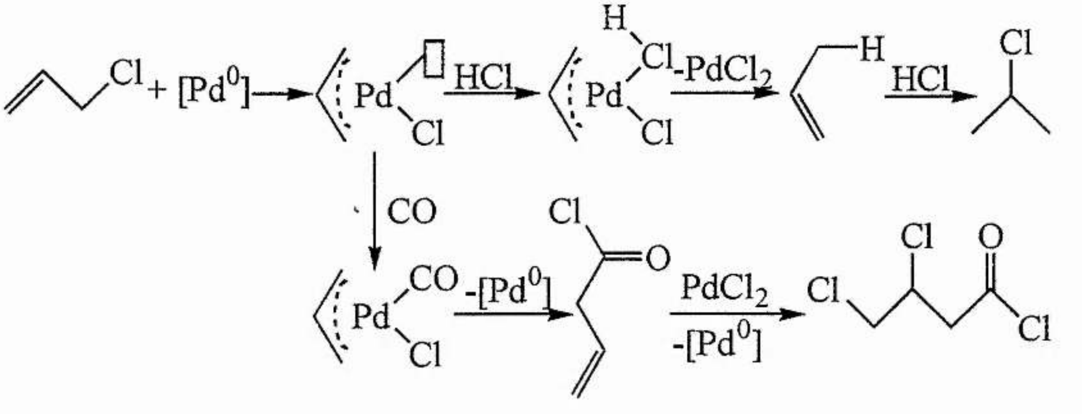
(fig. 1.43)

The simultaneous chlorination-carbonylation of allyl chlorides was a reaction first recorded by Tsuji *et al.* (see above). This reaction was, however, stoichiometric. Tkatchenko *et al.* obtained chloroacyl halides under mild conditions by catalytic carbonylation of 3-chloroprop-1-ene under CO (12-48 bar) and anhydrous HCl (9-24 bar).[82] The reactions were catalysed by various palladium compounds but mainly $PdCl_2$. The highest yields were obtained when aprotic solvents, such as CH_2Cl_2 or $C_2H_2Cl_2$, were used at temperatures above 60 °C. The products obtained from the reactions are given below in figure 1.44.



(fig. 1.44)

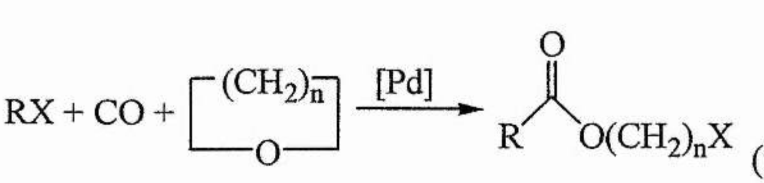
The dichlorinated acyl product, A, was formed in the greatest yields with propene and 2-chloropropane being formed in almost equal amounts. 3-butenoyl chloride, D, was formed in small amounts whilst only traces of E and the highly toxic phosgene, F, were formed in the reaction. The proposed mechanism of the reaction to give the dichlorinated acyl product is shown below (figure 1.45). The formation of the 3,4-dichlorinated ester was though to occur *via* reaction of the double bond of 3-butanoyl chloride with palladium dichloride.



(fig. 1.45)

1-chlorobut-2-ene and 3-chlorobut-1-ene gave the same product, methyl 3,4-dichloropentanoate, therefore it was reasonably assumed that the catalytic cycle involved a π-allylic palladium complex. However, at elevated temperatures an equilibrium existed between crotyl chloride and 3-chloro-1-butene thus the oxidative addition to the palladium complex of one of the isomers could be favoured thus pulling the equilibrium over to one side.

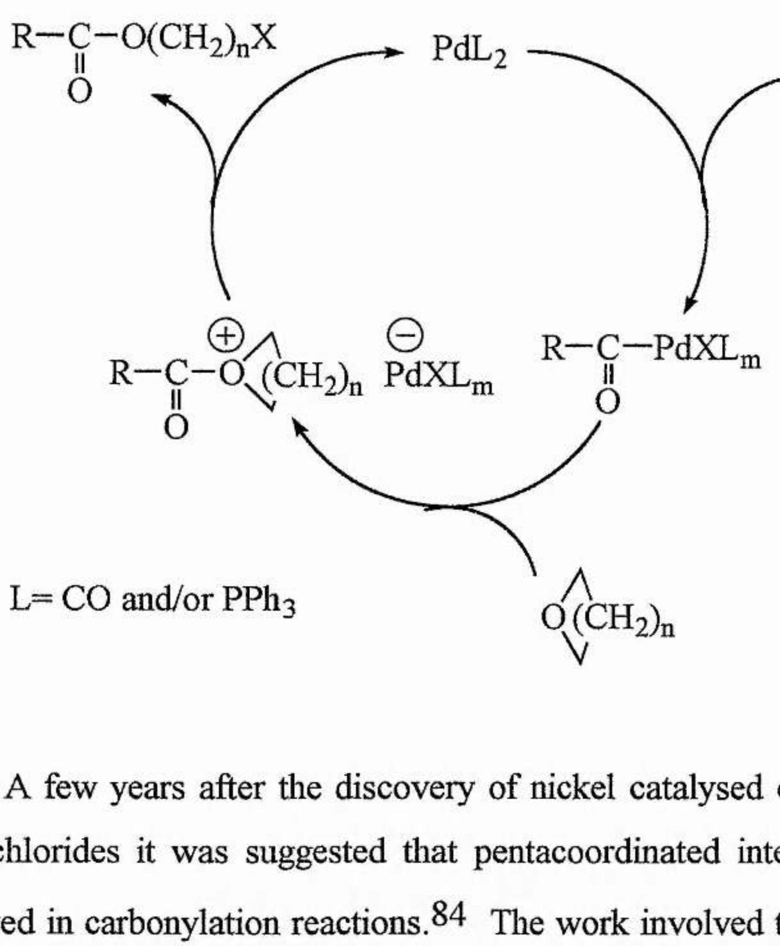
Halohydrin esters were formed when benzyl chloride was carbonylated in the presence of cyclic ethers, which were used as solvents for the reaction (figure 1.46).[79, 83] It was found that the smaller ringed cyclic ethers reacted more readily than the larger ringed ethers.



(fig. 1.46)

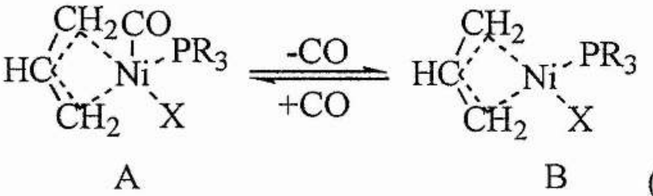
The reactions were carried out under 20 bar of CO at 130 °C for 16 hours using $[PhPdI(PPh_3)_2]$ as the catalytic precursor. Yields ranged from

8.1-71.9% with the greater yielding reactions carried out with the smaller ringed ethers. A possible mechanism for the system is shown in figure 1.47. The higher yields obtained when the smaller ringed ethers were used could have been due to the increased strain present in the ring system allowing easier cleavage of the C-O ether bond. It was noticed that when a small amount of water was added to the system the yields doubled. This could have been due to the water acting as a co-catalyst.



(fig. 1.47)

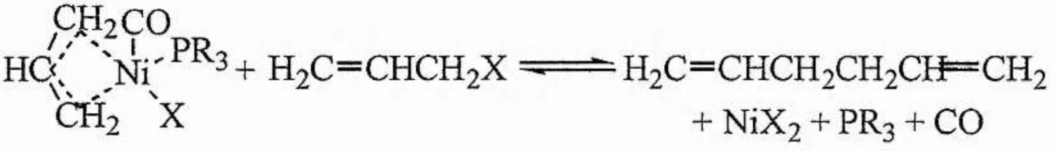
A few years after the discovery of nickel catalysed carbonylation of allyl chlorides it was suggested that pentacoordinated intermediates were involved in carbonylation reactions.[84] The work involved the use of triaryl (and trialkyl) phosphines and showed that 16 (A) and 18 (B) electron complexes involving CO were in equilibrium with each other (figure 1.48). Other equilibria involving CO, phosphine and σ- and π-allyl species were also thought to be operating involving 16 and 18 electron species.



(fig. 1.48)

It was found that when complex A was treated with CO in a solution of methanol, allyl methyl ether and methyl but-3-enoate were obtained. Therefore methanol could have reacted with A or B to give either the ester or the ether. HX was also produced in the reaction and 1,5-hexadiene would result, *via* the reaction shown in figure 1.49, if it was not neutralised.

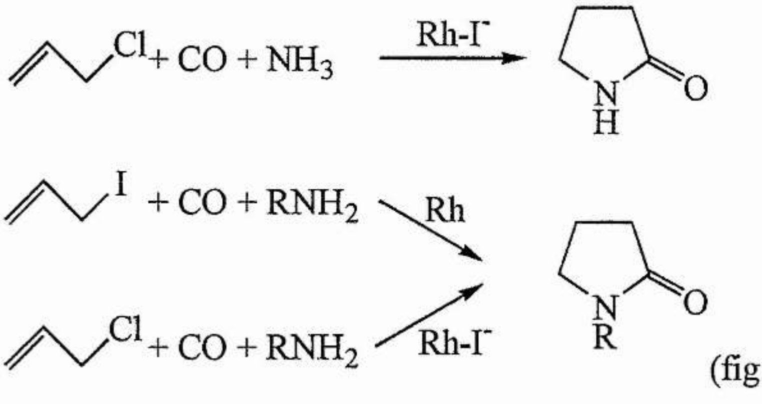
$$H_2C{=}CHCH_2OCH_3 + HX \rightleftharpoons H_2C{=}CHCH_2X + CH_3OH$$



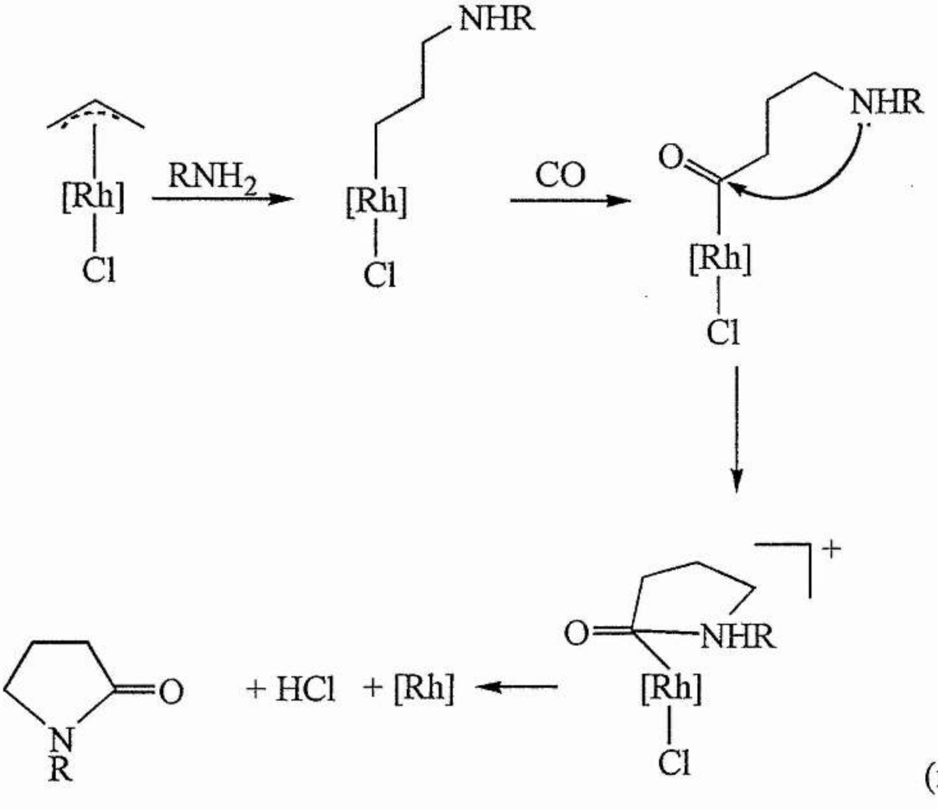
(fig. 1.49)

Scheben *et al.* showed that 3,7-dienoyl halides could be prepared by a platinum group metal catalysed carbonylation of allylic chlorides in the presence of a 1,3-butadiene.[85] The reactions took place between 35 and 110 °C and in a pressure range of 35-90 bar for about 40 hours. The catalysts for the reaction included platinum, palladium, osmium, iridium, rhodium and ruthenium as various salts, oxides, organic complexes and supported on an inert carrier. The best catalysts were obtained with the palladium halides which probably formed the halo-bridged bis-π-allyl palladium complex. Yields for the reaction were in the order of 24%.

Carbon monoxide insertion involving allylic halides may lead to the formation of both linear and cyclic products. The formation of these products was dependent upon the choice of catalyst and the presence or absence of a co-catalyst.[86] γ-lactams could be synthesised from allyl amines *via* carbonylation-cyclisation reaction using a rhodium based catalyst. The same compounds could be synthesised from allyl halides in the presence of ammonia or primary amines under 100-136 bar CO at 120 °C for 2-12 hours again using rhodium based catalysts e.g. $[RhCl(PPh_3)_3]$ and $[Rh(acac)_3]$ in CH_3CN (figure 1.50). These reactions gave the highest yields (which were comparable to the carbonylation reactions using allyl amines as the substrates) when allyl iodide was used or if an iodide promoter e.g. KI was used. A possible mechanism for the formation of the γ-lactams is given in figure 1.51.

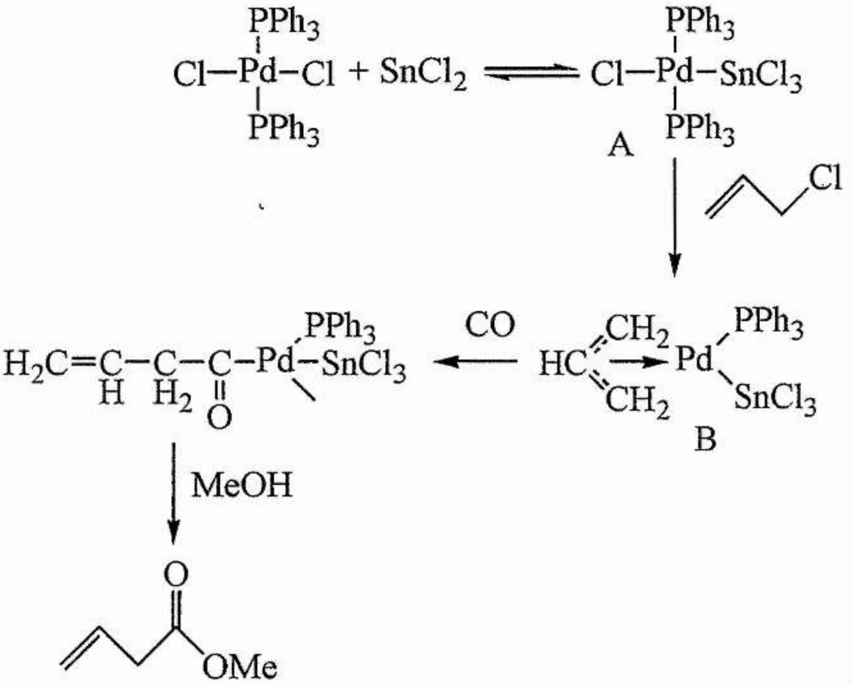


(fig. 1.50)



(fig. 1.51)

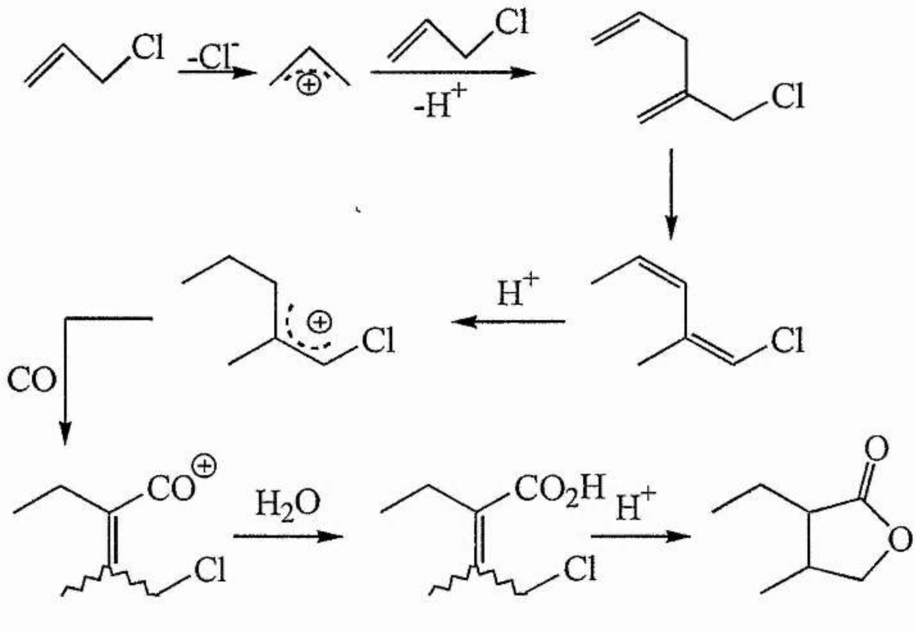
Vinylacetate esters could be synthesised from 3-chloroprop-1-ene using a palladium based bimetallic catalytic system in benzene-methanol. The reactions were carried out under 200 bar at 80 °C for 6 hours to yield approximately 75 mole % ester. Using [$PdCl_2(PPh_3)_2$] and $SnCl_2$ in benzene-methanol, 3-chloroprop-1-ene could be carbonylated to methyl but-3-enoate (figure 1.52) with methyl but-2-enoate as the by-product being produced *via* double bond isomerisation.



(fig. 1.52)

Complexes A and B could be isolated. The high *trans* effect of the $SnCl_3$ ligand labilised the coordinated chloride thus on addition of 3-chloroprop-1-ene complex B formed. The complex then went through π–σ rearrangement and CO insertion to produce the corresponding Pd-acyl species. This step was favoured by high CO pressures and the presence of strongly coordinating ligands such as PPh_3.

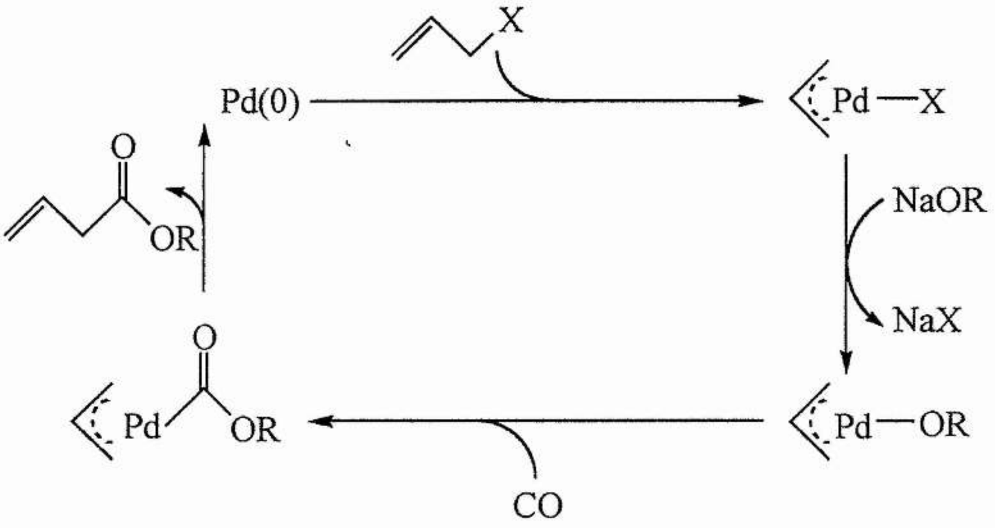
3-chloroprop-1-ene can be carbonylated under 69 bar CO at 50 °C to give 3-ethyl-4-methyl-2(5H)-furanone (a lactone) in 10% yield.[87] The reaction was carried out using a strong acid as both the solvent and the catalyst (no metals present at all!). The reaction was thought to proceed *via* the following mechanism (figure 1.53)



(fig. 1.53)

When 1-chloro-2-butene and 3-chloro-1-butene were carbonylated under the same conditions γ-valerolactone was the product, suggesting that a symmetrical allyl (cation, radical or anion, but most likely cation in the strong acidic medium) was the key intermediate.

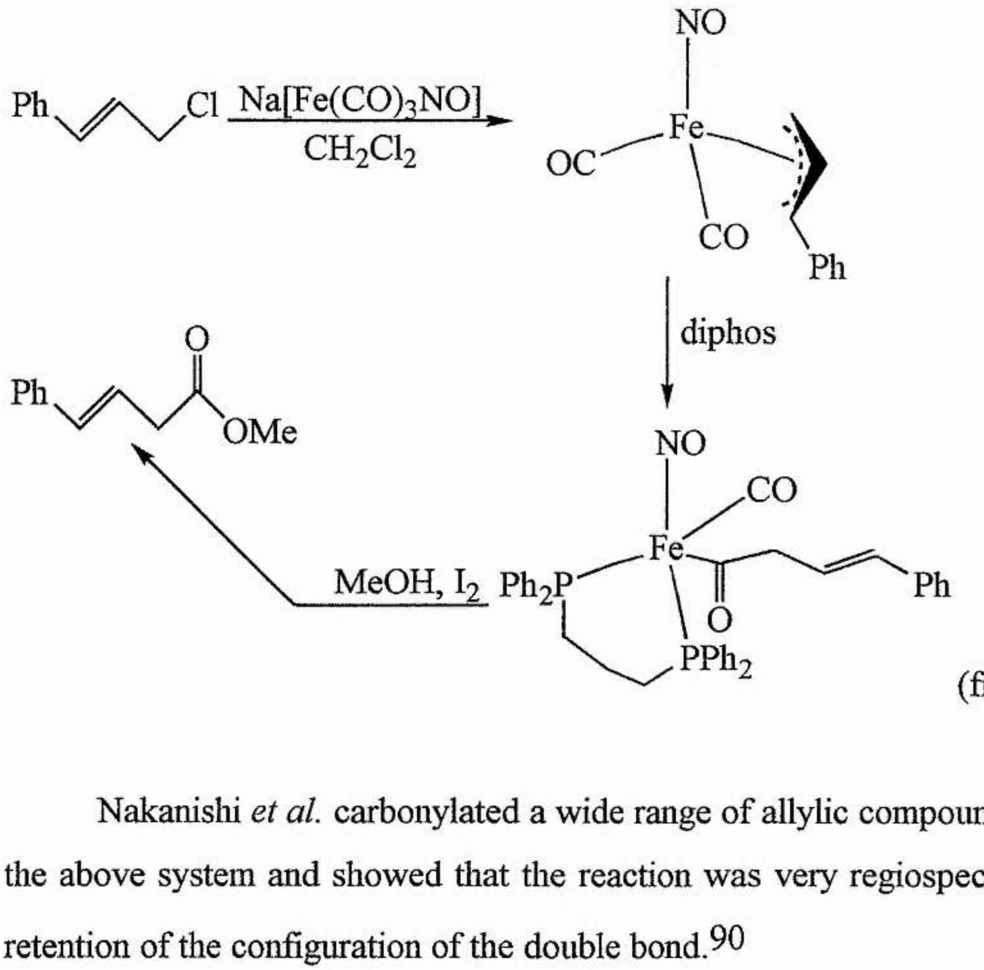
In order to expand the range of reactions discussed in the section on carboxylic acids, Okano *et al.* carried out alkoxycarbonylation reactions to synthesise esters rather than carboxylic acids.[88] These reactions were carried out in methanol (30 °C, 1 bar CO) with the phosphine free palladium complex, $[(\pi\text{-}C_6H_5CHCHCH_2)PdCl]_2$ being the best catalyst. Sodium methoxide was added dropwise to keep the concentration in the reaction solution low at all times. Yields with all the allylic compounds were high, with chlorides giving better yields than bromides. The suspected mechanism for the reaction is given in figure 1.54. The mechanism proposed was again one involving insertion of CO into the palladium-alkoxide bond rather than insertion into the palladium-alkyl bond.



(fig. 1.54)

Benzylic and allylic halides can be carbonylated in high yields using tricarbonylnitrosyl ferrate anion in stoichiometric amounts.[89] Sodium tricarbonylnitrosyl ferrate was prepared from iron pentacarbonyl, sodium methoxide and sodium nitrite, however, as this compound was *extremely* air sensitive and was found to decompose explosively, the more stable tetrabutylammonium salt was used in its place. The reactions took place at 50 °C under 4 bar CO with a three molar excess of base (K_2CO_3) for 15 hours, however, if triphenylphosphine was added to the system no CO was needed and the reaction took place at room temperature. With benzyl halides yields between 85 and 87% were obtained, however, when PhCH(Me)X were used the yields dropped to less than 50% due to the formation of styrene through β-hydride elimination. In order to produce β,γ-unsaturated esters from allylic halides a two step process was needed. An acyliron complex was first formed in a reaction of diphos and an allylic halide with the tricarbonylnitrosyl ferrate anion (figure 1.55). Methanol was added to the solution only after the first stage was complete to give the β,γ-unsaturated ester. If methanol was added without the presence of diphos the corresponding ether was obtained and not the ester.

The carbonylation of benzyl bromide was also attempted with a catalytic amount of tricarbonylnitrosyl ferrate anion. The system gave a maximum turnover of five over a six hour period. Increasing the temperature, time and CO pressure did not increase the amount of carbonylated product.



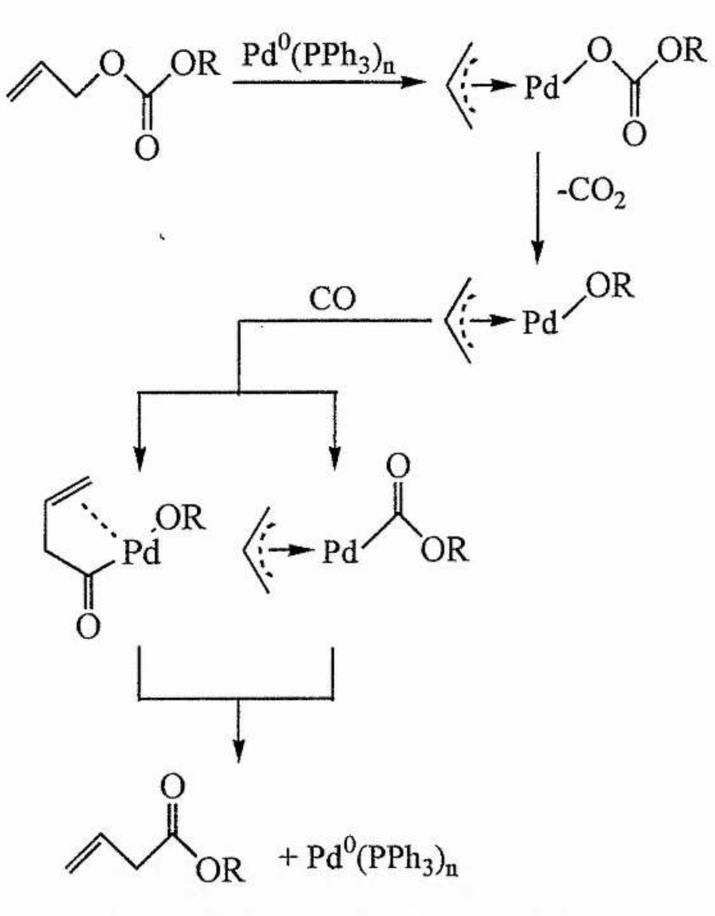
(fig. 1.55)

Nakanishi *et al.* carbonylated a wide range of allylic compounds using the above system and showed that the reaction was very regiospecific with retention of the configuration of the double bond.[90]

1.4.2 Carbonylation of Allylic Compounds Other Than Halocarbons to Yield Esters

It is worth mentioning the carbonylation of certain other allylic substrates to yield β,γ-unsaturated esters. Allylic carbonates are useful starting materials in palladium-catalysed carbonylation reactions. They undergo oxidative addition to palladium(0) compounds under mild conditions to form the corresponding π-allylic complexes by C-O cleavage. The alkyl carbonate anion then undergoes spontaneous decarboxylation to give the corresponding alkoxide (and CO_2). CO insertion must occur first. This can then act as a nucleophile, attacking the carbonylated π-allylic complex, to give the corresponding β,γ-unsaturated ester (figure 1.56).

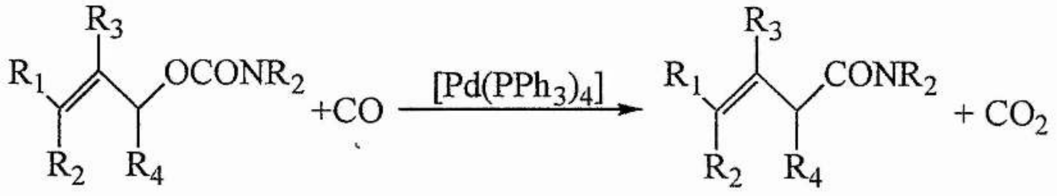
The stoichiometric carbonylation of allylic carbonates was first described by Milstein[91] and co-workers but Tsuji *et al.* described the first catalytic carbonylation.[92, 93] The reactions took place at 50 °C under 1-10 bar CO using $[Pd(OAc)_2]$ and PPh_3 as the catalyst precursors. If the temperature was increased to 80 °C exclusive formation of allyl alkyl ether resulted. No reaction took place in the absence of PPh_3. The best yields were obtained in the absence of solvents, in fact, reactions involving the use of solvents gave rather poor results. The reaction was thought to proceed *via* the mechanism shown in figure 1.56.



(fig. 1.56)

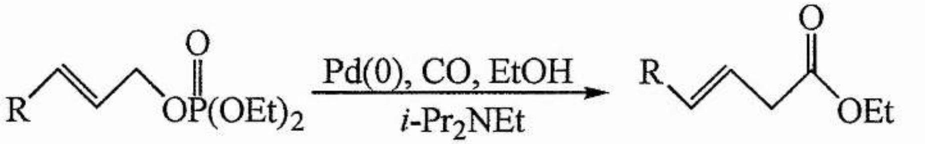
It is still unclear whether ester formation proceeded *via* carbon monoxide insertion into the metal-allyl bond followed by attack of the alkoxide or by alkoxide attack on the carbonyl ligand followed by reductive elimination.

Diethylcarbamic acid allylic esters are a very similar class of compound to allylic carbonates and these can also be carbonylated under relatively mild conditions.[94] The carbamates were prepared from the corresponding allyl alcohols and diethylcarbamoyl chloride. The decarboxylation-carbonylation reactions took place over 60 hours at 100 °C under 50-80 bar CO using [Pd(OAc)$_2$] and PPh$_3$ as the catalytic precursors (figure 1.57). The yields varied between 28 and 76% depending on the diethylallylcarbamate used.



(fig. 1.57)

Allylic phosphates can be catalytically alkoxycarbonylated to give the corresponding β,γ-unsaturated esters under mild conditions (figure 1.58).[95, 96] The reactions took place under 1 bar CO at 50 °C in ethanol in the presence of a tertiary amine using a palladium catalyst. The base was required to remove the phosphoric acid liberated from the reaction. No product was obtained without the use of a base.



(fig. 1.58)

1.5 Conclusions on the Carbonylation of Allylic and Benzylic Halides

The carbonylation of allylic and benzylic halides to yield aldehydes has not been extensively studied. The catalysts used for these reactions tended to be based mainly on cobalt and palladium. Hydroformylation of alkenes is by far the most widely studied and used technique for producing aldehydes *via* transition metal catalysis.

The production of ketones *via* transition metal catalysed carbonylation of allylic and benzylic halides has been more extensively studied. The reactions were very similar to those involved with the synthesis of aldehydes, the difference being that carbanions or carbocations were used in place of hydride or proton sources. As a result of this the reactions were more wide ranging and the catalysts more varied with iron and nickel being used along with the more common palladium and cobalt based systems. The production of cyclic ketones is now seen as an important subject due to their relevance to natural product chemistry with transition metal catalysed reactions now becoming a routine part of multistage syntheses.

Carboxylic acid synthesis is the most widely researched area of homogeneously catalysed carbonylation of halocarbons, one has only to look into the research into acetic acid production to verify this. The range of catalysts for the production of carboxylic acids is staggering, but again, most seem to be based on palladium systems. Recent trends of trying to 'heterogenise homogeneous catalysts' by using biphasic, phase-transfer and polymeric systems have tended to improve yields and allowed reaction conditions to become milder.

The synthesis of carboxylic acid esters is very similar to that of carboxylic acids the difference being that the reactions have usually been carried out in an alcoholic solvent in the absence of water.

The catalysts have changed quite dramatically since the early seventies. Pre 1970 most of the transition metal catalysts were based on the transition metal carbonyls. These catalysts required forcing conditions and most exhibited low activity as well as being highly toxic (nickel tetracarbonyl was the best example of this), very air-sensitive and very volatile. Thus they needed to be handled very carefully. This also meant that they were difficult to separate from the reaction mixture after the reaction was completed. However, post 1970 saw an evolution in the type of transition metal catalyst being used. The use of phosphine ligands became popular after the discovery that transition-metal/phosphine catalysts were very active, air-stable and involatile for a wide range of reactions (probably the best known and widely used are Wilkinson's catalyst for hydrogenation and $[RhH(CO)(PPh_3)_3]$ for hydroformylation reactions). These, on-the-whole were easily prepared and handled and hence within a short space of time were being found on the laboratory benches of organic chemists.

The catalysts most commonly used for the carbonylation of halocarbons seem to be based on palladium. Cobalt and nickel based systems are also used but not nearly as frequently. Iron based catalysts are not used very often for carbonylation reactions. Catalytic systems for the carbonylation of allylic and benzylic halides based on rhodium systems are also not very common despite the fact that more than half of the world's acetic acid is produced by a process based on rhodium. One of the reasons for this could possibly be due to the high price of rhodium.

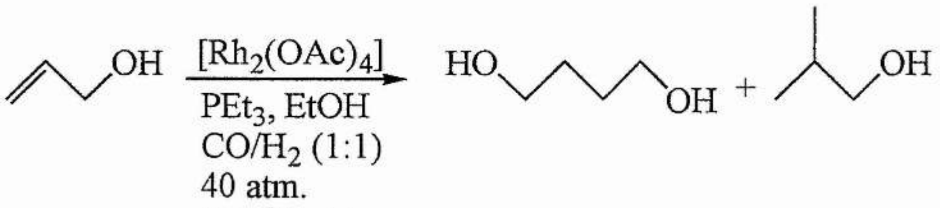
The mechanisms for the carbonylation of the allylic and benzylic halides have, on the whole, been very similar to each other. However, not much work seems to have been carried out on the elucidation of 'the suspected' mechanisms. Once one feasible mechanism was quoted on a particular type of reaction all other similar reactions 'were suspected' to follow the same mechanistic pathway. The mechanisms worked very well for the formation of the main product but what was lacking most was an explanation on the formation of the by-products from these reactions. If these were investigated in a little more detail then it may be possible to reduce the amount of by-products formed and enhance the production of the products.

CHAPTER 2

2. AUTOCLAVE REACTIONS

2.1 Introduction

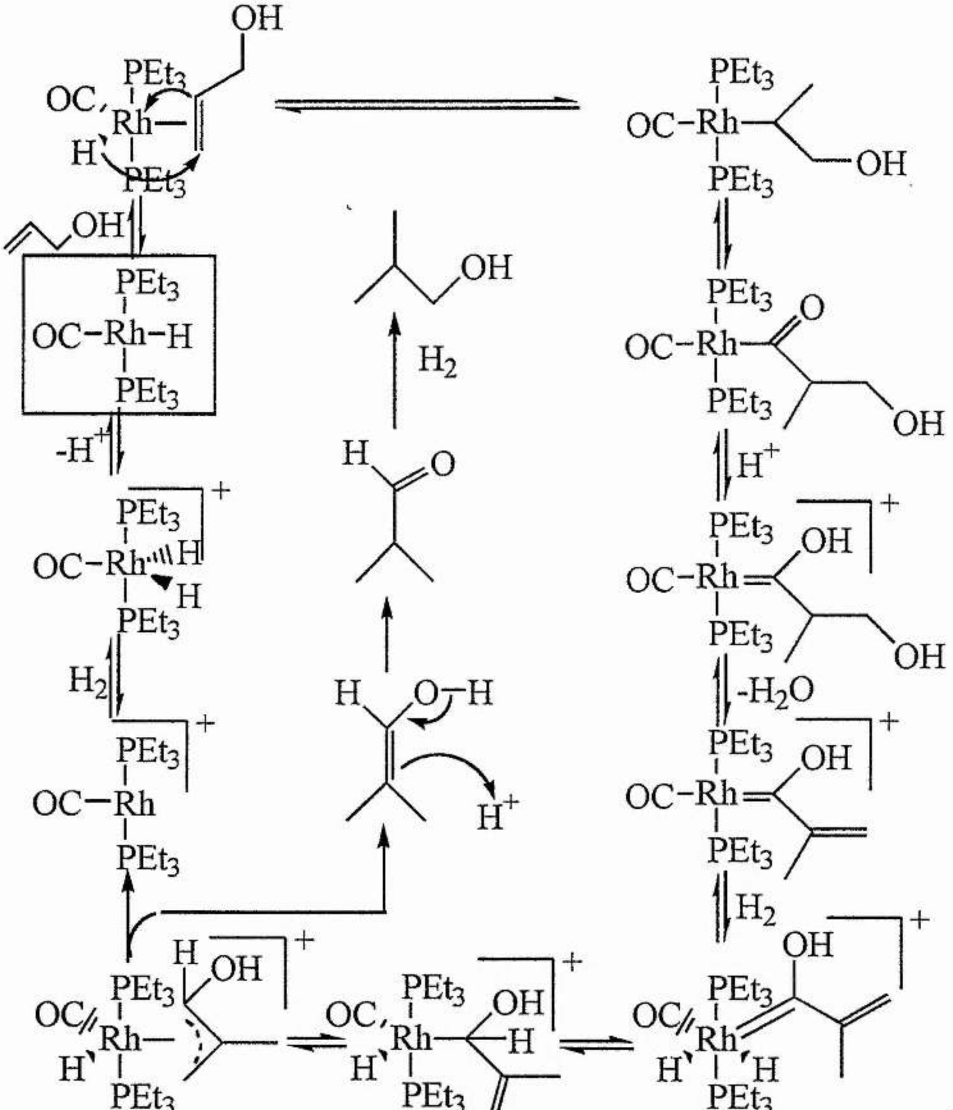
It is known that prop-2-en-1-ol can be hydrocarbonylated to butan-1,4-diol and 2-methylpropan-1-ol using a rhodium-triethylphosphine based catalyst in ethanol (figure 2.1).[97-99]



(fig. 2.1)

The initial aim of this project was to produce butan-1,4-diol from prop-2-en-1-ol thus bypassing the usual aldehyde intermediates. This was successfully achieved by using a rhodium-triethylphosphine catalytic system. An additional benefit of this system was obtaining 2-methylpropan-1-ol rather than 2-methylpropan-1,3-diol along with the butan-1,4-diol. This made the separation of the products very much simpler as the boiling points of the two components differed by approximately 130 °C.

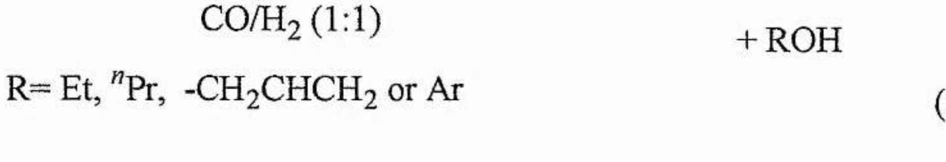
The mechanism for the formation of the branched chain alcohol using prop-2-ene-1-ol involved a carbene intermediate and loss of water thus stabilising the conjugated system which could then be hydrogenated (figure 2.2).[99]



(fig. 2.2)

Simpson investigated [97-99] the use of other substrates with the same propenyl functional group in an attempt to expand the catalytic system. Substrates investigated included propenyl halides, ethers and nitriles.

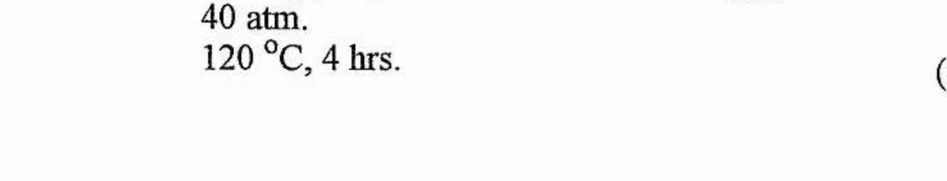
When aryl propenyl ethers were added to the system the products analogous to the prop-2-en-1-ol reaction were obtained along with butan-1-ol, the origin of which was not investigated. Similar products were obtained when alkyl propenyl ethers were used under the same conditions (figure 2.3).



R= Et, ^{n}Pr, -CH$_2$CHCH$_2$ or Ar

(fig. 2.3)

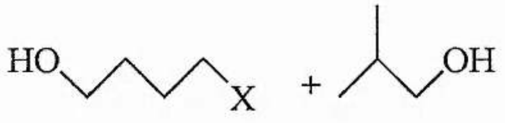
Prop-2-enylnitrile did not react in the same way as the alcohol and esters. The major product (>50%) of the reaction was propanenitrile through hydrogenation of the propenyl double bond. The other product was an acetal (figure 2.4). The mechanism of the formation of the acetal in this and other reactions is still under investigation. Other products from the reaction involving prop-2-enylnitrile included, in small quantities, straight and branched chain aldehydes and alcohols and also a branched chain acetal similar to the one in figure 2.4.



(fig. 2.4)

2.1.1 Attempted Hydrocarbonylation of Propenyl Halides

The hydrocarbonylation of propenyl halides was expected to produce products analogous to those obtained from prop-2-en-1-ol (figure 2.5).

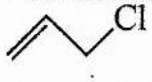
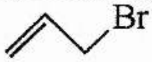
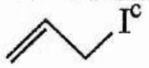
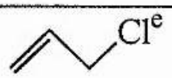
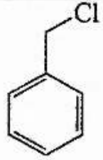
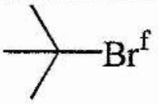
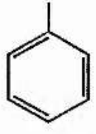


X= Cl, Br, I (fig. 2.5)

However, when the reaction was carried out using 1-chloroprop-2-ene under the same conditions as for the hydrocarbonylation of prop-2-en-1-ol none of the anticipated products were obtained. The products that were obtained appeared to have been formed via a carbonylation reaction, suggesting that the reaction should still proceed in the absence of hydrogen. When synthesis gas was replaced by CO the same products were produced, as was predicted. As can be seen in chapter 1, there is plenty of precedence for this type of reaction in the literature.

The main products obtained from the carbonylation of the propenyl halides, reported by Simpson, were ethyl but-3-enoate and ethyl propenyl ether along with substantial amounts of ethyl halides and propene (see table 2.1). Other substrates were also investigated in the system. The results are summarised in table 2.1.

Table 2.1 Simpson's Results from the Rhodium-Triethylphosphine Catalysed Carbonylation of Various Alkyl Halides[a]

R-X	Products (%)			
Substrate	Conversion %	RCO_2Et	ROEt	EtX
	64	33	7	b
	91	55	27	b
 [c]	88	16	57	91
 [d]	53	19	11	b
 [e]	sig.	0	sig.	b
	43	2	41	b
	0	-	-	-
	11	0	16	-
 [f]	15	0	13	b
	-	-	-	-

[a] $[Rh_2(OAc)_4.2MeOH]$ (2×10^{-5} mol), PEt_3 (4×10^{-4} mol), RX (1.0 cm^3), CO (40 bar), 120 °C, 4 hours. Propene was also detected as a reaction product. Due to its high volatility it was not quantified, propene is assumed to account for the mass imbalance seen on the table.

[b] Not quantified. Difficult to separate EtCl, EtBr and EtOH on glc column used.

[c] Trace of ethyl propanoate observed.

[d] No $[Rh_2(OAc)_4.2MeOH]$ or PEt_3; sig. = significant quantity (not quantified).

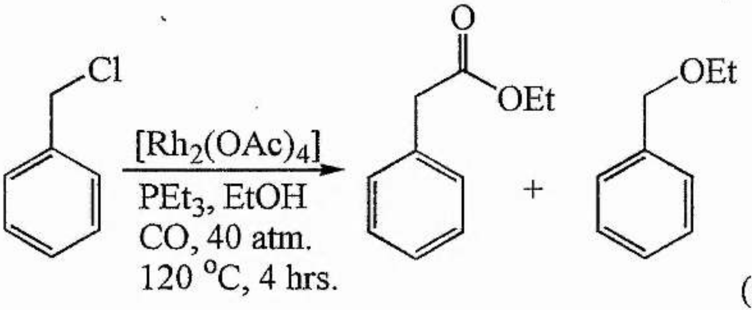
[e] $[RhCl(CO)PEt_3)_2]$ as catalyst with no added phosphine.

[f] Trace of 2-methylpropene observed.

These initial results suggested that the overall reactivity of the propenyl halides was in the order of RI > RBr > RCl (R= $-CH_2CHCH_2$) and that the selectivity towards the ester was determined by the extent of the ether forming reaction. A few points need to be noted from these initial reactions. The ester produced was mainly ethyl but-3-enoate with only a small amount of the isomerised product, ethyl but-2-enoate, present at the end of the reaction. The selectivities of $\beta,\gamma:\alpha,\beta$ were similar or better than the most selective of the carbonylation reactions reviewed in chapter 1. The carbonylation reactions were also carried out in the absence of a stoichiometric amount of base unlike the majority of the carbonylation reactions involving alkyl or aryl halides. Base is required to remove the HX formed in the reaction otherwise the catalyst could be deactivated *via* addition of HX across the metal centre. In this system, however, the HX reacted with the solvent to produce EtX and H_2O, thus effectively removing it from the catalytic cycle.

Attempts were made to carbonylate a variety of other halides using this new system in order to test the scope of the reaction. Chloropropane gave no carbonylation products and no ether was detected. Similarly no carbonylation products were obtained for either iodoethane or *tert*-butyl bromide but a significant amount of the corresponding ethyl ethers were obtained from these reactions. Therefore it was assumed that the allyl moiety from the allylic halides had some sort of stabilising influence on the intermediate Rh(III) complexes.

In order to test the above assumption Simpson used benzyl chloride as a substrate. As can be seen from table 2.1 a carbonylated product, ethyl phenylacetate, was obtained from the reaction along with benzyl ethyl ether (figure 2.6).

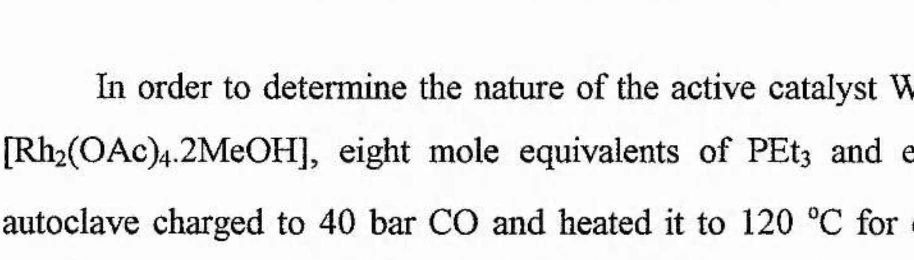


(fig. 2.6)

The carbonylation of chlorobenzene was attempted to complete the series of reactions involving halocarbons. As expected no reaction of any kind was observed.

2.2 Reactions using [$Rh(OAc)(CO)(PEt_3)_2$] as the Catalyst

In order to determine the nature of the active catalyst Weston placed [$Rh_2(OAc)_4.2MeOH$], eight mole equivalents of PEt_3 and ethanol in an autoclave charged to 40 bar CO and heated it to 120 °C for one hour.100 The rhodium complex obtained at the end of the reaction was the square planar acetatocarbonylbis(triethylphosphine) rhodium (I) (figure 2.7).



$$[Rh_2(OAc)_4.2MeOH] + 2PEt_3 \xrightarrow[120\ ^{\circ}C]{EtOH,\ CO} OC{-}\underset{\underset{PEt_3}{|}}{\overset{\overset{PEt_3}{|}}{Rh}}{-}OAc$$

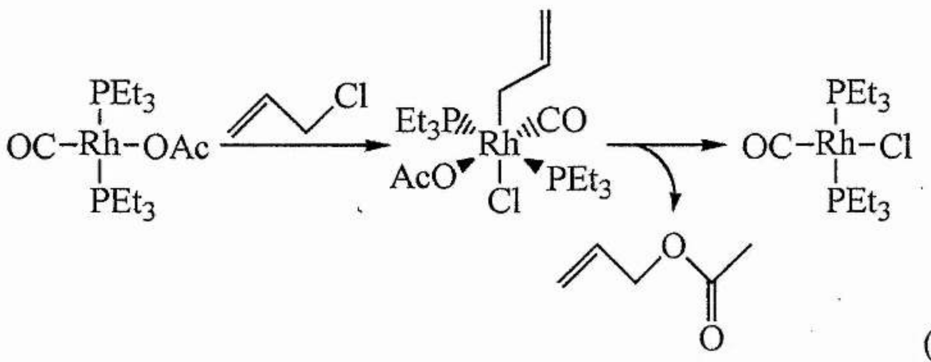
(fig. 2.7)

It was decided that subsequent experiments would be carried out using the preformed catalyst complex rather than the catalytic precursors to eliminate the possible effects of adding excess triethylphosphine to the system e.g. the formation of propenyltriethylphosphonium halides. This also made the study of the mechanistic aspects of the system much less complicated.

Another change was made in the method of heating the autoclaves. Simpson's method involved placing charged autoclaves in an oven preheated to 120 °C. Studies showed that the time taken for the inside of the autoclave to reach 120 °C was approximately 2 hours. In order for this time to be reduced heating bands were employed. Thus the time taken for the inside of the autoclave to reach 120 °C was now only in the order of 10-15 minutes.

2.2.1 Carbonylation of 1-chloroprop-2-ene

The carbonylation of 1-chloroprop-2-ene in the presence of $[Rh(OAc)(CO)(PEt_3)_2]$ gave ethyl but-3-enoate, propenyl ethyl ether, chloroethane and propene in the similar quantities as for the reaction carried out by Simpson using *in situ* formation of the catalyst from $[Rh_2(OAc_4).2EtOH]$ and PEt_3. The only difference was that a small amount of prop-2-enyl ethanoate was formed in the reaction. Quantitative analysis showed the amount to be equivalent to that of $[Rh(OAc)(CO)(PEt_3)_2]$ (~0.0001 mole) that was added to the autoclave at the beginning of the reaction. A possible explanation for this was that the 1-chloroprop-2-ene had oxidatively added to the rhodium (I) complex and immediately reductively eliminated the ester, forming $[RhCl(CO)(PEt_3)_2]$, as shown in figure 2.8.



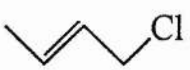
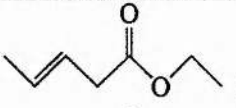
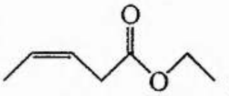
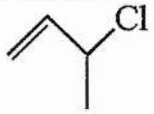
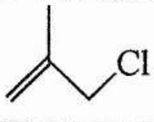
(fig. 2.8)

The above reaction suggested that if chloride-acetate exchange on the rhodium complex could be effected, the catalytic production of prop-2-enyl ethanoate from 1-chloroprop-2-ene and e.g. sodium acetate should be possible. To test this theory a range of reactions of simple salts with 1-chloroprop-2-ene or benzyl chloride in the presence of catalytic amounts of $[Rh(OAc)(CO)(PEt_3)_2]$ were investigated. All the reactions were carried out with an 8.0×10^{-3} mol dm^{-3} solution of the catalyst in ethanol with a 200 times mole excess of both the substrate and the salt. The solutions were heated under an atmosphere of argon either under reflux or in a sealed bottle for four hours. The results for these experiments are discussed in section 2.5.

2.2.2 Carbonylation of Unsymmetrical Allylic Halides

Various carbonylation reactions were carried out with unsymmetrical halides to try and establish if η^3-allyl intermediates were involved in the catalytic system. The allylic halides used for these reactions were 1-chlorobut-2-ene, 1-bromobut-2-ene, 3-chlorobut-1-ene and 3-chloro-2-methylprop-1-ene. The reactions were all carried out at 120 °C under 40 bar carbon monoxide using ethanol as the solvent and [Rh(OAc)(CO)(PEt_3)$_2$] as the catalyst. Reactions were also carried out in the absence of the catalyst. Results from these reactions are shown in table 2.2.

Table 2.2 Products and Yields from Carbonylation of Unsymmetrical Allylic Halides[a]

RX	Conversion	Products
	100%	 (47%) (0%)^{u}  (8%) (0%)^{u}  (17%)^{b} (2%)^{u} C_8 Dimers (10%) (11%)^{u}
	100%	Ethyl *E*-pent-3-enoate (31%) (0%)^{u} Z-Ethyl pent-3-enoate (8%) (0%)^{u} Ethyl 1-methylprop-2-enyl ether (22%)^{b} (5%)^{u} C_8 Dimers (19%) (19%)^{u}
	100%	Ethyl *E*-pent-3-enoate (61%) (0%)^{u} Z-Ethyl pent-3-enoate (9%) (0%)^{u} Ethyl 1-methylprop-2-enyl ether (16%)^{b} (7%)^{u} C_8 Dimers (14%) (16%)^{u}
	~10%	Ethyl 3-methylbut-3-enoate (< 4%) (0%)^{u} Ethyl 2-methylprop-1-enyl ether (sig.)^{c} (sig.)^{u} Dimers (sig.)^{a} (sig.)^{u}

[a] [Rh(OAc)(CO)(PEt_3)$_2$] (0.05 g, 0.0001 mol), RX (1.0 cm^3), EtOH (4.0 cm^3), CO (40 bar), 120 °C, 4 hours.

[b] Small amounts (< 3%) of the corresponding straight chain ether were also produced.

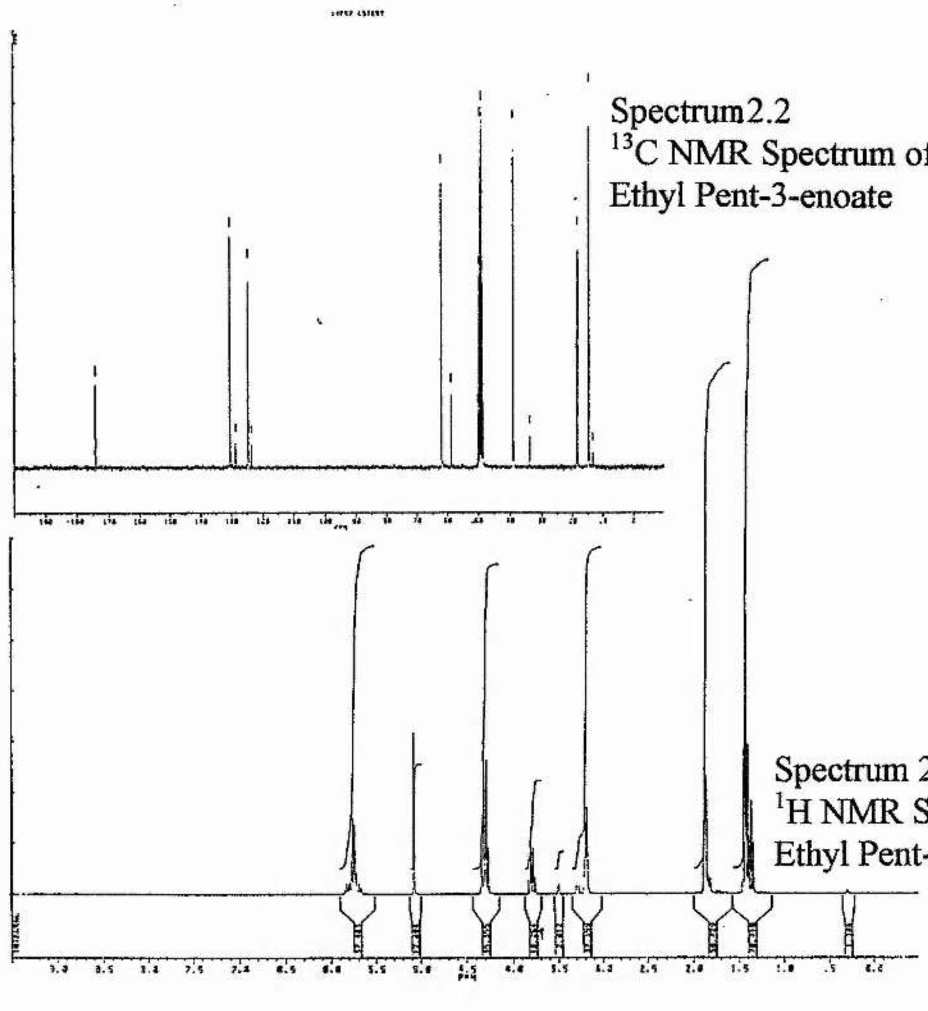
[c] Not quantified, although a significant quantity was detected.

[u] Products from uncatalysed reaction (same conditions as for the catalysed reactions but omitting [Rh(OAc)(CO)(PEt_3)$_2$]).

The reactions carried out using 1-chlorobut-2-ene and 1-bromobut-2-ene gave the expected results. The same β,γ-unsaturated ester obtained for both substrates with the chloride giving a better yield of the ester. This was similar to the result obtained for the carbonylation of the propenyl halides. The ether was obtained in greater yield when 1-bromobut-2-ene was used as the substrate. The fact that the ether was branched came as a surprise but it was assumed that it could only have been produced *via* a catalysed reaction. In order to calibrate the GC, ethyl 1-methylprop-2-enyl ether and ethyl but-2-enyl ether were respectively synthesised from 3-chlorobut-1-ene and 1-chlorobut-2-ene and sodium ethoxide. In both cases only the expected products were obtained from the reactions. This supports the theory that the production of the ethers in the carbonylation reaction must have occurred catalytically.

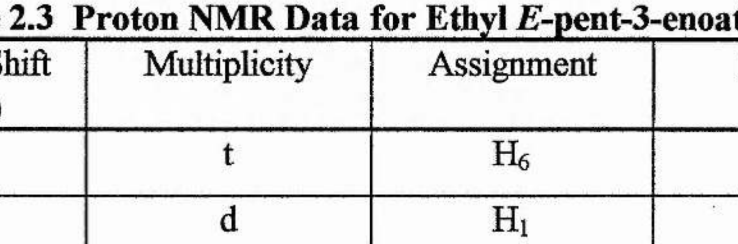
The difference in yields of the ethers had an effect on the yields of the esters obtained from both of the reactions. Thus it seems that the selectivity towards the ester is controlled by the rate of the etherification reaction. By using allylic chlorides the selectivity towards the ester is high but decreases when bromides and iodides are used.

When 3-chloro-1-butene was carbonylated the ester obtained from the reaction was predominantly ethyl *E*-pent-3-enoate and a little of the Z-isomer not the expected ethyl 2-methylbut-3-enoate. This was the same ester as produced in the catalysed reaction between 1-chloro-2-butene and carbon monoxide. As well as being identified by GCMS and GC data the compound was distilled from the autoclave reaction mixture and its identity verified by ^{1}H and ^{13}C NMR spectra. See ^{1}H NMR data spectrum 2.1, table 2.3 and figure 2.9 and ^{13}C NMR data spectrum 2.2, table 2.4 and figure 2.10.



Spectrum2.2
^{13}C NMR Spectrum of
Ethyl Pent-3-enoate

Spectrum 2.1
^{1}H NMR Spectrum of
Ethyl Pent-3-enoate

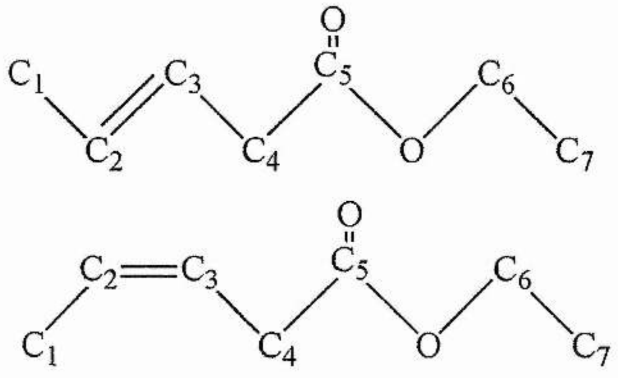


(fig. 2.9)

Table 2.3 Proton NMR Data for Ethyl *E*-pent-3-enoate

Chemical Shift (δ ppm)	Multiplicity	Assignment	Integral
1.40	t	H_6	3
1.87	d	H_1	3
3.19	d	H_4	2
4.30	q	H_5	2
5.75	m	H_2 & H_3	2

The ^{13}C NMR spectrum of ethyl pent-3-enoate showed the seven pairs of signals. In each pair one signal was much less intense than the other. These were due to the Z- and E-isomers of the unsaturated ester with the more intense lines being assigned to the E-isomer in agreement with the GC results.



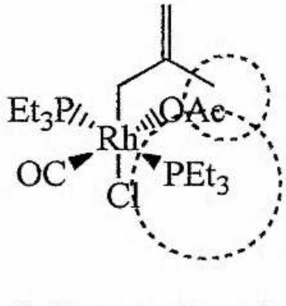
(fig. 2.10)

Table 2.4 ^{13}C NMR Data for E and Z Ethyl Pent-3-enoate

Ethyl *E*-pent-3-enoate		Ethyl *Z*-Pent-3-enoate	
Chemical Shift (δ ppm)	Assignment	Chemical Shift (δ ppm)	Assignment
14.79	C_1	13.29	C_1
18.35	C_7	18.66	C_7
39.10	C_4	33.72	C_4
61.91	C_6	58.59	C_6
124.47	C_2	123.36	C_2
130.35	C_3	129.52	C_3
174.14	C_5	173.96	C_5

The same spectra were obtained from the carbonylation of 1-chloro-2-butene. Therefore, from the evidence presented by the GCMS, ^{1}H and ^{13}C NMR spectra it could be concluded that the same straight chain ester was produced from both reactions. Attempts were also made to isolate the ether produced in the reactions in order to obtain NMR data. However, the ethers could not be isolated from ethanol because of the similarity in boiling points and the small quantities involved.

In the carbonylation reaction carried out with 3-chloro-2-methylprop-1-ene the yield of the expected β,γ-unsaturated ester, ethyl 3-methylbut-3-enoate, was less than 4% (see table 2.3). A large proportion of the starting material remained in the reaction solution. A possible explanation for this was that the methyl group on the 3-chloro-2-methylprop-1-ene was orientated such that it was experiencing a large steric hindrance from the groups on the rhodium complex thus could not form a σ-bond with the metal centre (figure 2.11). It was not possible for the alkyl group to rearrange to give the straight chain σ-allylic intermediate as suspected for the reactions involving 1-chlorobut-2-ene and 3-chlorobut-2-ene.



(fig 2.11)

It was noticed in all the reactions, both catalysed and uncatalysed, that a small proportion of the allylic halides dimerised to give either C_6 or C_8 dienes depending on the substrate used. The dimers corresponded to classical head-to-head, tail-to-tail and head-to-tail reactions involving allylic radicals that could be formed upon loss of a halide radical upon heating. The proportion of dimers in the products did not vary greatly between the chloride or bromide nor with the presence or absence of $[Rh(OAc)(CO)(PEt_3)_2]$.

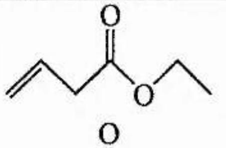
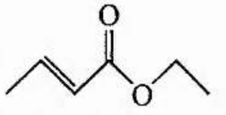
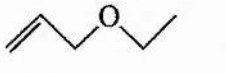
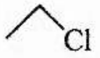
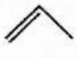
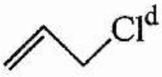
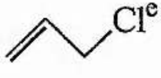
2.3 Reactions Using [RhCl(CO)(PEt$_3$)$_2$] as the Catalyst

The catalytic system was modified by replacing [Rh(OAc)(CO)(PEt$_3$)$_2$] with [RhCl(CO)(PEt$_3$)$_2$] and by modifying the autoclave liners to keep the catalytic solution away from the walls of the autoclave. The technique for pressurising the autoclaves was also modified. One of the reasons for changing the catalyst was that the [RhCl(CO)(PEt$_3$)$_2$] was shown to be the active catalyst in the system; thus using this complex simplified the reaction (see chapter 3). The [RhCl(CO)(PEt$_3$)$_2$] was also easier and quicker to synthesise than the [Rh(OAc)(CO)(PEt$_3$)$_2$], requiring only one step and a single recrystallisation. Finally [Rh(OAc)(CO)(PEt$_3$)$_2$] was in the form of a thick oily liquid and was very air sensitive, and possibly thermally sensitive; thus handling and weighing the compound was difficult and quite tedious. The [RhCl(CO)(PEt$_3$)$_2$], on the other hand, was crystalline and quite air stable; accurate weighing and handling of the compound was quick and easy.

2.3.1 Carbonylation of Propenyl Halides

Using the modified autoclave liners, the revised pressurising techniques and [RhCl(CO)(PEt$_3$)$_2$] instead of either [Rh(OAc)(CO)(PEt$_3$)$_2$] or [Rh$_2$(OAc)$_4$.2MeOH] / PEt$_3$, the carbonylation the propenyl halides was repeated. It was hoped that these modifications would improve the selectivity towards the ester over the ether. The results for these reactions are given in table 2.5.

Table 2.5 Products Obtained from the [RhCl(CO)(PEt$_3$)$_2$] Catalysed Carbonylation of Various Alkyl Halides[a]

Substrate	Conversion %	Products
	64	 (37%)  (~ 12%)  (2.7%)  (c)  (b) C_6 Dimers (sig.)
	51	Ethyl but-3-enoate (25%) Ethyl but-2-enoate (~ 8%) Ethyl prop-1-enyl ether (4.8%) Bromoethane (c) Propene (b) C_6 Dimers (sig.)
	92	Ethyl but-3-enoate (20%) Ethyl but-2-enoate (~ 6%) Ethyl prop-1-enyl ether (33%) Iodoethane (c) Propene (b) C_6 Dimers (sig.)
[d]	sig.	Ethyl but-3-enoate (0%) Ethyl but-2-enoate (0%) Ethyl prop-1-enyl ether (2%) Chloroethane (c) Propene (b) C_6 Dimers (sig.)
[e]	53	Ethyl but-3-enoate (19%) Ethyl prop-1-enyl ether (11%) Chloroethane (c) Propene (b)

[a] [RhCl(CO)(PEt$_3$)$_2$] (1 x 10^{-4} mol), RX (1.0 cm^3), CO (40 bar), 120 °C, 4 hours.

[b] Propene, due to its high volatility, was not quantified, propene is assumed to account for the mass imbalance seen on the table.

[c] Not quantified. Difficult to separate EtCl, EtBr and EtOH on glc column used.

[d] No [RhCl(CO)(PEt$_3$)$_2$]; sig. = small but significant quantity (not quantified).

[e] Work carried out by Simpson.

As expected the selectivities towards the esters all increased over the initial reactions carried out by Simpson (see table 2.1). A few new products were seen in these reactions that may have been present previously but were not detected. Reasons are thought to be due to the fitting of new and/or different glc columns both in the GCMS and the GC that enabled better separation of the products. Thus by keeping the catalytic solution in the glass liner and away from the autoclave walls a greater selectivity towards the carbonylated product was achieved.

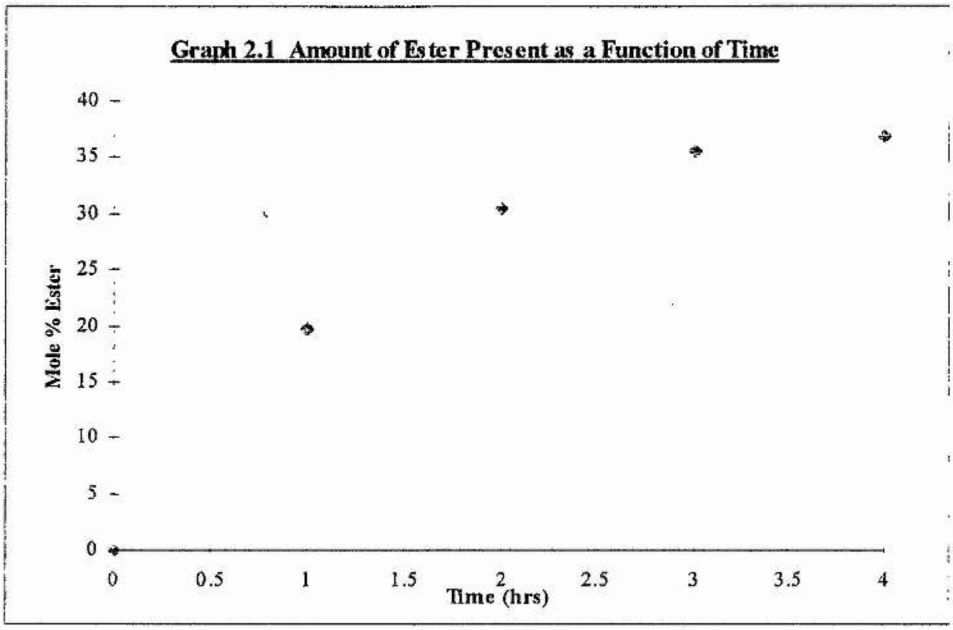
The catalyst was thought to be deactivated by reaction with the walls of the autoclave; hence the colour change of the solution. The solution that remained in the glass liner was bright yellow thus the catalyst was active. By keeping all of the reaction solution inside the glass liner a greater concentration of catalyst was present; therefore, greater ester:ether ratio was obtained.

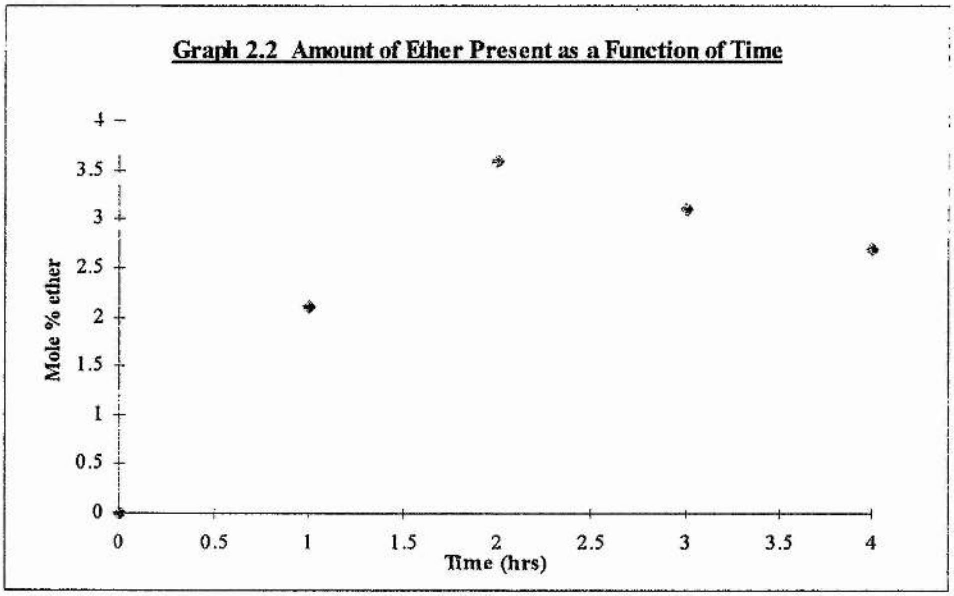
The reactions carried out using the revised system had two extra products compared to those carried out using the old system using the catalytic precursors. Ethyl but-2-enoate accounted for approximately one quarter of the total ester produced in all the reactions. This was produced *via* a catalysed isomerisation of the double bond in ethyl but-3-enoate. There is much literature precedence for this type of reaction which can be catalysed by protons, bases, photochemically, metal carbonyls or even complex ions containing Pt, Ru or Rh.[54] In this system two of the possible catalysts (protons and Rh(I)) for the isomerisation reaction were present thus it was of no surprise that this reaction occurred. The isomerised product is more thermodynamically stable because the internal double bond is in conjugation with the carbonyl group. However, compared with most of the reactions quoted in the literature, the selectivity of β,γ:α,β esters is much greater for this system (see chapter 1). This is presumably because most of the other systems require a stoichiometric amount of base which seems to be a more efficient catalyst for the isomerisation reaction.

The presence of C_6 propenyl dimers found in the catalytic system were typical of free radical reactions. Products formed by these radical reactions could be produced both in the presence and absence of $[RhCl(CO)(PEt_3)_2]$ just by heating an autoclave containing 1-chloroprop-2-ene. Most of the dimers were hexadienes formed by head-to-head, head-to-tail and tail-to tail dimerisation reactions of the propenyl radicals, however, small amounts of dihalogenated hexenes were also detected. The mechanism for the formation of propene in this system is unknown though it could also be derived from a free radical process.

2.3.2 The Effect of Time on the Carbonylation of 1-Chloroprop-2-ene

Autoclave reactions were run at various times in order to examine the formation of ethyl but-3-enoate and ethyl prop-1-enyl ether in the carbonylation system involving 1-chloroprop-2-ene. The results are shown in graphs 2.1 and 2.2.





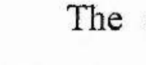
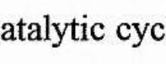
It can be seen from graph 2.1 that the rate of the production of the ethyl but-3-enoate is greatest near the beginning of the reaction but starts to slow down after 1.5 hours. The rate begins to level off after 2.5 hours. This was probably because of the drop in concentration of the 1-chlorobut-2-ene. It was unlikely that the drop in CO pressure would have been great enough to cause the rate to drop by such an extent.

The amount of ether present in the reaction is shown in graph 2.2. The initial rate of ether production is initially high but after approximately 2 hours the amount present begins to drop. A possible explanation for this is that the HCl produced in the reaction starts to react with the ether to produce 3-chloroprop-1-ene and ethanol.

2.3.3 Carbonylation of 1-Chloroprop-2-ene in the Presence of a Radical Trap

The carbonylation of 1-chloroprop-2-ene was carried out in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a free radical scavenger, in order to test the theory that the oxidative addition step of the catalytic cycle occurred *via* a free radical pathway. The BHT was present in 50 mole % of the amount of substrate present at the beginning of the reaction. The results for the reaction are given in table 2.6.

Table 2.6 Products Obtained from the Carbonylation of 1-chloroprop-2-ene in the Presence of BHT[a] with Standard Carbonylation Run for Comparison[b]

Substrate	Conversion %	Products
	64	Ethyl but-3-enoate (37%) Ethyl but-2-enoate (~ 12%) Ethyl prop-1-enyl ether (2.7%) Chloroethane (c) C_6 Dimers (sig.)
 + BHT	78	Ethyl but-3-enoate (14%) Ethyl but-2-enoate (< 1%) Ethyl prop-1-enyl ether (6.1%) Chloroethane (c) C_6 Dimers (very little present)

[a] $[RhCl(CO)(PEt_3)_2]$ (1×10^{-4} mol), 1-chlorobut-2-ene (1.0 cm^3, 0.0122 mol), BHT (1.35 g, 0.0061 mol), CO (40 bar), 120 °C, 4 hours.

[b] $[RhCl(CO)(PEt_3)_2]$ (1×10^{-4} mol), 1-chlorobut-2-ene (1.0 cm^3), CO (40 bar), 120 °C, 4 hours.

[c] Not quantified. Difficult to separate EtCl and EtOH on glc column used.

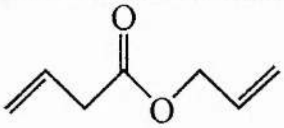
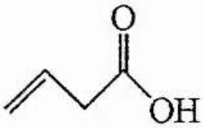
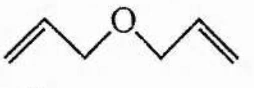
sig. = small but significant quantity (not quantified).

The results from the table indicate that the BHT did have an effect on the reaction. The yield of the ester dropped by 62% whereas the conversion of 1-chloroprop-2-ene increased by 18%. The other noticeable effect of adding the BHT to the reaction was that the amount C_6 dimers possibly produced by free radical dimerisation of 1-chloroprop-2-ene had decreased substantially. These results would seem to support the theory that the oxidative addition of 1-chloroprop-2-ene to $[RhCl(CO)(PEt_3)_2]$ did occur *via* a free radical pathway. However, care must be taken in drawing too many conclusions from this reaction as the addition of a radical inhibitor to a catalysed reaction can alter it by an effect as simple as changing the polarity of the medium or reacting with the substrate at a greater rate than the catalyst because of its greater concentration in the solution.

2.3.4 Carbonylation of prop-2-en-1-ol

A desirable goal for the carbonylation of allylic halides would be to eliminate the wasteful production of haloethanes from the reaction. The problem lay in the use of ethanol for the solvent. As long as this was used then haloethanes would always be produced in this system. The system would still require a protic solvent in order to pull the equilibrium over in favour of the ester thus keeping the cycle turning. The answer to this problem was to use prop-2-en-1-ol as the solvent instead of ethanol in the presence of a small amount of 1-chloroprop-2-ene. The HCl produced in the cycle could react with the prop-2-en-1-ol to produce more 1-chloroprop-2-ene thus producing a halide that could be converted into a ester. This followed the same principle as the Monsanto Process. The results from the reaction are shown in table 2.7.

Table 2.7 Products Obtained from the [RhCl(CO)(PEt$_3$)$_2$] Catalysed Carbonylation of prop-2-en-1-ol[a]

Substrate	Conversion %	Products	
	~ 96		(78%)[b]
			(~ 3%)
			(4%)
			(c)
		C$_6$ Dimers	(sig.)

[a] [RhCl(CO)(PEt$_3$)$_2$] (1 x 10^{-4} mol), 1-chloroprop-2-ene (1.0 cm^3), prop-2-en-1-ol (4 cm^3), CO (40 bar), 120 °C, 4 hours.

[b] 2 moles of substrate react to give 1 mole of product.

[c] Propene, due to its high volatility, was not quantified.

sig. = small but significant quantity (not quantified).

The conversion of substrates to carbonylated products was much greater in this reaction than the analogous one carried out in ethanol. Only a very small amount of prop-2-en-1-ol remained at the end of the reaction. A small amount of but-3-enoic acid was present because of water, produced in the reaction between HCl and prop-2-en-1-ol. The ratio of ester:ether (almost 20:1) was also much higher than for the analogous reaction carried out in ethanol. The amount of C_6 dimers present at the end of the reaction was similar to that observed in the other carbonylation reactions.

2.4 Other Substrates

In a further attempt to test the limits of this catalytic system two other potential substrates were investigated, 1-fluoroprop-2-ene and 1,4-dichlorobut-2-ene. The former was studied in an attempt to activate a carbon-fluorine bond and the latter in an attempt at a double carbonylation reaction.

2.4.1 The Attempted Carbonylation of 1-Fluoroprop-2-ene

In the previous examples of carbonylation all the substrates were commercially available and easy to handle using standard Schlenk techniques. The only propenyl halide that had not been used as a substrate was 1-fluoroprop-2-ene. The reasons for this were that it was not commercially available and it was a gas at room temperature (b.p. -12 °C) which meant there would be considerable handling problems.

The synthesis of 1-fluoroprop-2-ene was, however, very straightforward. 1-bromoprop-2-ene and potassium fluoride were heated to 120 °C in diethylene glycol. A tube was attached to the top of the condenser and connected to the side arm of a Schlenk tube which was immersed in an acetone/$CO_{2(s)}$ bath at -78 °C. This was connected in series to another cooled Schlenk tube which in turn was connected to a $CaCl_2$ drying tube. As the 1-fluoroprop-2-ene was produced it was condensed in the first cooled Schlenk tube. The second Schlenk tube only contained negligible amounts of the product. Once produced the 1-fluoroprop-2-ene was stored at -30 °C in a sealed Schlenk tube.

All the equipment used for handling and containing the 1-fluoroprop-2-ene was precooled to -50 °C before use. The autoclaves and syringes were deoxygenated and then cooled using external $CO_{2\ (s)}$. The Schlenk tubes were deoxygenated and immersed in an acetone/$CO_{2(s)}$ bath at -50 °C.

The first reaction carried out was the attempted carbonylation of 1-fluoroprop-2-ene using $[Rh(OAc)(CO)(PEt_3)_2]$ as the catalyst at 120 °C, under 40 bar CO in ethanol for four hours. The expected products from the reaction were ethyl but-3-enoate and ethyl prop-1-enyl ether, as with the carbonylation of the other propenyl halides. However, no reaction occurred and the starting materials remained in solution. This suggested that the carbon-fluorine bond was too strong to allow the oxidative addition of the molecule across the rhodium centre.

The C-X bond strengths of the organo halides decreases down the group (table 2.8):[67]

Table 2.8 Approximate C-X bond Strengths for Similar Aliphatic Molecules

C-X	Bond Strength (kJ mol^{-1})
C-F	452
C-H	409
C-OH	388
C-Cl	343
C-Br	284
C-I	226

$$F > Cl > Br > I$$

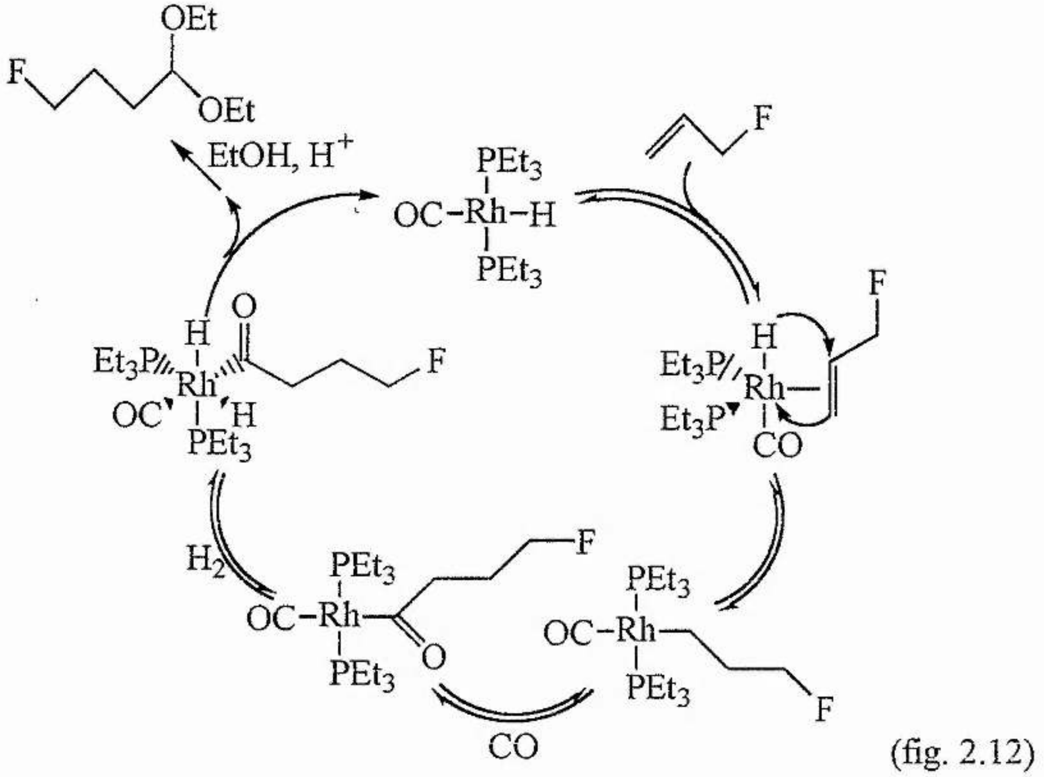
Therefore it can be reasonably assumed that because the bond strength of the C-F bond is greater than that of the analogous hydrocarbons, a carbonylation reaction would not occur using this catalytic system. However, a hydrocarbonylation reaction similar to the ones carried out with prop-2-en-1-ol by Simpson may be possible for this compound.

The first reaction of this type was carried out using $[Rh(OAc)(CO)(PEt_3)_2]$ as the catalyst and CO/H_2 (1:1) 40 bar. As with the carbonylation reaction it did not work and only the starting materials remained at the end of the reaction. The reasons for this are unclear but could be due to the failure of $[Rh(OAc)(CO)(PEt_3)_2]$ to convert to the active catalyst.

The second reaction was carried out using $[Rh_2(OAc)_4.2MeOH]$, PEt_3 and CO/H_2 (1:1) added separately at the start of the reaction to form the active catalyst species *in situ*. This reaction was successful and gave a mixture of 1,1-diethoxybutane, 1,1-diethoxy-2-methylpropane and 1,1-diethoxy-4-fluorobutane. These results were a little unexpected as alcohols rather than acetals were the expected products.

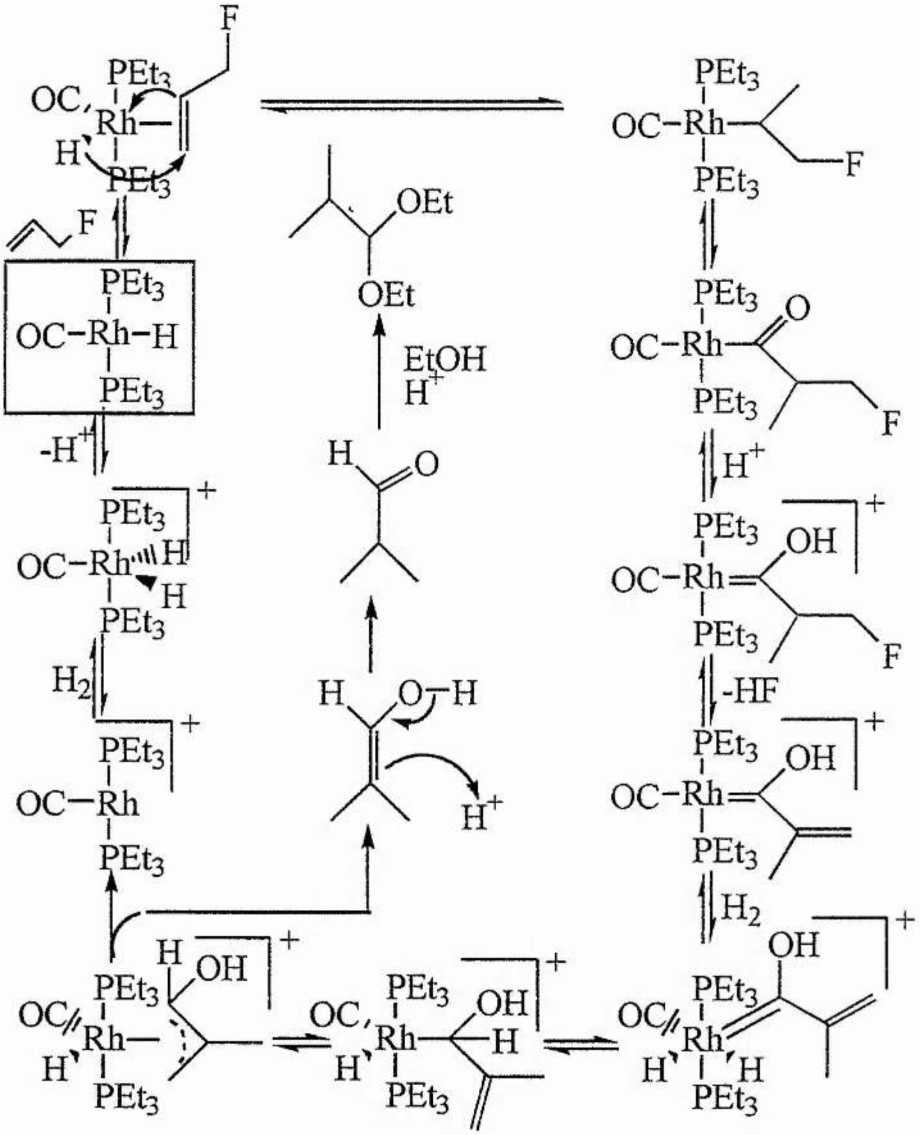
Work carried out by Andersen[101], on the hydroformylation of 1-hexene using rhodium/trialkylphosphine complexes has suggested that stirring has an effect on the nature of the products of the reactions. It was found that acetals and aldehydes were produced when the reactions were stirred but alcohols were produced in the absence of stirring. Work carried out by Simpson on the hydrocarbonylation of prop-2-en-1-ol also produced alcohols but the reactions were stirred. Work carried out by Rosi[102] has shown that alcohols were produced during hydroformylation reactions involving prop-2-enyl ethanoate which were stirred. At present no explanation can be offered for these results.

A possible mechanism for the formation of the 1,1-diethoxy-4-fluorobutane is the standard Union Carbide hydroformylation mechanism (figure 2.24). The reasons for the failure of the acetyl complex to hydrogenate to produce the alcohol (as in Simpson's work on prop-2-en-1-ol) after the migratory insertion reaction are unclear. This mechanism could also be applied to the formation of 4,4-diethoxybutane nitrile given in figure 2.12.



(fig. 2.12)

The suggested mechanism for the formation of the branched acetal is based on Simpson's mechanism for the formation of the of the branched alcohol from the hydrocarbonylation of prop-2-en-1-ol (figure 2.13).

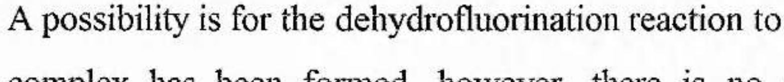


(fig. 2.13)

The first part of the mechanism is quite straight forward. The 1-fluoroprop-2-ene coordinated to the hydridocarbonylbis(triethylphosphine) rhodium(I) via the double bond. This rearranges to the branched chain intermediate and migratory insertion of carbon monoxide occurs. The next part of the mechanism in a series of eliminations and rearrangements.

A proton adds to the oxygen to produce a carbene intermediate. The complex then eliminates a molecule of hydrogen fluoride. The driving force for this step is the increase in conjugation which enhances the stability of the carbene and is the key step to the formation of the branched product. The HF would immediately react with ethanol to produce ethyl fluoride and water. After the hydrogen molecule is added to the complex the carbene rearranges to form a η^3-intermediate which reductively eliminated as the aldehyde in its enol form. The catalyst is regenerated by the addition of another molecule of hydrogen and elimination of a proton. The enol tautomerises to the keto form of the aldehyde which catalytically reacts with ethanol in the presence of an acid to produce the branched acetal.

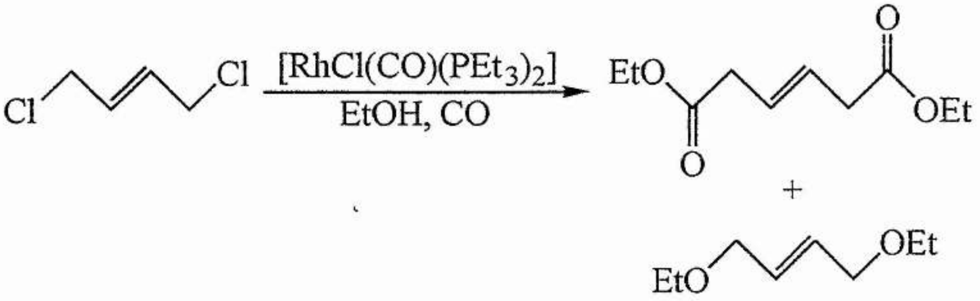
A straight chain dehydrofluorinated acetal was also produced in the reaction. However, a mechanism for this reaction was not easy to suggest. A possibility is for the dehydrofluorination reaction to occur after the σ-alkyl complex has been formed, however, there is no driving force for this reaction (fig 2.14).



(fig. 2.14)

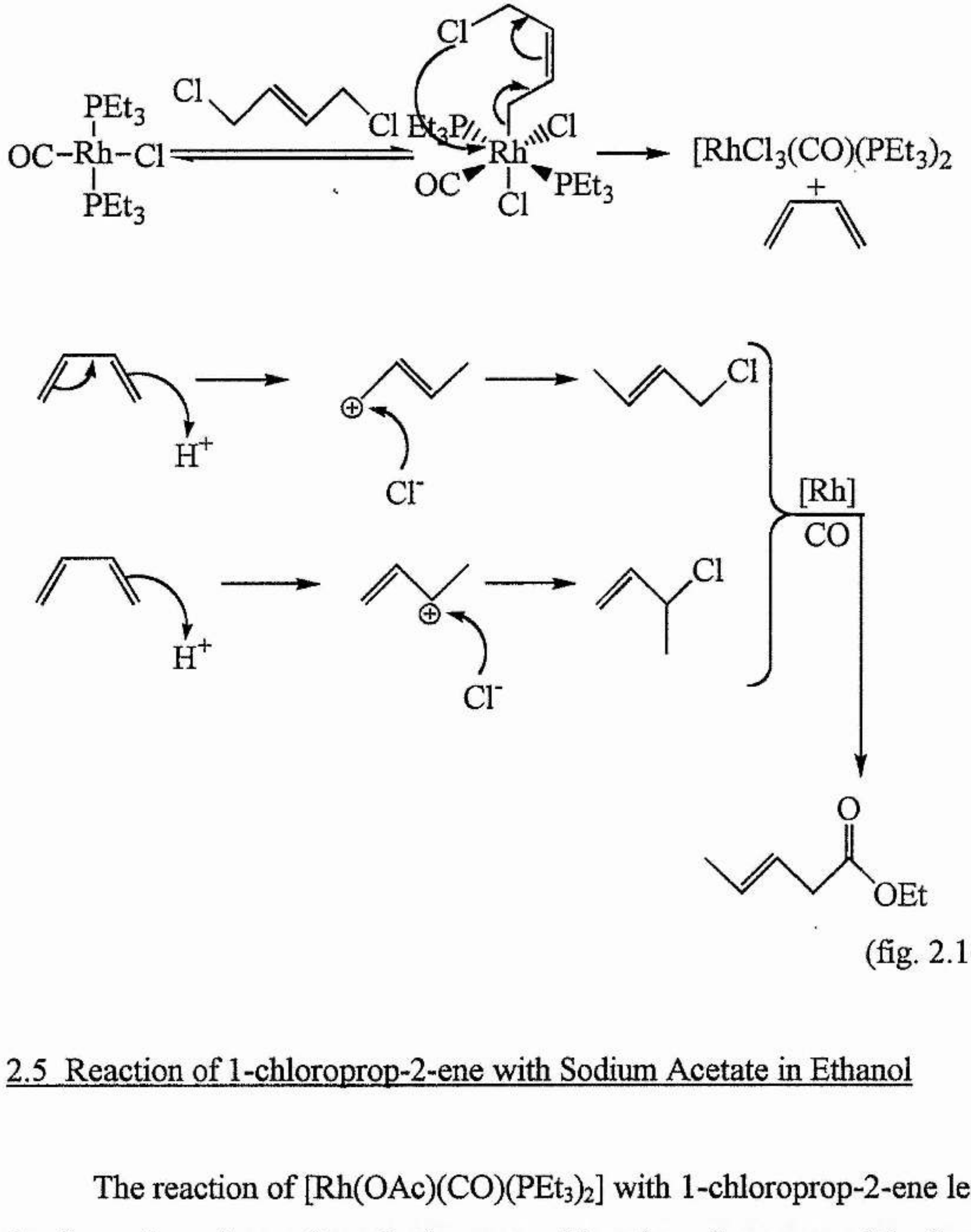
2.4.2 The Attempted Carbonylation of 1,4-Dichlorobut-2-ene

As mentioned previously the carbonylation of 1,4-dichlorobut-2-ene was an attempt at a double carbonylation reaction using this catalytic system. The expected products for this reaction were diethyl hex-3-en-1,6-dioate and 1,4-diethoxybut-2-ene (figure 2.15).



(fig. 2.15)

However, the products obtained were ethyl pent-3-enoate and a smaller amount of pent-3-enoic acid. Surprisingly these were very similar to those produced in the carbonylation of 1-chlorobut-2-ene. None of the expected diether was obtained from the reaction. This reaction, therefore, did not give any of the expected dicarbonylated product. A possible explanation for this reaction involves the formation of 1-chlorobut-2-ene from buta-1,3-diene (figure 2.16)



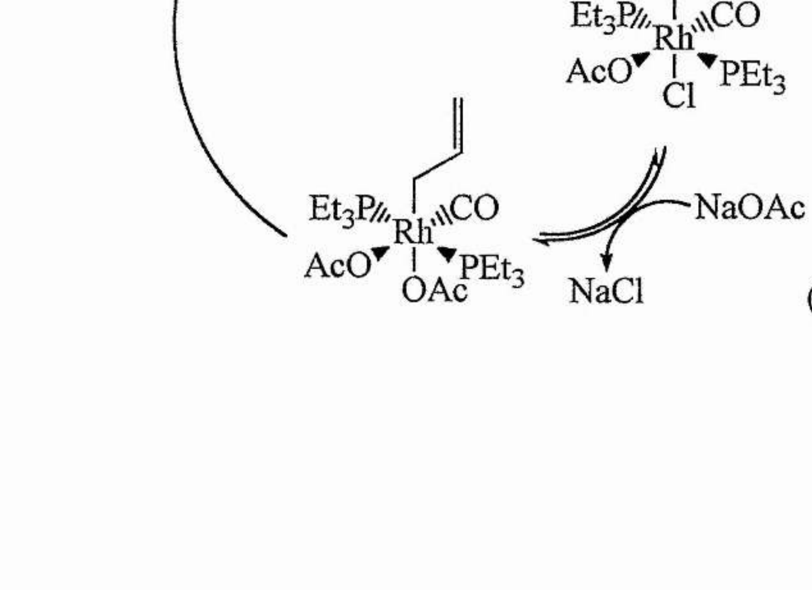
(fig. 2.16)

2.5 Reaction of 1-chloroprop-2-ene with Sodium Acetate in Ethanol

The reaction of [Rh(OAc)(CO)(PEt$_3$)$_2$] with 1-chloroprop-2-ene led to the formation of prop-2-enyl ethanoate. Therefore, it was possible for this reaction to be made catalytic. When 1-chloroprop-2-ene and sodium acetate were reacted together in the presence of [Rh(OAc)(CO)(PEt$_3$)$_2$] GCMS analysis showed the complete conversion of reactants into products. Two peaks of approximately the same size and area were present in the GCMS trace which were assigned to prop-2-enyl ethanoate and prop-1-enyl ethyl ether. The ether was assumed to have been produced *via* direct reaction of the propenyl chloride with ethanol but as will be discussed later this may have not been the case.

When the analogous reaction was carried out in the absence of the rhodium complex far smaller yields of prop-2-enyl ethanoate and prop-1-enyl ethyl ether were obtained. In addition there was a considerable quantity of unreacted 1-chloroprop-2-ene remaining.

From the two experiments it could be assumed that the rhodium complex was indeed catalysing the conversion of the 1-chloroprop-2-ene to prop-2-enyl ethanoate because of the complete conversion of the starting materials seen in the reaction carried out in the presence of [Rh(OAc)(CO)(PEt_3)$_2$]. Thus the presence of the [Rh(OAc)(CO)(PEt_3)$_2$] increased the rate of the reaction. The catalytic cycle could have proceeded as shown in figure 2.17.



(fig. 2.17)

In an attempt to prevent the formation of the ether the reaction was carried out in THF under similar conditions. As predicted prop-2-enyl ethanoate was produced in the absence of prop-1-enyl ethyl ether; however, there was not complete conversion of the 1-chloroprop-2-ene. This could have been because the anhydrous sodium acetate was slightly soluble in ethanol whereas it was insoluble in THF. Thus the formation of the Rh(III) diacetate complex would have occurred at a slower rate in the THF solution than in the ethanolic solution due to the availability of soluble acetate species in the latter solution.

2.5.1 Reaction of Benzyl Chloride with Sodium Acetate

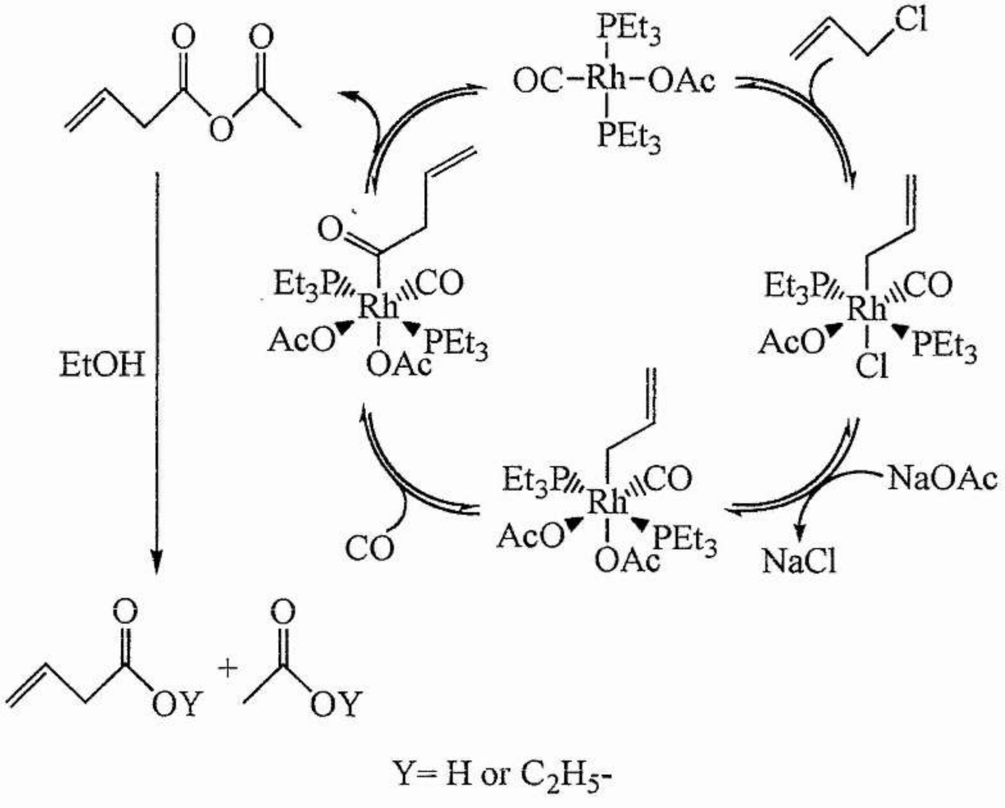
The analogous reaction between benzyl chloride and sodium acetate was carried out in ethanol under similar conditions to the previous reactions. Again, as with the other reactions carried out in ethanol, two products were obtained namely benzyl acetate and benzyl ethyl ether. From the GCMS trace it could be seen that a little benzyl chloride was left in solution. In comparison, the reaction carried out in the absence of $[Rh(OAc)(CO)(PEt_3)_2]$ gave a smaller yield of benzyl acetate with more unreacted benzyl chloride left in the solution. The yields of benzyl ethyl ether were similar for the two reactions. These, as with the corresponding reactions involving 1-chloroprop-2-ene, show that $[Rh(OAc)(CO)(PEt_3)_2]$ catalyses the reaction between benzyl chloride and sodium acetate though not very efficiently.

2.5.2 Reaction of 1-chloroprop-2-ene or Benzyl Chloride with Salts other than Sodium Acetate

As indicated in the previous sections, reactions between 1-chloroprop-2-ene or benzyl chloride and sodium acetate in the presence of a catalytic amount of [Rh(OAc)(CO)(PEt_3)$_2$], the corresponding acetate esters could be obtained in reasonable yields. Attempts were made to expand the above reactions to obtain a wider variety of compounds anions such as cyanide, cyanate and thiocyanate were used. However, these reactions were unsuccessful.

2.5.3 Reaction of 1-chloroprop-2-ene or Benzyl Chloride with Sodium Acetate under Carbon Monoxide

The following reactions were carried out in order to investigate the insertion of carbon monoxide at relatively low pressures (2 bar) into the Rh-C bond of the oxidative addition complex. In the presence of sodium acetate, acetic but-3-enoic anhydride could have been a possible product but, if formed, it would immediately react with ethanol on reductive elimination to produce a mixture of esters and carboxylic acids. A possible mechanism for this reaction is given in figure 2.18.



(fig. 2.18)

The products obtained from the reaction carried out under an atmospheric pressure of CO were identical to those obtained when the reaction was carried out under argon (i.e. the corresponding acetates and ethers). This was true for both the 1-chloroprop-2-ene and the benzyl chloride. Therefore no insertion of CO was observed for either substrate at atmospheric pressure. The same results were obtained when the reaction were carried out under 2.2 bar of carbon monoxide.

Propan-2-ol and 2-methylpropan-2-ol were substituted for ethanol and the above reactions repeated for 1-chloroprop-2-ene. Prop-2-enyl ethanoate and the corresponding ethers were obtained along with propene or 2-methylprop-1-ene, the dehydration products of the alcohols, in low yields.

The substitution of ethanol by the secondary and tertiary alcohols had no effect on the reaction.

The failure of the above reactions to produce any carbonylated products meant that higher carbon monoxide pressures had to be used. Thus 1-chloroprop-2-ene, sodium acetate and carbon monoxide (40 bar) were reacted together at 120 °C both in the presence and the absence of $[Rh(OAc)(CO)(PEt_3)_2]$. Two solvents (ethanol and DMF) were used for the reactions, the results of which were solvent dependent (table 2.9)

Table 2.9 Products from Catalysed and Uncatalysed Reaction of 1-chloroprop-2-ene with Sodium Acetate in Ethanol Under CO (40 bar)

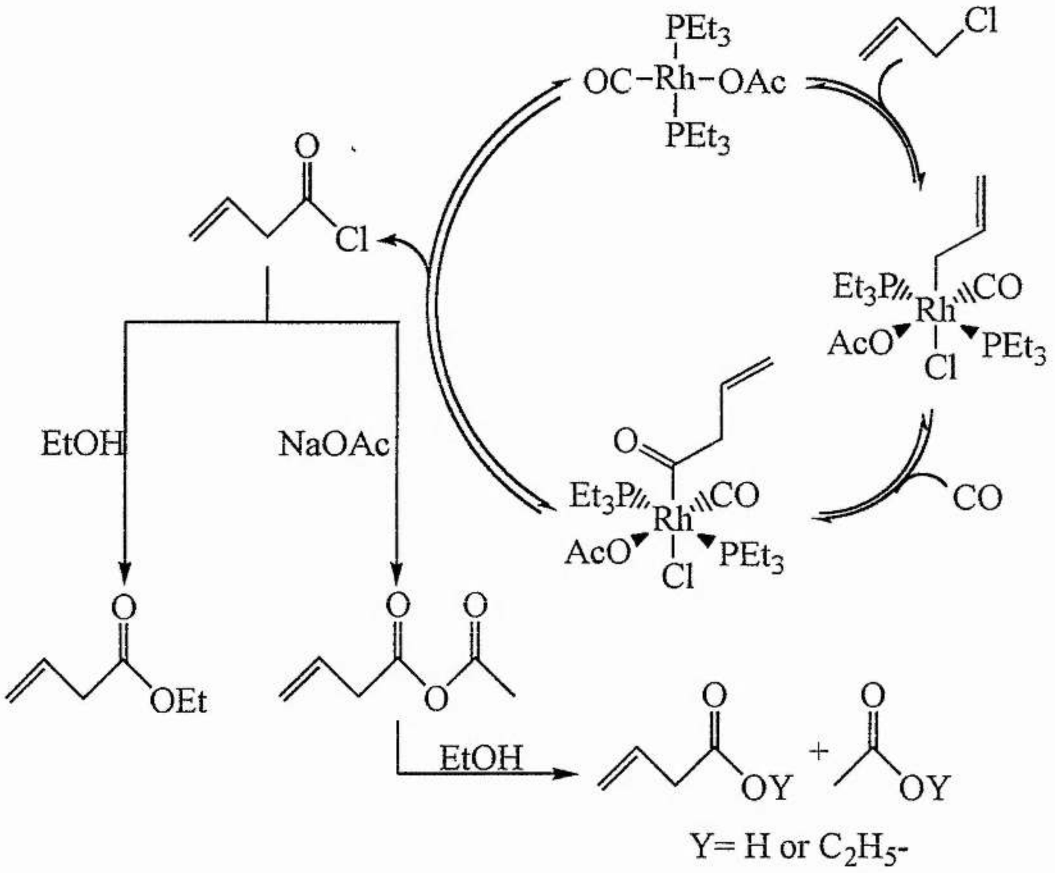
Solvent	Catalyst	Products
Ethanol	$[Rh(OAc)(CO)(PEt_3)_2]$	Ethyl but-3-enoate Ethyl ethanoate prop-2-enyl ethanoate prop-1-enyl ethyl ether
Ethanol	None	prop-2-enyl ethanoate prop-1-enyl ethyl ether 1-chloroprop-2-ene
DMF*	$[Rh(OAc)(CO)(PEt_3)_2]$	But-3-enoic acid prop-2-enyl ethanoate
DMF*	None	prop-2-enyl ethanoate 1-chloroprop-2-ene

* At 120 °C decomposition products from DMF were observed in small amounts in the GCMS trace.

In the reactions carried out in the absence of $[Rh(OAc)(CO)(PEt_3)_2]$ lower yields of products were obtained, as previously discussed. Prop-1-enyl ethyl ether was not obtained from the reactions carried out in DMF. The yield of the ether was higher in the reaction carried out in the presence of the rhodium complex than it was in its absence.

The products obtained from the reaction carried out in DMF seem to have been derived from both the acetate exchange reaction and the carbonylation reaction. The DMF or the sodium acetate must have been wet otherwise but-3-enoic acid would not have been a product. If the anhydride was formed in this reaction ethanoic acid, derived from cleavage of the anhydride with water, would also have been seen as a product of the reaction. Therefore, it was unlikely that acetic but-3-enoic anhydride was formed in this reaction.

When the reaction was carried out in ethanol in the presence of carbon monoxide two extra products were obtained compared with the reaction carried out in the absence of carbon monoxide. These were the ethyl ethanoate and ethyl but-3-enoate. The presence of ethyl ethanoate would seem to give some evidence in support of the formation of the unsymmetrical anhydride. However, as can be seen from figure 2.12, if acetic but-3-enoic anhydride was formed in the reaction carried out in ethanol, ethanoic acid and but-3-enoic acid should also have been present as products. Neither of these were detected by GCMS. A possible explanation for this could be that both of these products were esterified because of the large excess of ethanol. Either of two very similar mechanisms could have been operating in this system. The first could be as the one given in figure 2.12; a second possibility could be the reductive elimination of but-3-enoyl chloride from the rhodium complex, rather than the anhydride, and subsequent reaction with either ethanol (to produce ethyl but-3-enoate) or sodium acetate (to produce acetic but-3-enoic anhydride) and subsequent reaction with ethanol (figure 2.19).



(fig. 2.19)

2.5.4 Reaction Between But-3-enoyl Chloride, Ethanol and Sodium Acetate

In order to determine the possible products that could be obtained in the above catalytic system, a reaction was carried out between 3-butenoyl chloride and sodium acetate dissolved in ethanol. The reaction was set up to mimic the conditions of the catalytic system as closely as possible in the absence of pressure. Sodium acetate was dissolved in ethanol and the solution heated under reflux whilst but-3-enoyl chloride was added dropwise over a period of 45 minutes. The solution was heated for a further 2 hours, cooled and analysed by GCMS.

Five products were obtained from the reaction the most abundant of which was ethyl but-3-enoate. The most likely source for the production of this compound was *via* direct reaction of the acid chloride with ethanol. However, it could have possibly been formed by ethanol hydrolysis of the unsymmetrical anhydride. Support for this hydrolysis was given by the presence of both ethyl ethanoate and ethanoic acid. However, on closer examination of the system these products could have been derived *via* a different route involving HCl (figure 2.20). The acetic acid could also have been produced by ester hydrolysis.

$$\mathrm{HCl + NaOAc \xrightarrow{HCl} NaCl + AcOH}$$
$$\mathrm{AcOH + EtOH \xrightarrow{H^+} EtOAc + H_2O} \quad \text{(fig. 2.20)}$$

The equilibrium for the reaction between ethanol and sodium acetate usually lies to the side of the starting materials unless a strong acid is present. The HCl produced in the reaction between but-3-enoyl chloride and ethanol may have catalysed the reaction between sodium acetate and ethanol to give the ethyl ethanoate and may have been directly responsible for the production of ethanoic acid. The standing concentration of HCl in this reaction would have been low due to its reaction with ethanol as described by Simpson but may have been sufficient to catalyse the reaction. Another possibility for the formation of ethyl ethanoate could be the reaction of ethyl chloride with sodium acetate.

The two other products obtained from this reaction were but-2-enoic acid and ethyl but-2-enoate. The presence of these compounds was unexpected but were the result of isomerisation of the terminal double bonds. The resulting compounds were more thermodynamically stable due to having an internal double bond in conjugation with the carbonyl groups of either the acid or the ester. The yields of isomerised products were far less than the those obtained in many of the catalytic systems reviewed in chapter one. Those systems included a stoichiometric amount of base to neutralise the acid produced during the reaction. The base also catalysed the isomerisation of the external double bonds giving the thermodynamically more stable α,β-esters.

The products obtained from this reaction have shown that the synthesis of acetic but-3-enoic anhydride could have occurred. However, there was some discrepancy between the products obtained in this reaction and the catalysed reaction. The absence of carboxylic acids from the catalysed reaction would seem to suggest that the unsymmetrical anhydride was not formed and that ethyl ethanoate could have been formed via the reaction shown in figure 2.20.

2.5.5 Conclusions for the Reactions Involving Sodium Acetate

$[Rh(OAc)(CO)(PEt_3)_2]$ catalyses the reaction between 1-chloroprop-2-ene or benzyl chloride and sodium acetate to produce the corresponding acetate esters. In the presence of carbon monoxide, the products are consistent with competitive carbonylation and direct esterification.

The above reactions have neither proved or disproved the formation of acetic but-3-enoic anhydride in the catalytic system. It is still possible that anhydrides could be synthesised by this route but the system would have to be modified. Most importantly, alcoholic solvents would have to be replaced by a dry inert solvent system to prevent the cleavage of the anhydrides. The solvent would also have to be able to dissolve sodium acetate. A catalytic reaction carried out in dry ethanoic acid using dried reagents may still afford ethanoic but-3-enoic anhydride.

2.6 Conclusions

The carbonylation of 2-propenyl halides and 2-butenyl halides produces predominantly β,γ-unsaturated esters. Ethers are produced as by-products from the reaction. The β,γ-unsaturated esters undergo slight isomerisation to the α,β-unsaturated esters but not to the same extent as in previously reported reactions. The ester:ether selectivity seems to be dependent on the halide used for the reaction with chlorides giving the best selectivities and iodides the worst.

Both 1-chlorobut-2-ene and 3-chlorobut-1-ene produce the same straight chain ester and branched chain ether. Two possible mechanisms can be suggested for these reactions. One involves free radical intermediates and the other involves η^3-intermediates; experimental evidence seems to suggest that the mechanism is free radical. The formation of the branched chain ether is thought to take place on the metal centre.

Most other carbonylation reactions involving alkyl halides require stoichiometric amounts of base to remove the HX that is produced in the reaction. No added base is required in this system as EtX is produced in the reaction between HX and EtOH. However, the production of EtX is a wasteful reaction.

Prop-2-en-1-ol can be carbonylated in the presence of 1-chloroprop-2-ene in very good yields. This reaction cannot produce EtX because ethanol is not present in the system. Instead the HX reacts with prop-2-en-1-ol to produce more 1-chloroprop-2-ene (c.f. acetic acid production by the Monsanto Process).

The substrates that can be used in this system are limited to allylic or benzylic chlorides, bromides and iodides. No carbonylation reaction was observed when 1-fluoroprop-2-ene was used as a substrate. This system also does not seem to be active for double carbonylation reactions involving allylic dienes.

CHAPTER 3

3. OXIDATIVE ADDITION

3.1 Introduction[103]

Most organic reactions that are catalysed by transition metals occur by a series of steps, producing reactive intermediates, at least one of which contains a metal-carbon σ-bond. One important reaction type reaction type by which intermediates are formed is the oxidative addition of an organic substrate to a transition metal. The oxidative addition reaction is one in which there is a simultaneous increase in the formal oxidation state of the metal and its coordination number (figure 3.1).

$$L_nM^z + X\text{-}Y \longrightarrow L_n\overset{X}{\underset{Y}{M}}{}^{z+2}$$

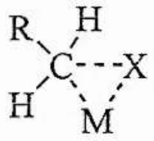
(fig. 3.1)

X-Y can be a wide variety of species including R-X, RCOX, X_2, H_2, H-X where X= F, Cl, Br, I and R= alkyl, aryl, vinyl, benzyl, allyl, etc..

The most widely studied reactions for transition metals are those of complexes of metals with the d^8 and d^{10} electron configuration. In addition to having this electronic configuration the complexes are coordinatively unsaturated, or have the ability to become so because of their lability. For example the square planar iridium complex *trans*-$[IrCl(CO)(PPh_3)_2]$ formally has two preformed vacant sites ready for reaction with the addition molecule but $[Pd(PPh_3)_4]$ must dissociate a triphenylphosphine ligand before it can react.

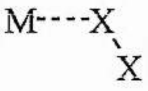
3.1.1 Oxidative Addition of Halocarbons to Metal Complexes[103, 104]

The simplest reaction that can occur between a metal complex and an alkyl halide which results in oxidative addition is one in which the metal site acts as nucleophile towards the carbon atom. This is analogous to the S_N2 reaction. However, the initial reaction need not be directed exclusively towards the carbon atom. It is possible for the metal complex to interact with both the carbon and the halide (figure 3.2)



(fig. 3.2)

Another possibility is for simple coordination *via* a lone pair of electrons, as in the oxidative addition reactions of halogens (figure 3.3).



(fig 3.3)

Radical oxidative addition pathways are also possible for halocarbons. There are two types of pathway possible, chain or non-chain. The non-chain mechanism is initiated by electron transfer to the organohalides (figure 3.4).

$$L_nM + RX \longrightarrow L_nM^{+\bullet}\,RX^{-\bullet} \longrightarrow L_nMX^{\bullet} + R^{\bullet} \longrightarrow L_nMXR \quad \text{(fig. 3.4)}$$

The initial interaction of the halocarbon in figure 3.4 occurs as in figure 3.3 *via* a lone pair of electrons followed by homolytic cleavage of the halogen-carbon bond (figure 3.5)

(fig. 3.5)

The chain mechanism involves single electron rather than two electron steps (figure 3.6).

$$L_nM + R\cdot \longrightarrow L_nMR\cdot \xrightarrow{RX} L_nMXR + R\cdot \quad \text{(fig. 3.6)}$$

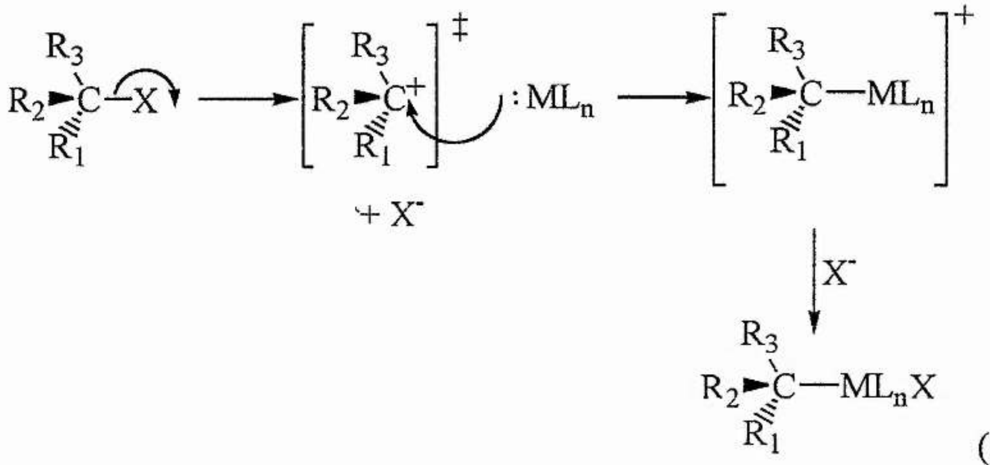
In reactions involving the S_N2 mechanism a polar transition state appears to be involved; the reaction is promoted by polar solvents. These reactions ought to proceed with inversion of configuration of the chiral centre when optically active organohalides are used; because of steric and electronic effects of other ligands e.g. phosphines this is not always the case. A generalised S_N2 mechanism is given in figure 3.7.

(fig. 3.7)

In the S_N2 mechanism for the oxidative addition, the reactivity of metal complexes towards alkyl halides will be the same as that of standard nucleophiles in organic chemistry, namely: RI > RBr > RCl; Me > primary > secondary > tertiary. However, oxidative addition reactions involving free radicals occur with a reverse order of reactivity with respect to the alkyl groups shown above: $PhCH_2$ > ^{t}Bu > ^{i}Pr > Et > Me. This order is reversed because groups such as benzyl and ^{t}Bu stabilise free radicals whereas methyl and ethyl groups do not. Oxidative addition reactions that are not clean and show products other than the expected alkyl complex may also indicate radical pathways. The rates of these reactions may also be sensitive to light, oxygen and paramagnetic impurities.

Unlike the S_N2 mechanism for oxidative addition, where the stereochemistry of a chiral carbon would be inverted, a radical mechanism would cause racemisation of the chiral centre; thus loss of all optical activity.

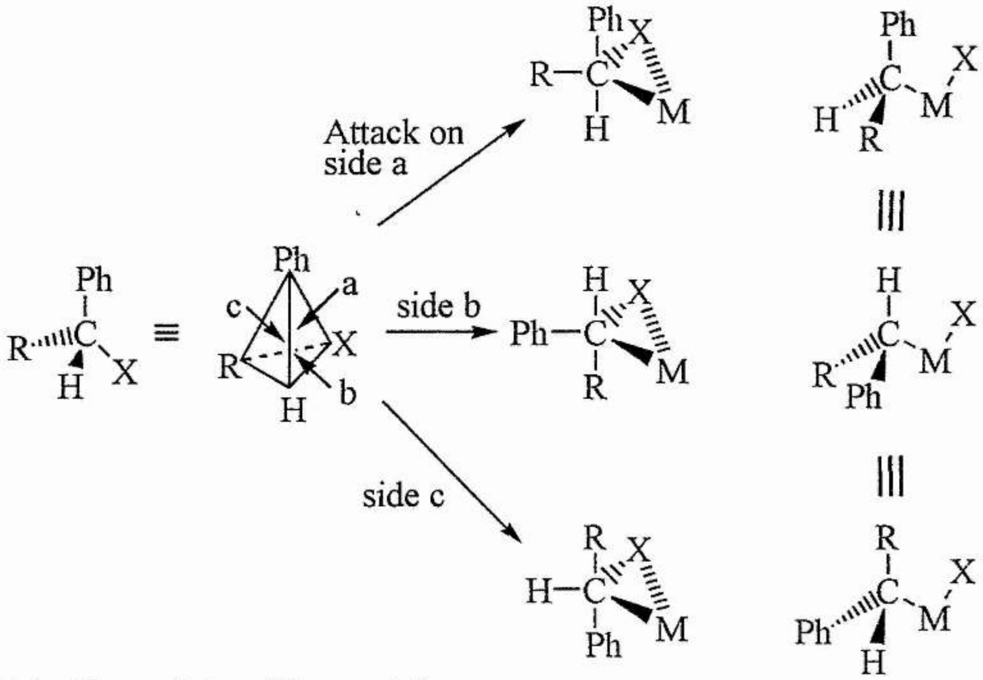
Another possible mechanism for the oxidative addition of halocarbons to metal complexes is an ionic reaction analogous to the S_N1 reaction in organic chemistry (figure 3.8).



(fig. 3.8)

In the S_N1 type reactions the order of reactivity towards RX is in the order I > Br > Cl as in the S_N2 type mechanism; the reactivity in respect to the R group is reversed (as for radical type mechanisms): tertiary > secondary ≈ benzyl ≈ allyl > primary > methyl. The allylic and benzylic groups have the ability to stabilise the positive charge of the transition state.

Another possible mechanism for the oxidative addition of halocarbons to group 8 transition metals involves concerted attack at the carbon-halogen bond at any one of three tetrahedral faces common to the carbon halogen bond resulting in a trigonal bipyramidal transition state (figure 3.9).[105] This mechanism accounts for many of the effects seen in the oxidative addition reactions of halocarbons to Group 8 metal complexes.



M= Group 8 transition metal

(fig. 3.9)

For steric reasons attack at face b would be preferred. If carbon-halogen bond scission occurs with least motion of the equatorial group and towards the palladium then the same enantiomer is always obtained. The enantiomer would have the opposite configuration to the starting material. This mechanism could possibly accommodate the loss of optical purity in the product and racemisation of the starting material. Motion of the equatorial group in the opposite direction and away from the palladium would result in the other enantiomer thus loss of optical purity. The extent of this loss would be dependent on steric factors. More importantly, the extent of bond making (M-C) and breaking (C-X) in the transition state would influence the enantiomer distribution. A pseudorotation of the trigonal bipyramid followed by either collapse to product or reversion to starting material would account for both reduction of optical yield in the product and racemisation of the starting material. If the C-X bond breaking precedes C-M bond making and occurs *via* a one-electron process then a radical pair is formed. Rotation of the alkyl radical followed by collapse to product or reversion to starting material would account for the loss of stereospecificity in the product or racemisation of starting material.

Despite all of the differences between the nucleophilic and free radical mechanisms for oxidative addition of a halocarbon to a metal complex it is not a simple matter to discriminate between the pathways. Metal complexes can react with subtly different halocarbons by completely different mechanisms. Changes in the ligands on the metal centre can also have an effect on the mechanism.

3.2 Oxidative Addition Reactions of 1-Chloroprop-2-ene

In order to elucidate the mechanism for the formation of ethyl but-3-enoate from 1-chloroprop-2-ene and carbon monoxide the reaction was broken down in parts. The first part of the mechanism to be studied was the oxidative addition of 1-chloroprop-2-ene to $[Rh(OAc)(CO)(PEt_3)_2]$.

3.2.1 Synthesis of $[Rh(OAc)(CO)(PEt_3)_2]$

This synthesis simply involved bubbling carbon monoxide through an ethanolic solution of $[Rh_2(OAc)_4.2EtOH]$ and triethylphosphine to produce the square planar $[Rh(OAc)(CO)(PEt_3)_2]$. The $[Rh(OAc)(CO)(PEt_3)_2]$ was handled under argon because of its sensitivity to oxygen. A reductant was not required for the reaction because the phosphine ligands and the ethanolic solvent were able to reduce the Rh(II) to Rh(I).

It was noticed in the synthesis that when the triethylphosphine was added to the $[Rh_2(OAc)_4.2EtOH]$ and allowed to stand for one hour the solution turned bright yellow within a few minutes when carbon monoxide was bubbled through it, indicating formation of the product. However, if the carbon monoxide was bubbled through the solution immediately after the addition of triethylphosphine it took up to an an hour for the solution to turn yellow. This suggested that the reduction of the $[Rh_2(OAc)_4.2EtOH]$ by the triethylphosphine and the ethanol was quite a slow step despite giving a rapid colour change from blue-green to dark orange on addition of triethylphosphine. This colour change was the result of the replacement of the terminal ethanol ligands with triethylphosphine. The final product was isolated by crystallisation at -100 °C giving microcrystals but was liquid at room temperature despite numerous attempts to crystallise it from every conceivable solvent.

The ^{31}P NMR spectrum of $[Rh(OAc)(CO)(PEt_3)_2]$ showed a doublet centred on δ 25.3 ppm ($^1J_{Rh\text{-}P}$ = 126.4 Hz) (table 3.1).

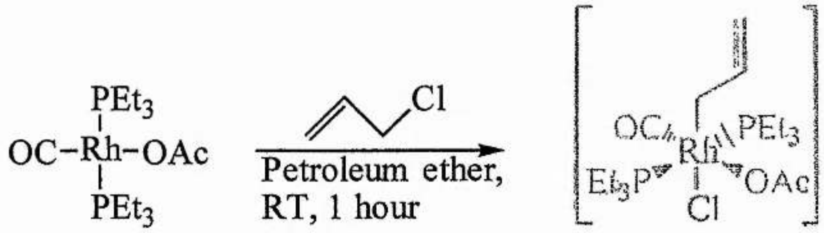
Table 3.1 ^{31}P NMR Data for $[Rh(OAc)(CO)(PEt_3)_2]$

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment
25.3	d	126.4	$^1J_{Rh\text{-}P}$ of *trans*-$[Rh(OAc)(CO)(PEt_3)_2]$

A very small singlet was also present in the spectrum at δ 53.3 ppm. This was assigned to triethylphosphine oxide which was present in a small quantity in the starting triethylphosphine.

3.2.2 Stoichiometric Addition of 1-chloroprop-2-ene to $[Rh(OAc)(CO)(PEt_3)_2]$

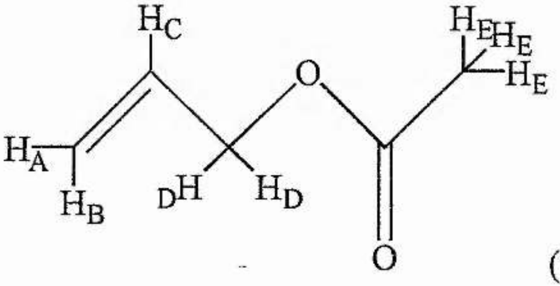
In an attempt to isolate the oxidative addition product from the addition of 1-chloroprop-2-ene to $[Rh(OAc)(CO)(PEt_3)_2]$ the reaction shown in figure 3.10 was carried out. However, the Rh(III) complex that was expected to have been formed in the reaction (shown in red) was not obtained.



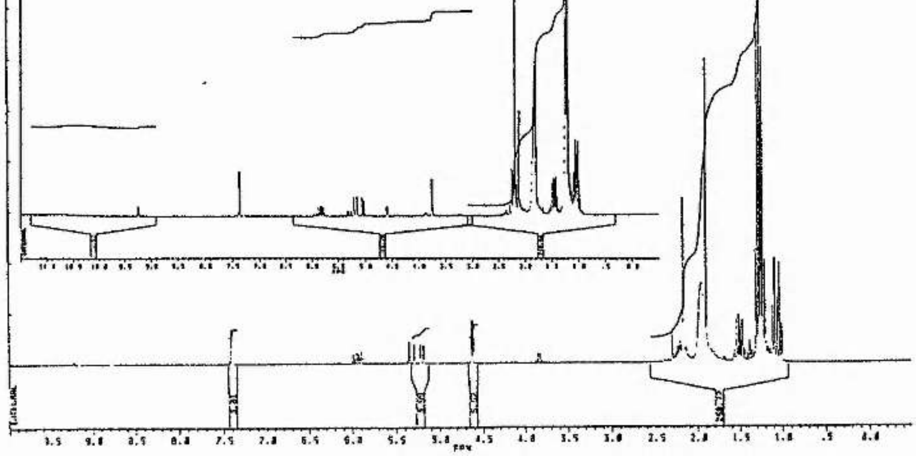
Expected product (fig. 3.10)

The reaction was carried out using a 1:1 mixture of 1-chloroprop-2-ene and the rhodium complex under an argon atmosphere. It was worked up by cooling the solution to -100 °C, filtering and drying the resulting oil *in vacuo* at room temperature. The ^1H NMR of the oil was almost identical to the starting material. However, it contained peaks of very low intensity between δ 3.5 - 7.0 ppm which were attributed to prop-1-enyl compounds.

In order to identify the unknown prop-1-enyl compounds formed in the previous experiment a reaction was carried out *in situ* in the NMR tube using d^6-benzene as the solvent. The 3-chloroprop-2-ene (0.0096 mol) was present in a four times excess over the [Rh(OAc)(CO)(PEt$_3$)$_2$] (0.0024 mol). One of the compounds was immediately identified as 3-chloroprop-2-ene and the other was identified as being prop-1-enyl ethanoate (see spectrum 3.1 and figure 3.11), by comparison with literature. The ratio of 1-chloroprop-2-ene to prop-1-enyl ethanoate was 4:1 thirty minutes after the addition of 1-chloroprop-2-ene to the NMR tube.



(fig. 3.11)



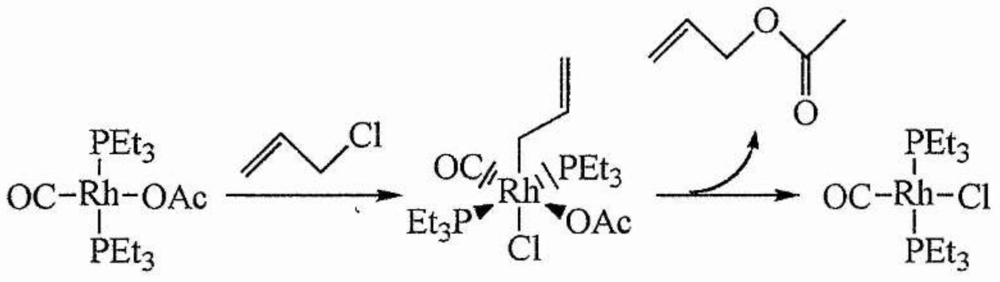
Spectrum 3.1
^{1}H NMR Spectrum of
the Conversion of 1-chloroprop-2-ene
to Prop-1-enyl Ethanoate

The inlayed spectrum shows the reaction 30 minutes after the addition of 3-chloroprop-2-ene. Peaks were present in this spectrum from both 3-chloroprop-2-ene and prop-1-enyl ethanoate. The singlet due to the protons on the ethanoate group of the rhodium complex (δ 2.20 ppm) was reduced in intensity. There was also another peak at δ 1.80 ppm due to the presence of the ethanoate group of prop-1-enyl ethanoate. Prop-1-enyl ethanoate was formed *via* the reductive elimination of the prop-1-enyl and ethanoate groups from the Rh(III) complex giving $[RhCl(CO)(PEt_3)_2]$. The main spectrum on the page is the reaction after 4 hours. It shows that the 1-chloroprop-2-ene had been completely converted to prop-1-enyl ethanoate. The conversion of $[Rh(OAc)(CO)(PEt_3)_2]$ to $[RhCl(CO)(PEt_3)_2]$ was confirmed by the presence of a doublet at δ 24.5 ppm in a ^{31}P NMR spectrum (table 3.2)

Table 3.2 ^{31}P NMR Data for $[RhCl(CO)(PEt_3)_2]$

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment
24.5	d	117.2	$^{1}J_{Rh\text{-}P}$ of *trans*-$[RhCl(CO)(PEt_3)_2]$

Therefore, instead of obtaining the expected Rh(III) product, as shown in figure 3.10, the oxidative addition of 1-chloroprop-2-ene was immediately followed by the reductive elimination of prop-1-enyl ethanoate as show in figure 3.12.



(fig. 3.12)

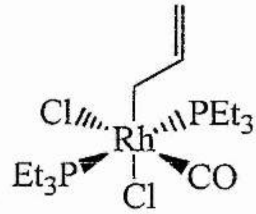
3.2.3 Reaction of [$RhCl(CO)(PEt_3)_2$] with 1-chloroprop-2-ene at -20 °C

An *in situ* NMR reaction was carried out between the 1-chloroprop-2-ene and [$RhCl(CO)(PEt_3)_2$] using a 4:1 excess of 1-chloroprop-2-ene. The reaction was carried out at -20 °C in an attempt to trap any intermediates formed in the reaction. The reactants and solvent were precooled before mixing and were kept at -50 °C in an NMR tube before being placed into the cooled NMR. On mixing it was noticed that the colour of the solution changed from bright yellow to pale cream. The pale colour was indicative of a Rh(III) complex. The first ^{31}P NMR was taken one hour after the addition of 1-chloroprop-2-ene to the catalytic solution and showed a single doublet at δ 14.54 ppm (table 3.3).

Table 3.3 ^{31}P NMR Data for Reaction of 1-Chloroprop-2-ene with [$RhCl(CO)(PEt_3)_2$]

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment
14.54	d	85.47	$^1J_{Rh-P}$ of *trans*-[$RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2$]

The coupling of 85.47 Hz was typical of a Rh(III) compound. It was now possible that the complex formed in the reaction was the one shown in figure 3.13.



(fig. 3.13)

There was no sign of any exchanging phosphine in the ^{31}P NMR spectrum. This would have been present as a broad peak at approximately δ -20 ppm and would have occurred if the prop-1-enyl group had been η^3-bonded rather than η^1-bonded. The presence of the excess 1-chloroprop-2-ene meant that the peaks from the complex in the ^{1}H NMR spectrum were hidden under much larger ones due to the 1-chloroprop-2-ene.

The solvent and the excess 1-chloroprop-2-ene were removed *in vacuo*, being careful to keep the temperature below -20 °C at all times. The resulting pale cream solid was redissolved in precooled d^8-toluene. The only signal that was expected in the ^{31}P NMR was that of the above complex; another doublet was present at δ 25.69 ppm which was attributed to [RhCl(CO)(PEt$_3$)$_2$] (table 3.4).

Table 3.4 ^{31}P NMR Data for Isolated [RhCl$_2$(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$]

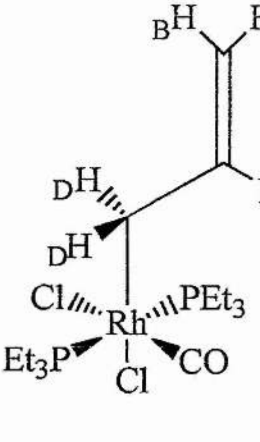
Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
14.69	d	85.41	$^1J_{Rh-P}$ of *trans*-[RhCl$_2$(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$]	47
24.4	d	117.3	$^1J_{Rh-P}$ of *trans*-[RhCl(CO)(PEt$_3$)$_2$]	9

From the relative intensities of the peaks it could be seen that the Rh(III) complex was present in a greater amount than the Rh(I) complex.

When the ^{1}H NMR was carried out the peaks due to the prop-1-enyl group on the rhodium complex could be seen clearly because there was no excess 1-chloroprop-2-ene present. These were readily assigned as a η^1-bonded prop-1-enyl group (table 3.5 and figure 3.14).

Table 3.5 ^{1}H NMR Data for the prop-1-enyl group of [RhCl$_2$(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$]

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Integral	Assignment
2.75	bm	-	2	H_D
4.90	d	10	1	H_A J_{AC}
5.15	d	17	1	H_B J_{BC}
6.10	ddt	9, 10, 17	1	H_C J_{CD}, J_{AC}, J_{BC}



(fig. 3.14)

If the prop-1-enyl group had been η^3-bonded to the rhodium complex then the signals from H_A and H_B would have been equivalent to those from H_D. The peak at δ 2.75 ppm was a complex multiplet and could not be resolved in this spectrum. Other complex peaks were present in the spectrum below δ 2.50 ppm. These were assigned to the ethyl groups on the triethylphosphine ligands.

When the solution was allowed to warm to room temperature (25 °C) the doublet at δ 25.69 ppm in the ^{31}P spectrum increased in intensity whilst peaks due to 1-chloroprop-2-ene appeared in the ^{1}H spectrum. This indicated that at high temperatures 1-chloroprop-2-ene reductively eliminated from the Rh(III) complex to leave $[RhCl(CO)(PEt_3)_2]$. After 24 hours the only significant peak present in the ^{31}P NMR spectrum was at δ 25.69 ppm, the doublet corresponding to the Rh(III) complex had almost completely disappeared. The ^{1}H NMR spectrum showed peaks mainly from 1-chloroprop-2-ene and $[RhCl(CO)(PEt_3)_2]$.

When a solution of 1-chloroprop-2-ene and $[RhCl(CO)(PEt_3)_2]$ in d^8-toluene were cooled down from room temperature to -50 °C and monitored by ^{31}P NMR the doublet due to $[RhCl(CO)(PEt_3)_2]$ disappeared and was replaced by a doublet at δ 14.69 ppm which was attributed to $[RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2]$. These experiments would seem to suggest that reaction of 1-chloroprop-2-ene with $[RhCl(CO)(PEt_3)_2]$ was completely reversible, with formation of the Rh(III) complex favoured by low temperatures.

3.2.4 Thermodynamic Data from the Reaction of 1-Chloroprop-2-ene with $[RhCl(CO)(PEt_3)_2]$

In order to obtain thermodynamic data for the oxidative addition of 1-chloroprop-2-ene to $[RhCl(CO)(PEt_3)_2]$ variable temperature ^{31}P NMR experiments were carried out. $[RhCl(CO)(PEt_3)_2]$ was used instead of $[Rh(OAc)(CO)(PEt_3)_2]$ in order to make the NMR spectra less complicated and because $[Rh(OAc)(CO)(PEt_3)_2]$ was rapidly converted to

$[RhCl(CO)(PEt_3)_2]$ on the addition of propenyl and benzyl chlorides and thus played no further part in the reaction. A slightly different approach was used for this experiment compared with the previous experiments. Instead of using an excess of substrate a slight excess of catalyst was used (0.95:1). This meant that there would always be a peak present in the spectrum that corresponded to the unreacted catalyst. The assignment of peaks was made easier using this technique.

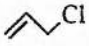
All the reactants and the solvent (CD_2Cl_2) were cooled to -50 °C before mixing in a precooled NMR tube. The ^{31}P NMR spectra were run at -20, -10, 0, 20 and 35 °C. Two doublets of varying intensity were seen in all the spectra (table 3.6).

Table 3.6 ^{31}P NMR Data for Variable Temperature Reaction of 1-Chloroprop-2-ene with $[RhCl(CO)(PEt_3)_2]$

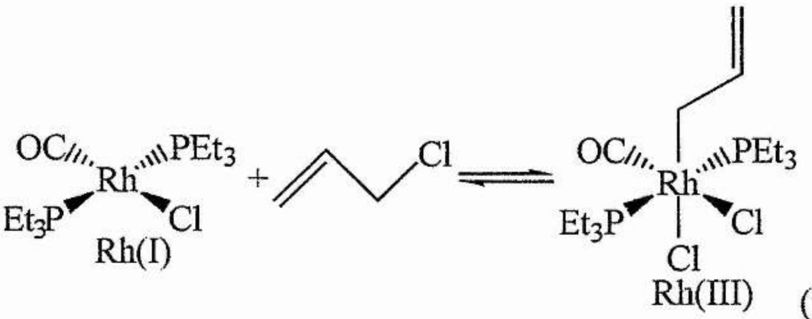
Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment
24.1	d	116	$^1J_{Rh\text{-}P}$ of *trans*-$[RhCl(CO)(PEt_3)_2]$
14.54	d	86	$^1J_{Rh\text{-}P}$ of *trans*-$[RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2]$

It was possible to work out the thermodynamic data for the reaction using the change in intensities of the peaks in the ^{31}P NMR spectra at different temperatures. As mentioned previously, the intensity of the doublet corresponding to $[RhCl(CO)(PEt_3)_2]$ increased whilst that of $[RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2]$ decreased with increasing temperature and vice-versa. The initial concentrations of the reactants were known at the beginning of the reaction, therefore, knowing these concentrations combined with the intensities of the peaks in the NMR spectra the concentration of each of the species could be calculated at each temperature (tables 3.7 and 3.8; figure 3.15; equations 3.1 and 3.2). It was assumed that the response obtained in the ^{31}P NMR spectra was the same for both the Rh(I) and Rh(III) complexes.

Table 3.7 Concentrations of Rh(I) and Rh(III) Complexes at Various Temperatures

Temperature (K)	Intensity Rh(I) (arb. Units)	Intensity Rh(III) (arb. Units)	Conc.  (mol dm^{-3})	Conc. Rh(I) (mol dm^{-3})	Conc. Rh(III) (mol dm^{-3})
253	93.582	172.874	0.0575	0.213	0.116
263	31.835	47.638	0.0738	0.197	0.132
273	48.006	42.751	0.1160	0.155	0.174
293	49.30	27.048	0.1544	0.117	0.212
308	47.151	4.963	0.2397	0.031	0.298

From the equations:



(fig 3.15)

$$K = \frac{[Rh(III)]}{[Rh(I)][1-chloroprop-2-ene]} \quad \text{(eqn. 3.1)}$$

$$\Delta G^{\circ} = -RT\ln K \quad \text{(eqn. 3.2)}$$

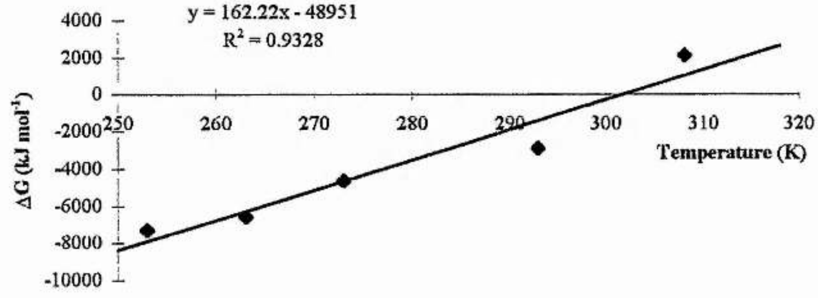
Table 3.8 Thermodynamic Data for the Equilibrium Shown in Figure 3.15 Derived From Table 3.11 and the above Equations

Temperature (K)	K	ln K	ΔG (kJ mol^{-1})
253	32.1	3.47	-7.30
263	20.3	3.01	-6.58
273	7.70	2.04	-4.63
293	3.60	1.27	-2.88
308	0.439	-0.824	2.11

A graph of ΔG versus temperature, in Kelvin, gives ΔS^{o} as the slope and ΔH^{o} as the intercept (graph 3.1) according to equation 3 (assuming that ΔH and ΔS are temperature invariant..

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad \text{(eqn. 3)}$$

Graph 3.1 Graph of ΔG versus Temperature for the Equilibrium Shown in Figure 3.15



$$\Delta S^{o} = -162.2\ \mathrm{JK^{-1}mol^{-1}}$$

$$\Delta H^{o} = -48.95\ \mathrm{kJmol^{-1}}$$

$$\Delta G^{o} = -0.6108\ \mathrm{kJmol^{-1}}$$

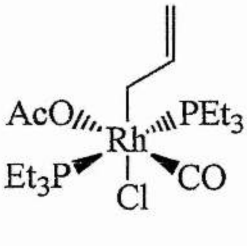
The negative value of ΔS^{o} meant that on oxidative addition of 1-chloroprop-2-ene to the [RhCl(CO)(PEt$_3$)$_2$] the system became more ordered. This can be easily visualised as the two reactants combined to give the one product. The slightly negative ΔG^{o} value meant that the reaction was favoured under the standard conditions (i.e. at 25 °C), however, it can be seen from the graph that at increased temperatures the ΔG value became positive. This meant that the equilibrium moved to the left i.e. back to the reactants. The negative enthalpy term meant that the reaction was exothermic because the formation of the new Rh-C and Rh-Cl bonds released more energy than it took to break the C-Cl bond of the 1-chloroprop-2-ene when the oxidative addition reaction occurred.

At the reaction temperature of 120 °C in a catalytic run involving 1-chloroprop-2-ene most of the catalyst would be in the Rh(I) oxidation state. Thus the standing concentration of the Rh(III) oxidative addition complex in the solution would be very small.

An attempt was made to measure the kinetics of the oxidative addition reaction using a spin-saturation transfer experiment carried out using ^{31}P NMR spectroscopy. This technique involved placing a magnetic label on the phosphines of one of the rhodium complexes by inverting the spin signal and then following the intensity of the phosphine signals on the other rhodium complex as the inverted signal relaxed back. If there was chemical exchange on the timescale of the relaxation process a reduction in intensity of the monitored signal should have been observed. However, in this experiment there was no decrease in the intensity of the signal between -50 and -10 °C. This showed that the oxidative addition reaction occurred either at a faster or slower rate than the NMR timescale. The absence of dynamic NMR line broadening indicated that the rate of the reaction must have been low. However, the rate was not low enough to follow the reaction by measuring the signal intensities as a function of time. Therefore, the reaction must have come into equilibrium soon after the desired temperature was reached but not rapidly enough to be measured by the spin-saturation transfer experiment.

3.2.5 Reaction of [Rh(OAc)(CO)(PEt$_3$)$_2$] with 1-chloroprop-2-ene at -20 °C

In an attempt to isolate the Rh(III) intermediate (shown in figure 3.16) formed from the oxidative addition of 1-chloroprop-2-ene to [Rh(OAc)(CO)(PEt$_3$)$_2$] a similar low temperature experiment to the one above was carried out.



(fig. 3.16)

The ^{31}P NMR spectrum showed two doublets at δ 12.79 and 14.64 ppm with coupling constants typical of Rh(III) complexes (table 3.9). The doublet at δ 14.64 ppm was due to the [RhCl$_2$(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$], shown in figure 3.13 in section 3.3.3. The doublet at δ 12.79 ppm was probably due to the complex shown above in figure 3.16.

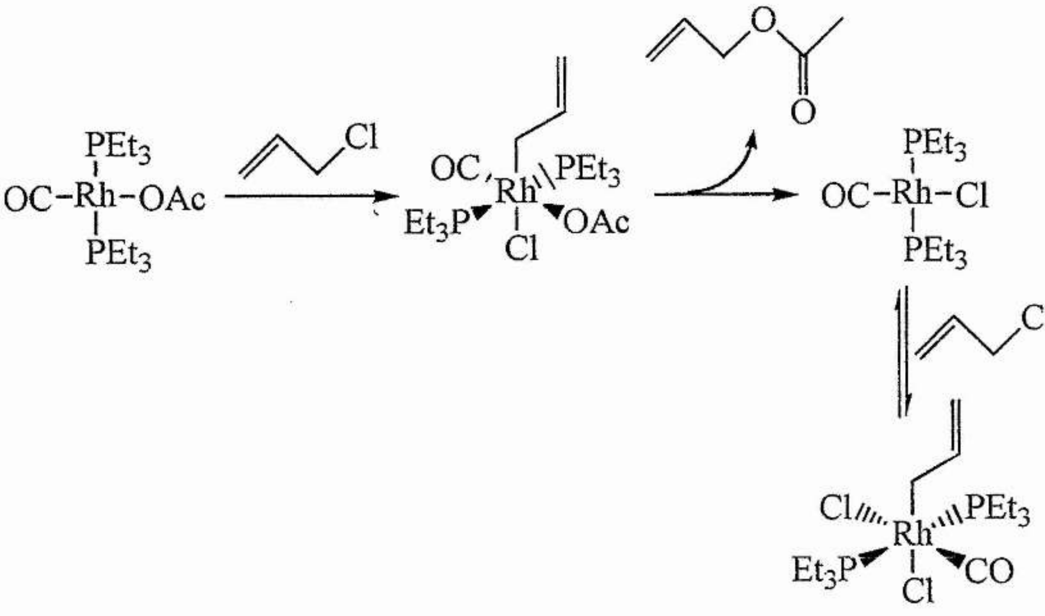
Table 3.9 ^{31}P NMR Data for Reaction of 1-chloroprop-2-ene with [Rh(OAc)(CO)(PEt$_3$)$_2$]

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment
12.79	d	86.16	$^1J_{Rh-P}$ of *trans*-[RhCl(OAc)(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$]
14.64	d	85.58	$^1J_{Rh-P}$ of *trans*-[RhCl$_2$(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$]

A fractional crystallisation of the mixture was attempted and crystals were obtained from the solution at -50 °C and again at -70 °C. However, a mixture of [RhCl(CO)(PEt$_3$)$_2$] and [RhCl(OAc)(CH$_2$CHCH$_2$)(CO)(PEt$_3$)$_2$] was obtained for both fractions.

3.2.6 Summary of Oxidative Addition Reactions Involving 1-Chloroprop-2-ene

When 1-chloroprop-2-ene was added to a solution containing [Rh(OAc)(CO)(PEt$_3$)$_2$] it oxidatively added to give the corresponding Rh(III) complex. This immediately reductively eliminated a molecule of prop-1-enyl ethanoate to give [RhCl(CO)(PEt$_3$)$_2$]. The [RhCl(CO)(PEt$_3$)$_2$] could also oxidatively add another molecule of 1-chloroprop-2-ene to give the corresponding Rh(III) complex (figure 3.17)



(fig. 3.17)

The intermediate Rh(III) complex, [$RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2$], was isolated from the reaction of [$RhCl(CO)(PEt_3)_2$] and 1-chloroprop-2-ene at -20 °C. However, on warming up to room temperature reductive elimination of 1-chloroprop-2-ene occurred. All of the σ-propenyl species seem to be thermally sensitive and lose the propenyl group on warming to give [$RhCl(CO)(PEt_3)_2$].

3.3 Reaction of Benzyl Chloride with [$Rh(OAc)(CO)(PEt_3)_2$]

The reaction between benzyl chloride and [$Rh(OAc)(CO)(PEt_3)_2$] was carried out in order to confirm that the benzyl group would react in the same way with the Rh complex as the prop-1-enyl group.

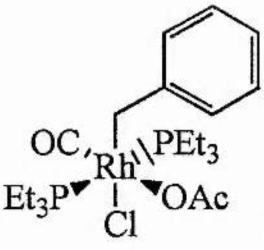
A 5:1 excess of benzyl chloride was added to [$Rh(OAc)(CO)(PEt_3)_2$] and the solution heated up to 60 °C for 30 minutes and the resulting Rh complex crystallised at -100 °C. It was identified as $[RhCl(CO)(PEt_3)_2]$ by ^{31}P NMR spectroscopy (δ 24.55 ppm, d, $^{1}J_{Rh\text{-}P} = 117.4$ Hz).

A second *in situ* NMR reaction was carried out in order to gain more information on the above reaction. The solution was heated up to 60 °C for 15 minutes in an NMR tube before being cooled to room temperature and placed in the NMR magnet. The ^{31}P NMR of the reaction showed two doublets (table 3.10). No evidence was present in this ^{31}P NMR spectrum for $[RhCl(CO)(PEt_3)_2]$.

Table 3.10 ^{31}P NMR Data for Reaction of $[Rh(OAc)(CO)(PEt_3)_2]$ with Benzyl Chloride

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
17.86	d	90.78	$^{1}J_{Rh\text{-}P}$ of *trans*-$[Rh(OAc)Cl(PhCH_2)(CO)(PEt_3)_2]$	14
25.29	d	126.17	$^{1}J_{Rh\text{-}P}$ of *trans*-$[Rh(OAc)(CO)(PEt_3)_2]$	44

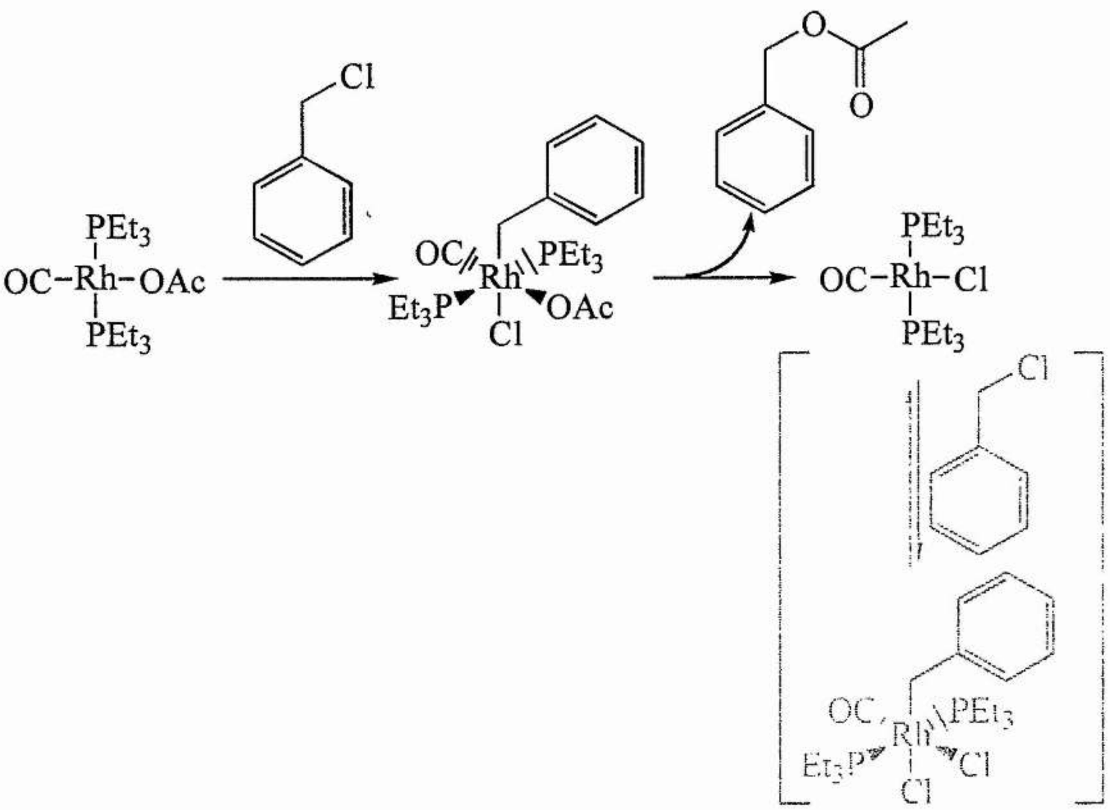
The doublet at δ 17.86 ppm was from the Rh(III) oxidative addition complex shown in figure 3.18. From the relative intensities of the peaks it could be seen that the Rh (I) was present in the greater amount.



(fig. 3.18)

The ^{1}H NMR spectrum of the reaction did not give a great deal of information about the reaction because of the presence of the excess benzyl chloride. The peaks that were expected to be present for the complex were hidden under the larger peaks due to the excess benzyl chloride. There were, however, two singlets due to the methyl groups on the ethanoate ligands of the Rh(I) and Rh(III) complexes present in the spectrum. These gave supporting evidence for the formation of the Rh(III) complex shown in figure 3.14. No peaks were present that could have been due to benzyl acetate.

From the above experiments it can be concluded that an analogous reaction takes place for the benzyl chloride as for the 1-chloroprop-2-ene when added to a solution containing [Rh(OAc)(CO)(PEt_3)$_2$] (figure 3.19). The part of the diagram shown in blue was not observed in the above experiments but, as with the reactions carried out with 1-chloroprop-2-ene, the formation of [RhCl_2(PhCH_2)(CO)(PEt_3)$_2$] could have been favoured by low temperatures.



(fig. 3.19)

3.4 Attempted Reaction of 1-Chloropropane and Chlorobenzene with $[Rh(OAc)(CO)(PEt_3)_2]$

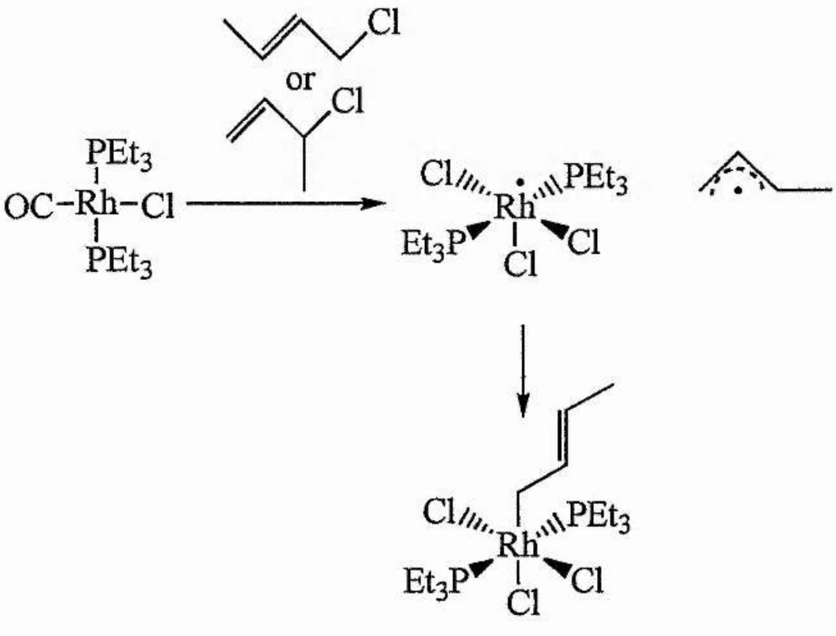
There was no evidence, either in the ^{31}P or ^{1}H NMR spectra, for the reaction between 1-chloropropane and $[Rh(OAc)(CO)(PEt_3)_2]$ (2:1). The only doublet present in the ^{31}P NMR spectrum occurred at δ 25.32 ppm ($^{1}J_{Rh\text{-}P}$ = 126.53 Hz). This was assigned to $[Rh(OAc)(CO)(PEt_3)_2]$. The starting materials from this reaction were recovered unchanged. As mentioned in the previous chapter, the attempted catalytic carbonylation involving 1-chloropropane was unsuccessful. This could, therefore, be attributed to the reluctance of 1-chloropropane to oxidatively add to $[Rh(OAc)(CO)(PEt_3)_2]$.

The attempted oxidative addition of chlorobenzene to $[Rh(OAc)(CO)(PEt_3)_2]$ was carried out under similar conditions to the reaction carried out with 1-chloropropane. As expected, no oxidative addition of chlorobenzene occurred. However, the ^{31}P NMR spectrum contained a small doublet at δ 17.80 ppm with a coupling constant of 90.81 Hz. The intensity of this doublet remained constant when more chlorobenzene was added to the NMR tube. This doublet was attributed to the Rh(III) complex obtained from the oxidative addition of benzyl chloride to $[Rh(OAc)(CO)(PEt_3)_2]$. Therefore, the NMR tube or syringes may have been contaminated with a small amount of benzyl chloride. No peaks were present in the ^{1}H NMR that could be attributed to the expected oxidative addition product of chlorobenzene to $[Rh(OAc)(CO)(PEt_3)_2]$.

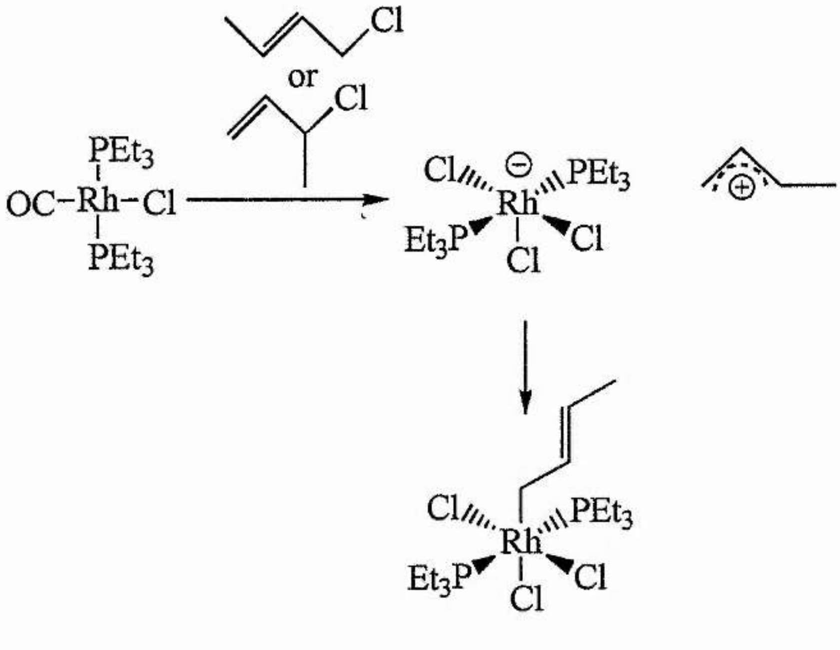
3.5 Reaction of 1-Chlorobut-2-ene and 3-Chlorobut-1-ene with $[RhCl(CO)(PEt_3)_2]$ at variable Temperature

The reactions of 1-chlorobut-2-ene 3-chlorobut-1-ene with $[RhCl(CO)(PEt_3)_2]$ were carried out in an attempt to elucidate the mechanism of the formation of the same straight chain ester from both compounds in catalytic reactions. The reactions were carried out at temperatures varying from -60 °C to 40 °C and were monitored *in situ* by ^{31}P and ^{1}H NMR.

Prior to these experiments it was suspected that either of two reactions was occurring. The first was oxidative addition *via* a free radical mechanism which gave an unsymmetrical stabilised allylic intermediate which would add to the rhodium complex at the least hindered end (figure 3.20). The second was an S_N1 type mechanism where a similar type of unsymmetrical intermediate was formed as in the radical mechanism which would again add to the rhodium complex at the least hindered end (figure 3.21). However, in the light of the results of the following experiments both of the above proposed mechanisms seem unlikely.



(fig. 3.20)

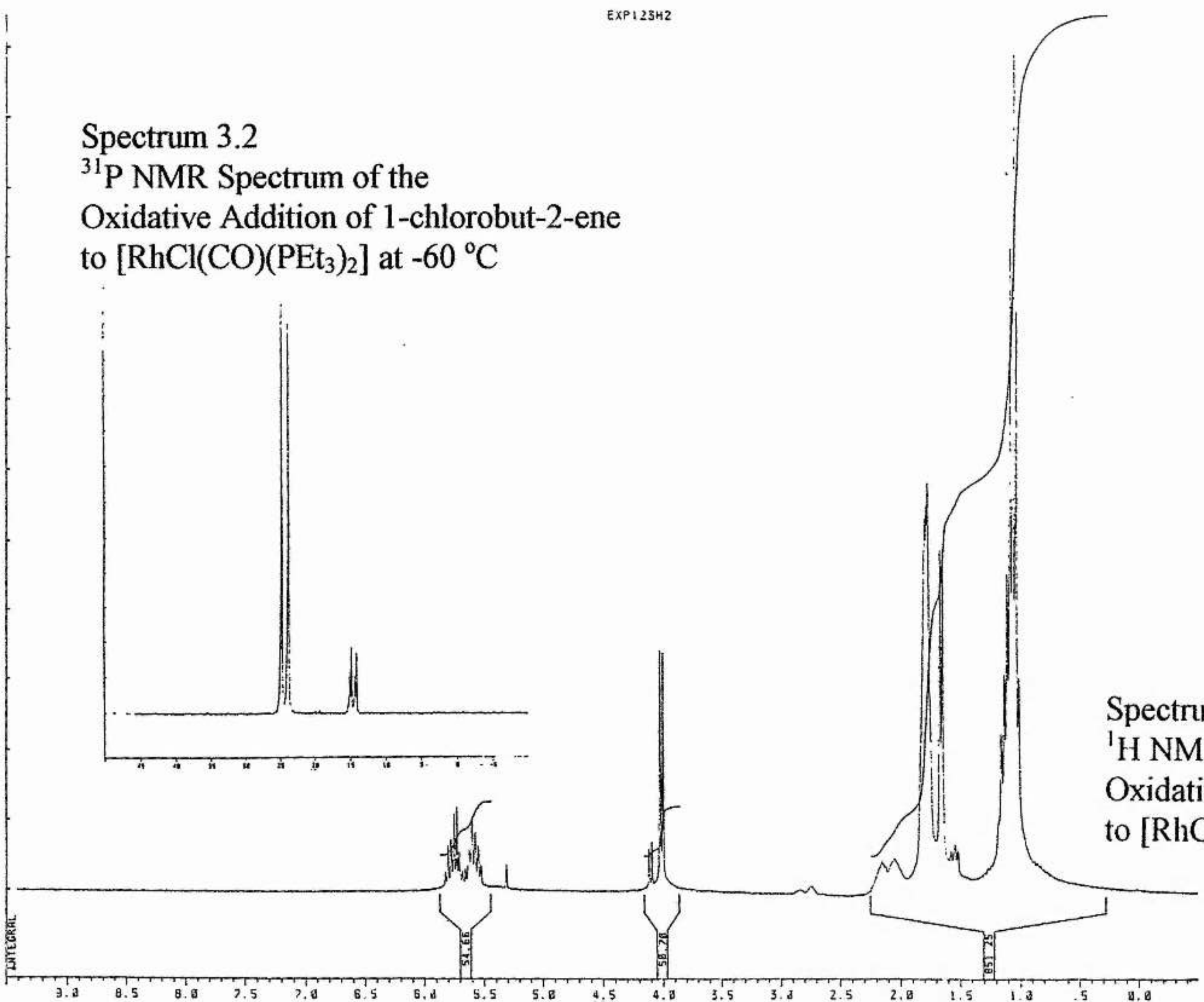


(fig. 3.21)

When 1-chlorobut-2-ene was added to a solution of [RhCl(CO)(PEt$_3$)$_2$] in CD$_2$Cl$_2$ at -60 °C two Rh(III) oxidative addition complexes were formed (table 3.11 and spectra 3.2 and 3.3).

Table 3.11 Products from the Oxidative Addition of 1-Chlorobut-2-ene to [RhCl(CO)(PEt$_3$)$_2$] at -60 °C

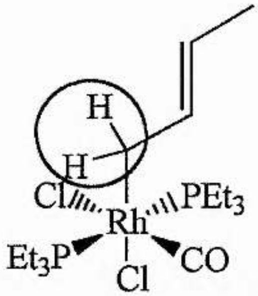
Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
14.42	d	86	$^1J_{Rh-P}$ of *trans*-[RhCl$_2$(CH$_2$CHCHCH$_3$)(CO)(PEt$_3$)$_2$]	7
14.67	d	86	$^1J_{Rh-P}$ of *trans*-[RhCl$_2$(CH$_2$CHCHCH$_3$)(CO)(PEt$_3$)$_2$]	4.5
24.17	d	113	$^1J_{Rh-P}$ of *trans*-[RhCl(CO)(PEt$_3$)$_2$]	48.3



Spectrum 3.2
^{31}P NMR Spectrum of the
Oxidative Addition of 1-chlorobut-2-ene
to $[RhCl(CO)(PEt_3)_2]$ at -60 °C

Spectrum 3.3
^{1}H NMR Spectrum of the
Oxidative Addition of 1-chlorobut-2-ene
to $[RhCl(CO)(PEt_3)_2]$ at -60 °C

The ^{1}H NMR spectrum of the reaction solution at this temperature showed a large amount of unreacted 1-chlorobut-2-ene. Both the *E*- and *Z*-isomers were present in the solution with the *E*-isomer being the most predominant. Two small, broad and unresolved multiplets were present at δ 2.77 and 2.85 ppm in a ratio of 2:1. These were assigned to the methylene protons of the but-2-enyl group joined to the Rh(III) centre (figure 3.22). The signal at δ 2.77 ppm was assigned to the *E*-isomer with the *Z*-isomer giving a signal at δ 2.85 ppm.



(fig. 3.22)

The presence of the two doublets in the ^{31}P NMR spectrum and the two multiplets at δ 2.77 and 2.85 ppm in the ^{1}H NMR spectrum could have been due to *E*- and *Z*-isomers of the but-2-enyl group on the Rh(III) complex.

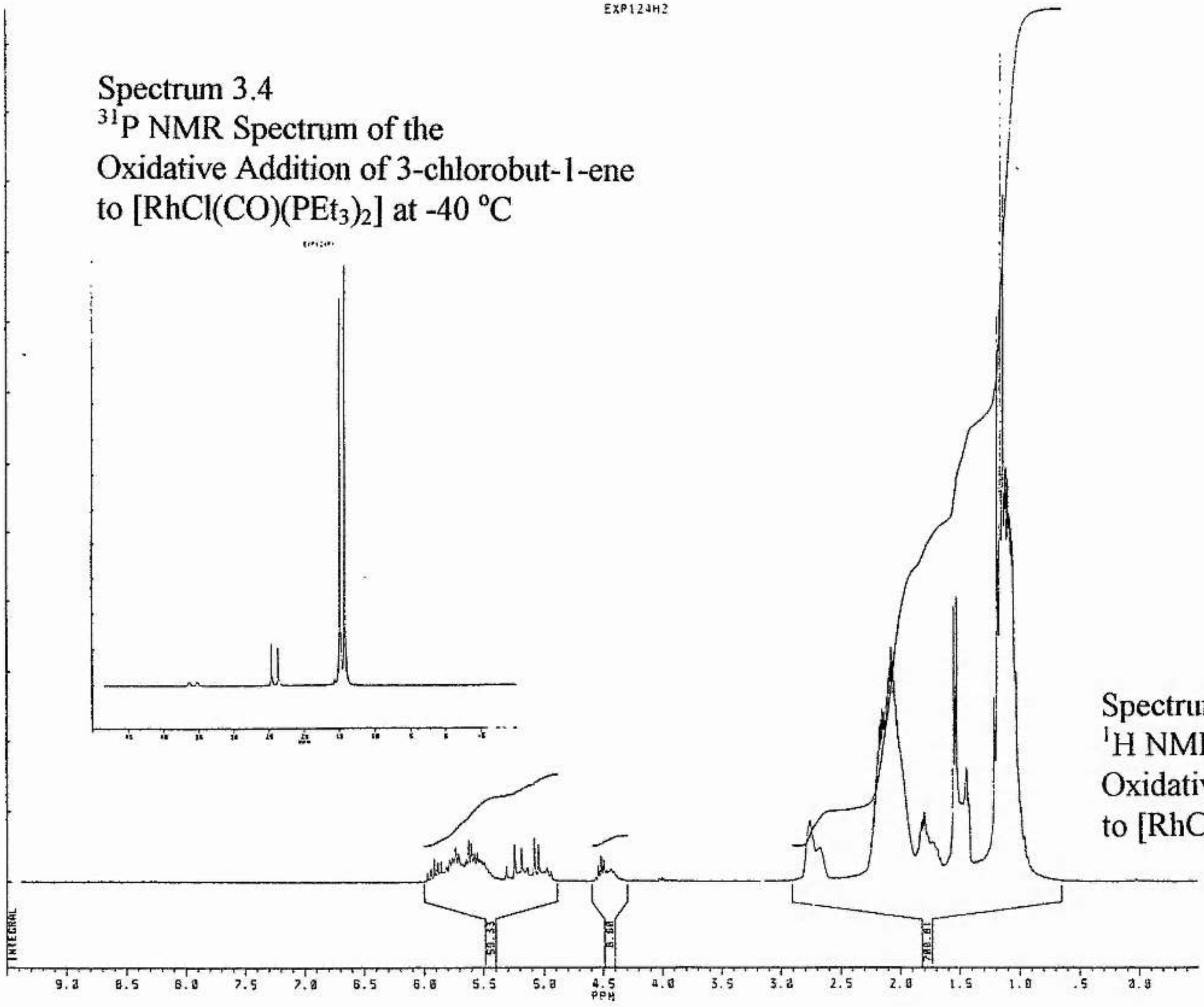
As the solution was warmed, the only change that occurred below 0 °C was the increasing in intensity of the peaks in the ^{31}P NMR spectrum due to the Rh(III) complexes. However, at 0 °C and above significant amounts of free 3-chlorobut-1-ene were observed in the solution. The broad multiplets at δ 2.77 and 2.85 ppm at 25 °C were in a ratio of approximately 2:1 in favour of the *E*-isomer. The *Z*-1-chlorobut-2-ene was present in the solution at less than 10% the concentration of the *E*-isomer, therefore, the oxidative addition of *Z*-1-chlorobut-2-ene seemed to be favoured over that of the *E*-1-chlorobut-2-ene. Peaks arising from a Rh(III) oxidative addition product containing the branched chain butenyl group were not seen.

When the above experiment was carried out by starting at room temperature and cooling to -60 °C, almost the reverse of the above process occurred. At room temperature both 1-chlorobut-2-ene and a small amount of 3-chlorobut-1-ene were present in the solution. The two peaks from the Rh(III) complexes seen in the previous reaction were present in the ^{31}P NMR spectrum. As the reaction was cooled the peaks in the ^{1}H NMR spectrum due to the free 3-chlorobut-1-ene diminished in intensity. Only the doublet at δ 14.42 ppm increased in intensity in the ^{31}P NMR spectra. This difference was also reflected in the ^{1}H NMR spectrum with only one broad multiplet at δ 2.77 ppm present, corresponding to the *E*-isomer.

When the analogous reaction was carried out with 3-chlorobut-1-ene an unexpected result was obtained. Instead of the two expected Rh(III) complexes being present there was only one. This was the same as the first Rh(III) complex listed in table 3.11. This reaction, unlike the previous two, had almost gone to completion at -40 °C (table 3.12 and spectra 3.4 and 3.5).

Table 3.12 Products from the Oxidative Addition of 3-Chlorobut-1-ene to $[RhCl(CO)(PEt_3)_2]$ at -40 °C

Chemical Shift δ (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
14.42	d	86	$^{1}J_{Rh-P}$ of *trans*-$[RhCl_2(CH_2CHCHCH_3)(CO)(PEt_3)_2]$	46.3
24.17	d	114	$^{1}J_{Rh-P}$ of *trans*-$[RhCl(CO)(PEt_3)_2]$	4.6



Spectrum 3.4
^{31}P NMR Spectrum of the
Oxidative Addition of 3-chlorobut-1-ene
to $[RhCl(CO)(PEt_3)_2]$ at -40 °C

Spectrum 3.5
^{1}H NMR Spectrum of the
Oxidative Addition of 3-chlorobut-1-ene
to $[RhCl(CO)(PEt_3)_2]$ at -40 °C

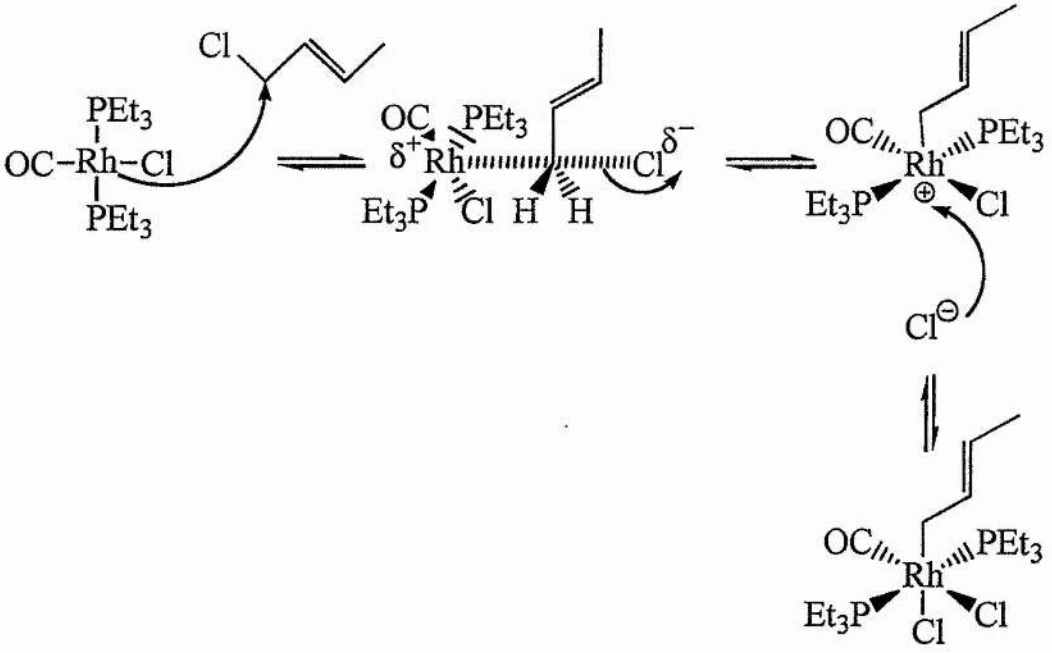
The ^{1}H NMR spectrum at -40 °C showed the solution contained free 3-chlorobut-1-ene and a very small amount of free 1-chlorobut-2-ene. The ^{1}H NMR spectrum also showed that the butenyl group on Rh(III) oxidative addition complex was the same as that for the previous reactions i.e. as shown in figure 3.22.

As the temperature was increased the amount of the Rh(III) oxidative addition complex present decreased and the amount of free 3-chlorobut-1-ene in the solution increased. This was unexpected as the compound that should have been reductively eliminated was 1-chlorobut-2-ene.

When the analogous reaction was carried out in d^8-toluene the amount of the Rh(III) oxidative addition complex present at -40 °C was approximately 0.26% that of the initial $[RhCl(CO)(PEt_3)_2]$ compared with approximately 90% when the reaction was carried out in CD_2Cl_2. This suggested that the reaction was occurring *via* a mechanism with ionic intermediates rather than *via* a radical based mechanism. The more polar CD_2Cl_2 would have been able to stabilise the ionic intermediates more effectively than the relatively non-polar d^8-toluene.

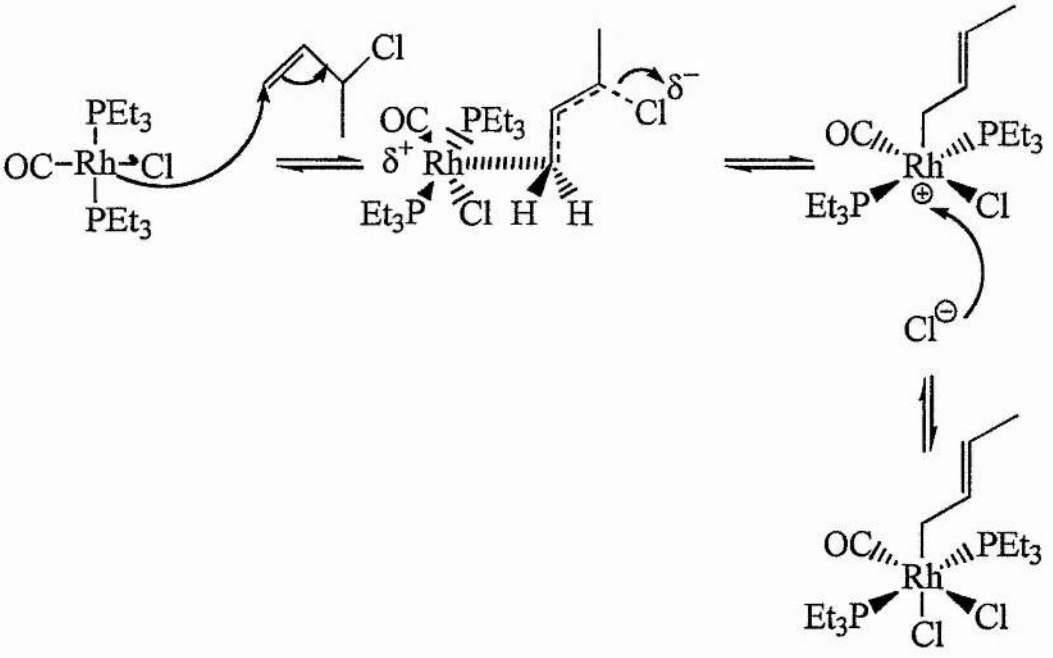
The oxidative addition of 1-chlorobut-2-ene to $[RhCl(CO)(PEt_3)_2]$ resulted in the formation of two very similar Rh(III) complexes (^{31}P NMR: δ 14.42 and 14.67 ppm ($^1J_{Rh-P} = 86$ Hz)). The ^{1}H NMR spectrum showed two broad multiplets at δ 2.77 and 2.85 ppm from the methylene groups adjacent to the rhodium centre. The two complexes were thought to be the *E*- and *Z*-isomers of the straight chain oxidative addition complex. The oxidative addition of 3-chlorobut-2-ene to $[RhCl(CO)(PEt_3)_2]$ resulted in the formation of only one Rh(III) complex. The ^{31}P NMR spectrum showed this to be the same as the one of the complexes formed from the oxidative addition of 1-chlorobut-2-ene to $[RhCl(CO)(PEt_3)_2]$ (δ 14.42 ppm ($^{1}J_{Rh-P}$ = 86 Hz)). The ^{1}H NMR spectrum showed only one broad multiplet at d 2.77 ppm. This was attributed to the *E*-isomer.

The oxidative addition of 1-chlorobut-2-ene to $[RhCl(CO)(PEt_3)_2]$ could have occurred *via* an S_N2 reaction (figure 3.23). The stereochemistry of the double bond was maintained during the reaction.



(fig. 3.23)

The mechanism for the oxidative addition of 3-chlorobut-1-ene is not as straight forward. The same ester, ethyl *E*-but-3-enoate, was obtained from the catalytic run as for 1-chlorobut-2-ene. One of the possible mechanisms that could explain this reaction is oxidative addition by a radical intermediate. However, because of the nature of the oxidative addition products seen in the NMR reactions and the retarding of the reaction when it was carried out in toluene, free radicals have been discounted as intermediates. An S_N1 type mechanism is also unlikely because both the 1-chlorobut-2-ene and 3-chlorobut-1-ene would have given similar NMR spectra and product ratios because the same intermediates would have been present. An S_N2 mechanism would give a branched chain intermediate which was not seen in the NMR spectra. However, the S_N2' mechanism for the oxidative addition of 3-chlorobut-1-ene would give the straight chain intermediate (figure 3.24).

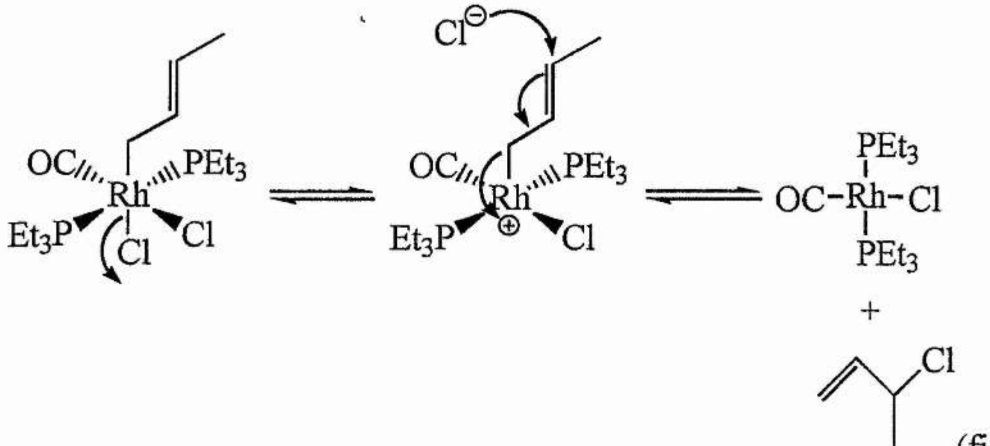


(fig. 3.24)

The S_N2' mechanism usually occurs where normal S_N2 conditions hold but where α-substitution sterically retards the normal S_N2 mechanism. Thus there are few cases of the S_N2' mechanism on substrates of the type $C{=}C{-}CH_2X$, while compounds in the form $C{=}C{-}CR_2X$ give the S_N2' almost exclusively. Increasing the size of the nucleophile can also increase the extent of the S_N2' mechanism at the expense of the S_N2 mechanism.[106]

In this system the [RhCl(CO)(PEt$_3$)$_2$] acts as the nucleophile towards the chlorobutenes. The complex is much larger than any of the usual organic nucleophiles. The normal S_N2 mechanism operates for the 1-chlorobut-2-ene because there is very little steric hindrance at the α-position thus there is room for the nucleophile to attack the carbon atom directly attached to the chlorine. However, the 3-chlorobut-1-ene has a methyl group at the α-position. This, along with the size of the nucleophilic complex, would retard the S_N2 mechanism at this position. Therefore, the reaction will occur at the terminal end of the double bond, which unlike the 1-chlorobut-2-ene is unsubstituted, to give the straight chain intermediate. From the catalytic reactions it can be seen that the yield of ester obtained from the 3-chlorobut-1-ene is slightly greater than that obtained from the 1-chlorobut-2-ene. The NMR reactions also show that far more oxidative addition product is present with 3-chlorobut-1-ene. Thus it seems that the S_N2' mechanism is far more efficient in this system than the S_N2 mechanism. The inefficiency of the carbonylation of 2-methyl-3-chloroprop-1-ene perhaps suggests that a substituent on the centre carbon atom of the allylic group inhibits attack of the nucleophile by S_N2 or S_N2' routes.

It was noticed that 3-chlorobut-1-ene was formed when 1-chlorobut-2-ene was heated in the presence of [RhCl(CO)(PEt$_3$)$_2$]. However, when 3-chlorobut-1-ene was heated in the presence of [RhCl(CO)(PEt$_3$)$_2$] very little 1-chlorobut-2-ene was produced. This could be rationalised by the Rh(III) oxidative addition complex eliminating a chloride ion which would attack the double bond of the allylic group thus reductively eliminating 3-chlorobut-1-ene (figure 3.25).



(fig. 3.25)

3.6 Conclusions

[$Rh_2(OAc)_4.2MeOH$], PEt_3 and CO spontaneously form [$Rh(OAc)(CO)(PEt_3)_2$] in ethanol. Propenyl, butenyl and benzyl halides can undergo oxidative addition to this complex followed by immediate reductive elimination of the corresponding acetates giving [$RhCl(CO)(PEt_3)_2$]. This reaction does not work with chlorobenzene and 1-chloropropane suggesting that the allylic and benzylic moieties are an essential part of the mechanism of oxidative addition. [$RhCl(CO)(PEt_3)_2$] can oxidatively add a further alkenyl halide. Therefore, this complex is thought to be the active catalyst for the catalytic cycle.

The oxidative addition of 1-chloroprop-2-ene is favoured at low temperatures. This meant that at the standard reaction temperature of 120 °C only a very low concentration of the Rh(III) oxidative addition complex was present in the solution. The entropy change of the reaction under standard temperature and pressure was negative, therefore, the system became more ordered after the oxidative addition i.e. two reactants giving one product.

Steric effects appear to control the detailed mechanism of the oxidative addition reaction so that allylic halides substituted on the α-carbon (3-chlorobut-1-ene) undergo S_N2' type reactions whilst those substituted on the γ-carbon undergo the S_N2 type reaction. For 3-chloroprop-1-ene, with no substituents on either carbon atom, we do not have direct evidence for the mechanism of oxidative addition, but the equilibrium constant for the formation of the oxidative addition product is more similar to that observed for 3-chlorobut-1-ene, which probably indicates that an S_N2' mechanism predominates in this case.

The oxidative addition of the propenyl, butenyl and benzyl halides to $[RhCl(CO)(PEt_3)_2]$ can be compared to that of MeI to $[Rh(CO)_2I_2]^-$. This reaction is the rate determining step in the cycle to produce acetic acid from methanol and obeys second-order kinetics (first order in both [MeI] and $[[Rh(CO)_2I_2]^-]$. The mechanism proceeds *via* an S_N2 process. The reaction rate was enhanced by polar solvents with protic solvents giving the best rates. Addition of iodide salts also gave enhanced rates, thought to be due to the formation of the highly nucleophilic dianion, $[Rh(CO)_2I_3]^{2-}$ or the effects of iodide on the transition state complexes [107].

The oxidative addition of the propenyl, butenyl and benzyl halides to $[RhCl(CO)(PEt_3)_2]$ is also enhanced by polar solvents. However, there are some major differences in the two reactions. The oxidative addition reaction in this system is reversible and there is no migratory insertion of carbon monoxide into the Rh-C bond in the absence of added carbon monoxide. After MeI oxidative addition, the insertion reaction occurs immediately to give the acetyl complex.

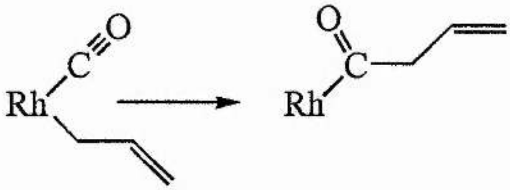
The next stage of the catalytic process is the migratory insertion of carbon monoxide into the Rh-C bond of the Rh(III) complex. It is evident from the experiments on the oxidative addition of the halocarbons to the Rh(I) complex that the migratory insertion reaction does not occur in the absence of added carbon monoxide. No complexes due to migratory insertion were present during the low temperature oxidative addition studies.

CHAPTER 4

4. MIGRATORY INSERTION

4.1 Introduction[108, 109]

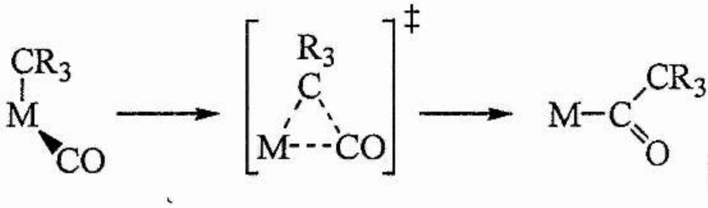
In Chapter 3, the oxidative addition of allylic halides to a rhodium(I) centre was discussed. In the catalytic carbonylation of allylic halides, the likely next step would be the migratory insertion of carbon monoxide into the M-C bond to produce the corresponding acyl species. The overall reaction is shown in figure 4.1.



(fig. 4.1)

Much work has been carried out, mainly with $[Mn(CH_3)(CO)_5]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]$ and ^{13}CO, into determining which group moves. There are three possibilities: the alkyl group moves; the carbon monoxide moves; they both move. It has been shown by using these compounds that it is a coordinated carbon monoxide ligand that becomes the acyl CO and not an external CO. The inserted CO has to be *cis* to the alkyl group and can be effected by addition of ligands other than CO e.g. triethylphosphine.

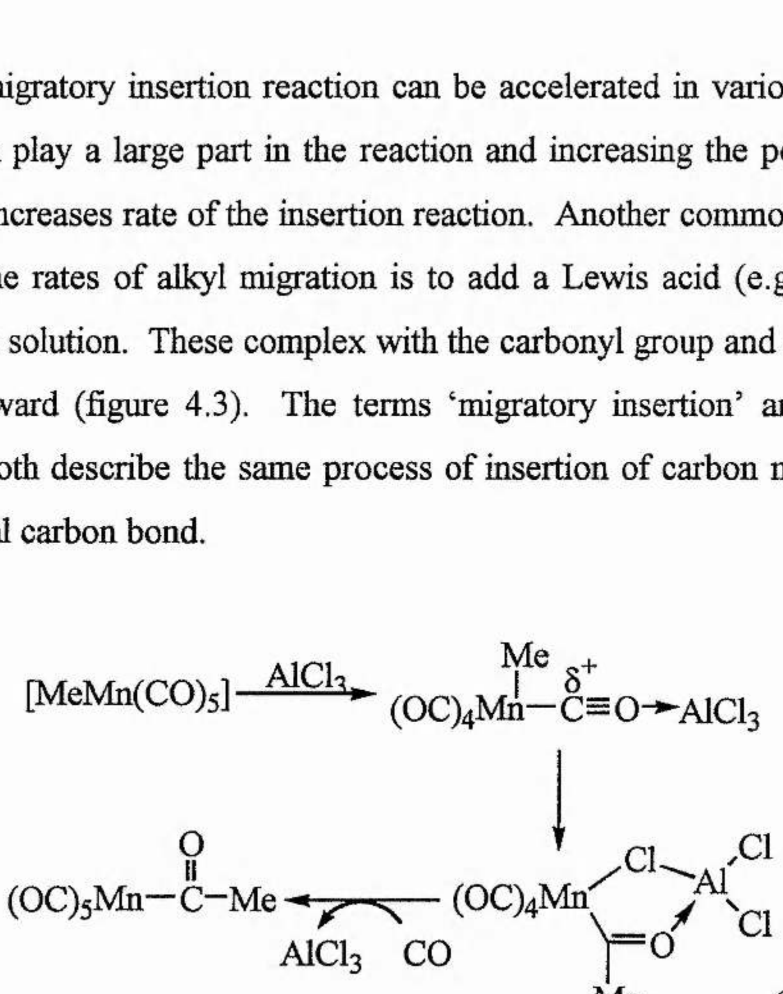
The carbon monoxide insertion reaction is a 1,2-migration of the alkyl group to the *cis* coordinated CO and proceeds through a three centred transition state (figure 4.2).



(fig. 4.2)

With the use of chiral ligands it has been shown that the migratory insertion reaction proceeds with retention of configuration of the alkyl group.

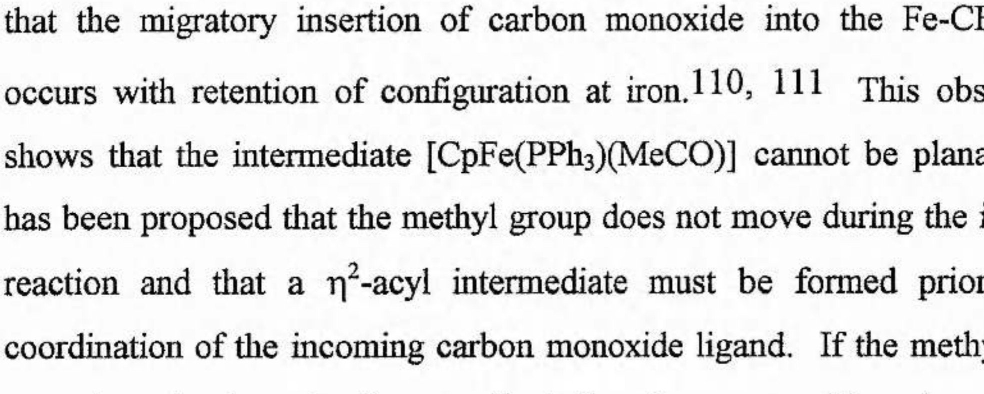
The migratory insertion reaction can be accelerated in various ways. Solvents can play a large part in the reaction and increasing the polarity of the solvent increases rate of the insertion reaction. Another common way of increasing the rates of alkyl migration is to add a Lewis acid (e.g. BF_3 or $AlCl_3$) to the solution. These complex with the carbonyl group and drive the reaction forward (figure 4.3). The terms 'migratory insertion' and 'alkyl migration' both describe the same process of insertion of carbon monoxide into the metal carbon bond.



(fig. 4.3)

The migratory insertion reaction can also be accelerated or initiated by electrochemical or chemical oxidation (using Ag^+ or Ce^{IV}). The transfer is more facile in the oxidised state. In solvent dependent reactions, protonic acids (e.g. HBF_4) may be used to increase the rate of the insertion reaction. Finally halide ions, especially iodide, can promote the migratory insertion reaction. A possible reason for their effectiveness may be because the acyls are better electron acceptors than the alkyls and thus may be able to stabilise the extra electron density donated by the halide ion.

Using the chiral iron complex shown in figure 4.4, it has been shown that the migratory insertion of carbon monoxide into the Fe-CH_3 bond occurs with retention of configuration at iron.[110, 111] This observation shows that the intermediate [CpFe(PPh_3)(MeCO)] cannot be planar and it has been proposed that the methyl group does not move during the insertion reaction and that a η^2-acyl intermediate must be formed prior to the coordination of the incoming carbon monoxide ligand. If the methyl group were to migrate onto the coordinated carbon monoxide , inversion of configuration at the metal would occur even if a η^2-acyl intermediate were formed.



(fig. 4.4)

4.2 Insertion of Carbon Monoxide into [$RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2$]

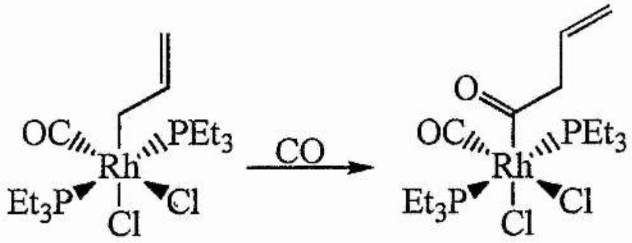
The insertion of carbon monoxide into the Rh-C bond of [$RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2$] was not observed under atmospheric pressure. In order to study this reaction three techniques were used:

1. High pressure NMR (HPNMR) using a titanium capped sapphire crystal cell.
2. High pressure infrared (HPIR) using a SpectraTech CIR cell with a silicon (or zinc selenide) rod inserted through the side. The reaction was monitored at the surface of the rod.
3. Attempted isolation and characterisation of the acyl intermediate.

The rhodium complexes were ideal for study by both NMR and IR spectroscopies. The phosphine and CO ligands enabled the complex to be studied by ^{1}H, ^{13}C and ^{31}P NMR. The IR gave information on the nature of the rhodium complexes *via* the carbon monoxide ligand and the formation of the acyl complexes.

4.2.1 Migratory Insertion Reactions of $[RhCl_2(CO)(CH_2CHCH_2)(PEt_3)_2]$ under Carbon Monoxide Monitored by HPNMR

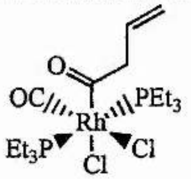
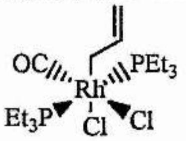
In order to study the insertion of carbon monoxide into the Rh-C bond of the oxidative addition complex the HPNMR cell was charged with 1-chloroprop-2-ene and $[RhCl(CO)(PEt_3)_2]$ in a ratio of 0.95:1 in CD_2Cl_2 (figure 4.5). The cell was then pressurised at room temperature with carbon monoxide to 40 bar. As none or very little insertion product was present in the solution at room temperature or lower then the temperature was raised, in stages to 100 °C to study the insertion reaction (spectra 4.1a-f).

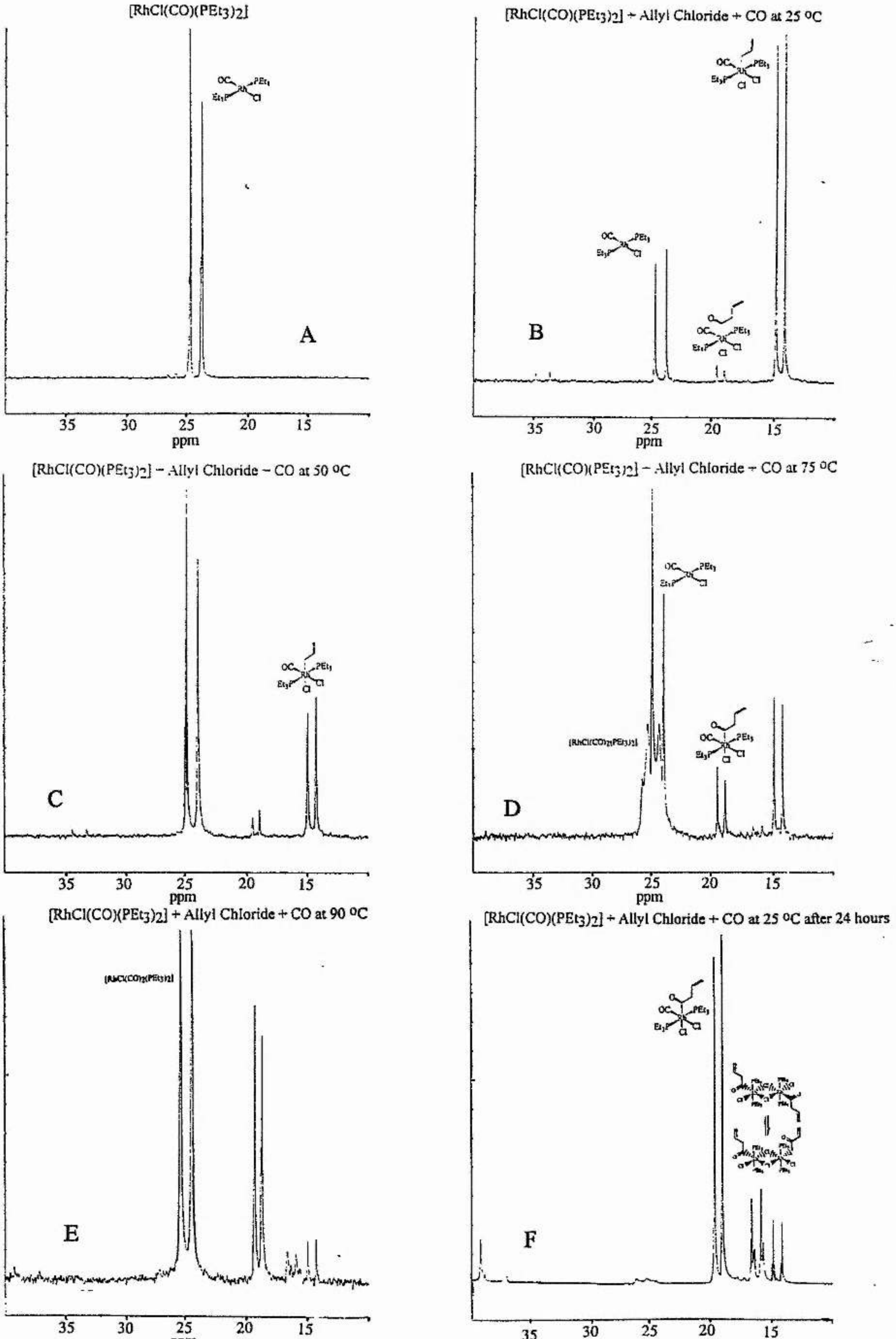


(fig. 4.5)

At room temperature three doublets were present in the ^{31}P NMR spectrum (Table 4.1).

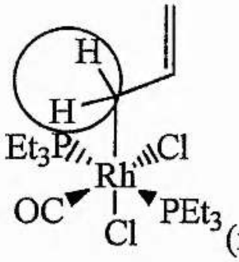
Table 4.1 Species Present at Room Temperature During Investigation into the Above Insertion Reaction

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
24.1	d	116	[RhCl(CO)(PEt$_3$)$_2$]	53
19.3	d	67		7
14.6	d	84		145



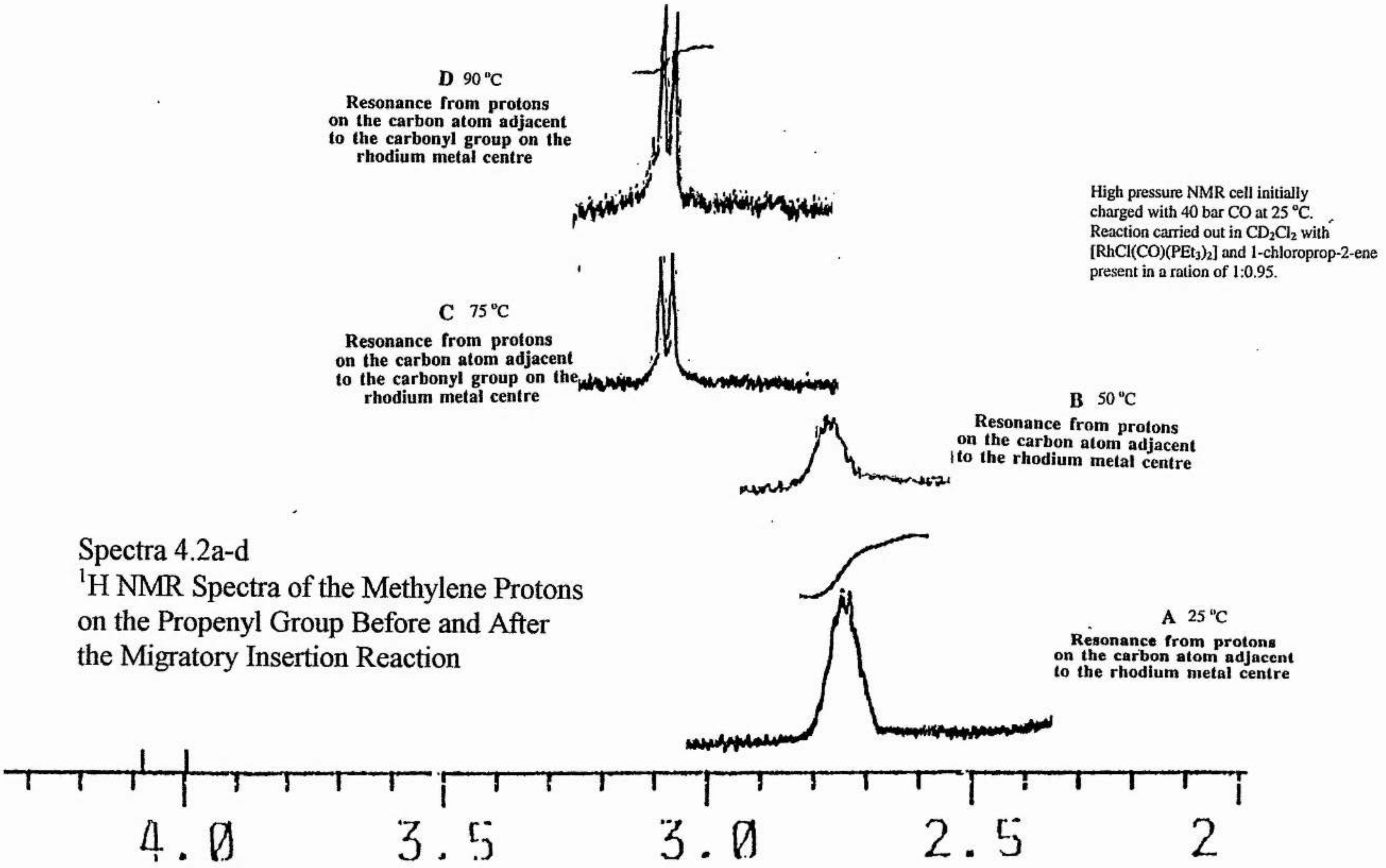
Spectra 4.1a-f
Variable Temperature, High Pressure ^{31}P NMR
Spectra of $[RhCl(CO)(PEt_3)_2]$ and 1-chloroprop-2-ene
in the Presence of Carbon Monoxide

At 25 °C the predominant species present in the solution was [RhCl(CO)(PEt$_3$)$_2$]. There was also a little of the oxidative addition product present in the solution. The very small doublet present in the ^{31}P NMR spectrum at δ 19.3 ppm (rel. int. 7) was thought to correspond to the migratory insertion product shown in figure 4.5. Therefore, at room temperature only a very small amount of this complex was present. The ^{1}H NMR spectrum at this temperature showed peaks for the free 1-chloroprop-2-ene and the oxidatively added η^1-prop-1-enyl group. The peak for the two protons on the carbon atom nearest the rhodium centre (figure 4.6) appeared as a broad, unresolved multiplet centred on δ 2.7 ppm.



(fig. 4.6)

On heating the solution up to 50 °C the intensity of the peak in the ^{31}P NMR spectrum at δ 19.3 ppm (rel. int. 9) increased slightly in intensity. This meant that the concentration of the insertion product was increasing with the rise in temperature. The doublet for the [RhCl(CO)(PEt$_3$)$_2$] also broadened at this temperature. It was thought that carbon monoxide was rapidly exchanging with the Rh(I) complex. This will be discussed later. The broad multiplet at δ 2.7 ppm in the ^{1}H NMR spectrum decreased in intensity and another broad peak started to appear at δ 3.2 ppm. The sequence for this is shown in spectra 4.2a-d.

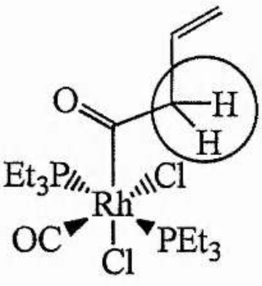


High pressure NMR cell initially charged with 40 bar CO at 25 °C. Reaction carried out in CD_2Cl_2 with $[RhCl(CO)(PEt_3)_2]$ and 1-chloroprop-2-ene present in a ration of 1:0.95.

Spectra 4.2a-d
^1H NMR Spectra of the Methylene Protons on the Propenyl Group Before and After the Migratory Insertion Reaction

At 75 °C there was no change in the intensity of the doublet at δ 14.6 ppm (rel. int. 58) in the ^{31}P NMR spectrum whilst the doublet at δ 19.3 ppm (rel. int. 27) had increased in intensity. The Rh(I) complexes were still present in the solution at a much greater concentration than the Rh(III) complexes

The ^{1}H NMR spectrum showed that there was free 1-chloroprop-2-ene present in the solution. The broad multiplet at δ 2.7 ppm had completely disappeared and was replaced by a sharp doublet at δ 3.2 ppm. This corresponded to the protons nearest the carbonyl group on the acyl complex (figure 4.7).



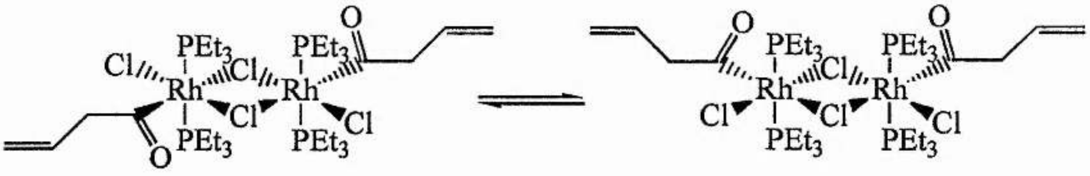
(fig. 4.7)

The broad peak resulting from the coupling between these protons and the rhodium and phosphorus atoms in the prop-2-enyl complex was no longer present because the carbonyl group was now between the rhodium and the methylene group. The downfield shift of the signal due to the methylene group also indicated that insertion had occurred.

At 90 °C the amount of the insertion product had increased but there was still quite a significant amount of Rh(I) complex present. However, two small doublets had appeared in the ^{31}P NMR spectrum at δ 16.5 and 17.0

ppm with ${}^{1}J_{Rh\text{-}P}$ of 85 Hz (rel. int. 8 and 13 respectively). A similar spectrum was obtained at 100 °C.

The solution was cooled down and a ${}^{31}P$ NMR spectrum was run after it had been allowed to stand for 24 hours. There was only a very small amount of Rh(I) complex present in the solution. The Rh(III) insertion complex was the most abundant species present in the solution. The two small doublets present at δ 16.5 and 17.0 ppm (rel. int. 15 and 37 respectively) had increased in intensity indicating that these species had increased in concentration. These species were suspected to be Rh(III) dimers of the type shown in figure 4.8, though no direct evidence for the formation of these complexes was obtained.

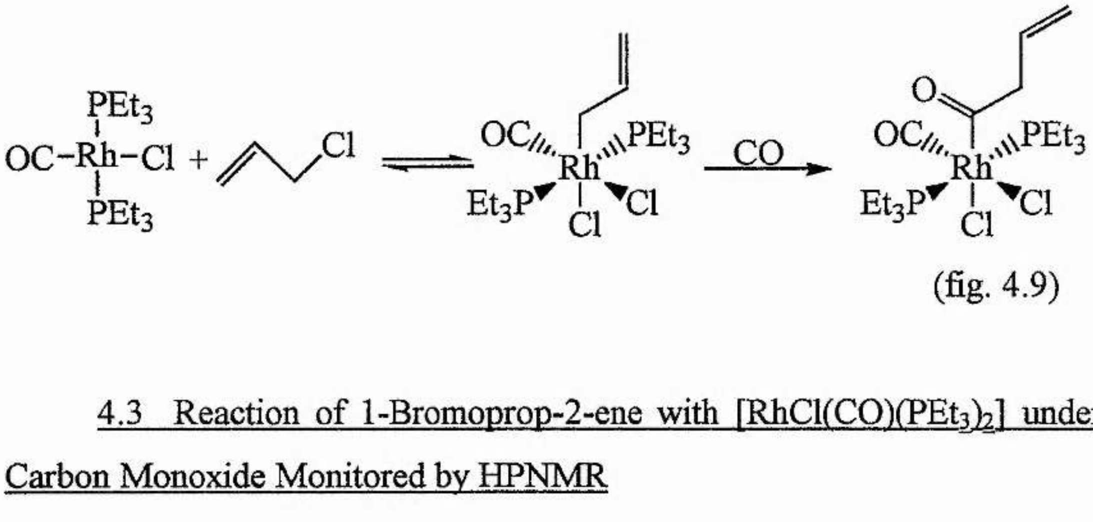


(fig. 4.8)

These dimers were thought to have been formed because the pressure of carbon monoxide in the HPNMR cell dropped. Thus there was not enough carbon monoxide present to fill the vacant site left after the migratory insertion reaction. Solvent molecules could have coordinated with the complexes but because of the presence of the two doublets in the ${}^{31}P$ NMR spectrum the formation of the *cis* and *trans* isomers shown above was thought to be more likely.

The presence of the migratory insertion product at room temperature after 24 hours suggests that the migration of the 1-propenyl group is under kinetic rather than thermodynamic control. It has been shown that once this complex is formed, in the absence of either water or a protic solvent, it is quite stable and does not undergo the reverse reaction at room temperature under argon.

The oxidative addition product was favoured by low temperatures but high temperatures were needed for the migratory insertion to occur. Thus at high temperatures the standing concentration of the oxidative addition product was very low because it could either reductively eliminate 1-chloroprop-2-ene, which was favoured by high temperatures, or migratory insertion could take place (figure 4.9).



(fig. 4.9)

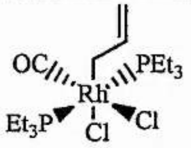
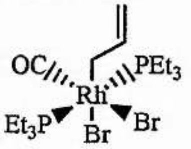
4.3 Reaction of 1-Bromoprop-2-ene with $[RhCl(CO)(PEt_3)_2]$ under Carbon Monoxide Monitored by HPNMR

The reaction of 1-bromoprop-2-ene with $[RhCl(CO)(PEt_3)_2]$ under carbon monoxide was carried out in order to try and establish the intermediates present in the carbonylation reaction. The C-Br bond is weaker than the C-Cl bond; oxidative addition of the 1-bromoprop-2-ene to

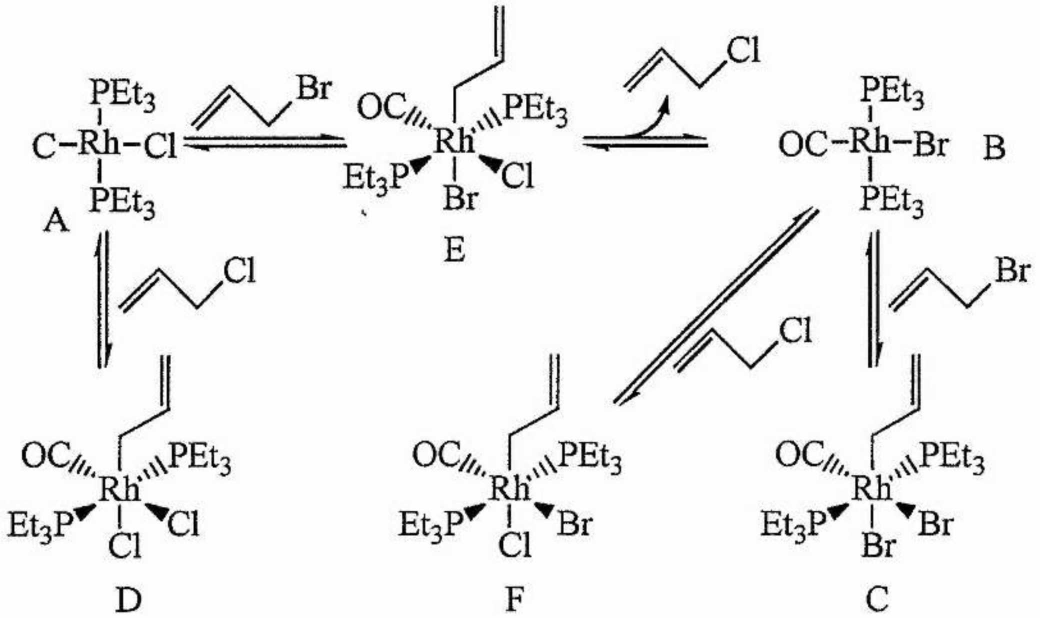
$[RhCl(CO)(PEt_3)_2]$ should have occurred more readily than that of 1-chloroprop-2-ene.

When the ^{31}P NMR spectra taken at -40 °C were examined and compared with those from the oxidative addition of 1-chloroprop-2-ene this was the case. However, there was a mixture of four Rh(III) and two Rh(I) compounds (table 4.2) (Spectra 4.3a and b).

Table 4.2 Products from the Oxidative Addition of 1-bromoprop-2-ene to $[RhCl(CO)(PEt_3)_2]$

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
24.1	d	116	$[RhCl(CO)(PEt_3)_2]$	20.7
22.5	d	113	$[RhBr(CO)(PEt_3)_2]$	15.2
14.4	d	85		19.5
12.2	d	85	$[RhClBr(CH_2CHCH_2)(CO)(PEt_3)_2]$	47.8
11.3	d	85	$[RhBrCl(CH_2CHCH_2)(CO)(PEt_3)_2]$	3.8
8.80	d	85		8.4

From the ^{31}P NMR spectrum the following equilibria were present in the solution (figure 4.10).



(fig. 4.10)

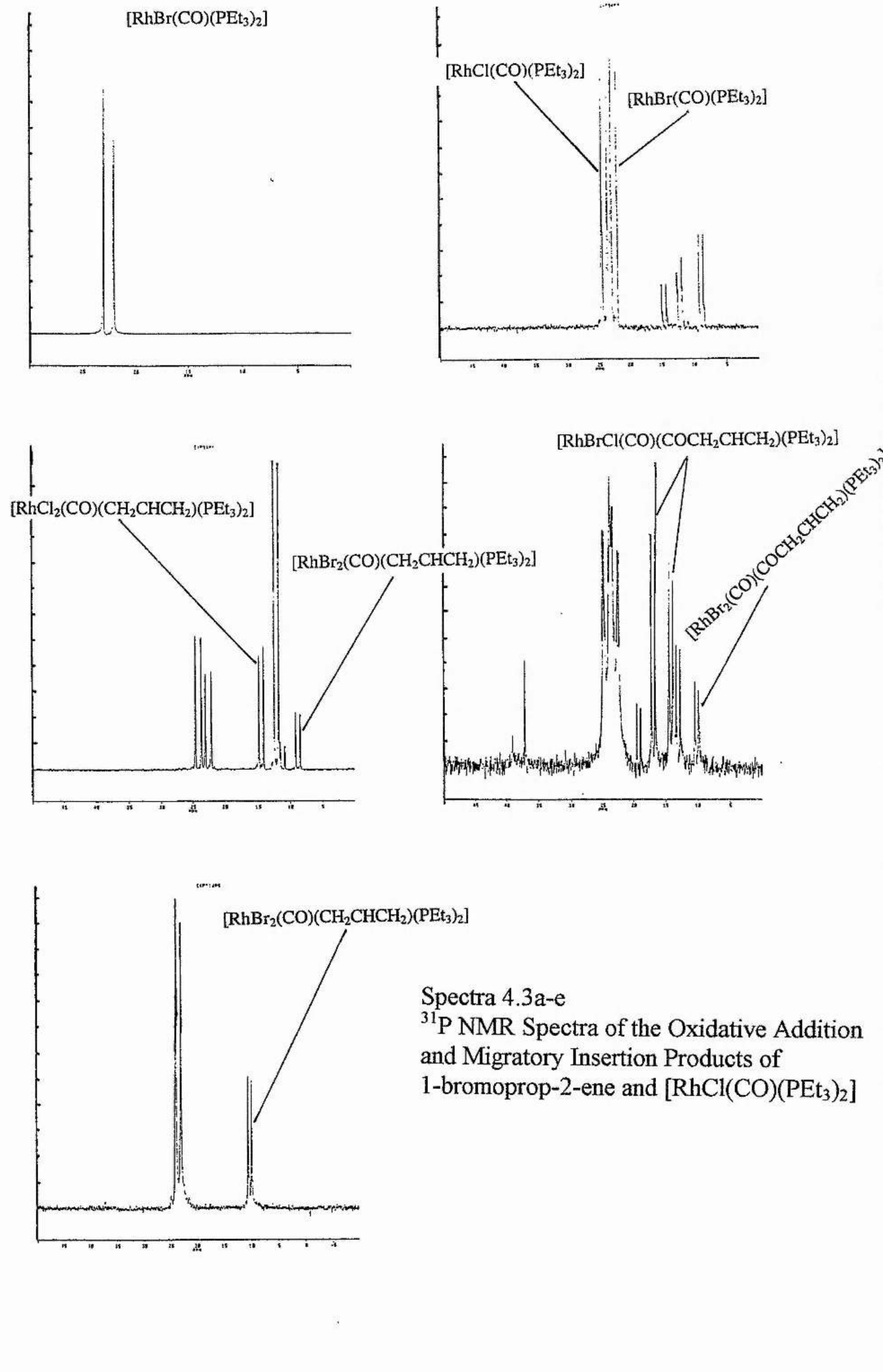
At -40 °C the most predominant species present was E, from the oxidative addition of 1-bromoprop-2-ene onto [RhCl(CO)(PEt$_3$)$_2$]. Species D was from the oxidative addition of 1-chloroprop-2-ene which was present in the solution from the reductive elimination reaction of species E. Species F and C were present in the solution to a lesser extent than the other two Rh(III) complexes. It was determined from the NMR spectrum that at this temperature the oxidative addition complexes were present in the solution at greater concentrations compared with the analogous reaction carried out with 1-chloroprop-2-ene.

As the reaction was heated it followed the same general trend as the oxidative addition reaction of 1-chloroprop-2-ene to [RhCl(CO)(PEt$_3$)$_2$]. The concentrations of the four Rh(III) species decreased whilst those of the two Rh(I) complexes increased. However, at 30 °C the concentration of [RhBr(CO)(PEt$_3$)$_2$] was greater than that of [RhCl(CO)(PEt$_3$)$_2$]. At -40 °C species E followed by D were the most abundant. At 30 °C species C, the dibromo Rh(III) complex, was the most abundant followed by E and then D. This meant that on increasing the temperature the equilibria involving the Rh(III) species favoured the dibromo complex (Spectrum 4.3 c).

When the NMR tube was charged with carbon monoxide (40 bar) at ambient temperature no reaction was observed. The ^{31}P NMR spectrum was the same as that taken at 30 °C under argon. The ^{1}H NMR showed a broad unresolved multiplet at δ 2.87 ppm confirming that no migratory insertion products were present in the solution.

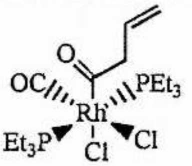
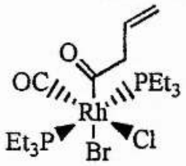
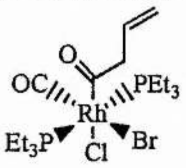
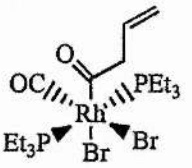
At 40 °C two things occurred in the ^{31}P NMR spectrum. The two Rh(I) doublets broadened and overlapped and a small doublet appeared at δ 14.1 ppm with a coupling constant of 73 Hz. The new doublet was attributed to a migratory insertion complex although no evidence for this was present in the ^{1}H NMR spectrum.

When the temperature was increased beyond 60 °C four new doublets appeared between δ 20 and 5 ppm (table 4.3) in the ^{31}P NMR spectra whilst the peaks due to the Rh(III) oxidative addition complexes disappeared (Spectrum 4.3 d). The two Rh(I) doublets remained broad and overlapped. The ^{1}H NMR spectrum at these temperatures showed sharp doublets at δ 3.20 and 3.18 ppm but no broad peak at δ 2.87 ppm. Therefore, only the migratory insertion complexes were present in the solution.



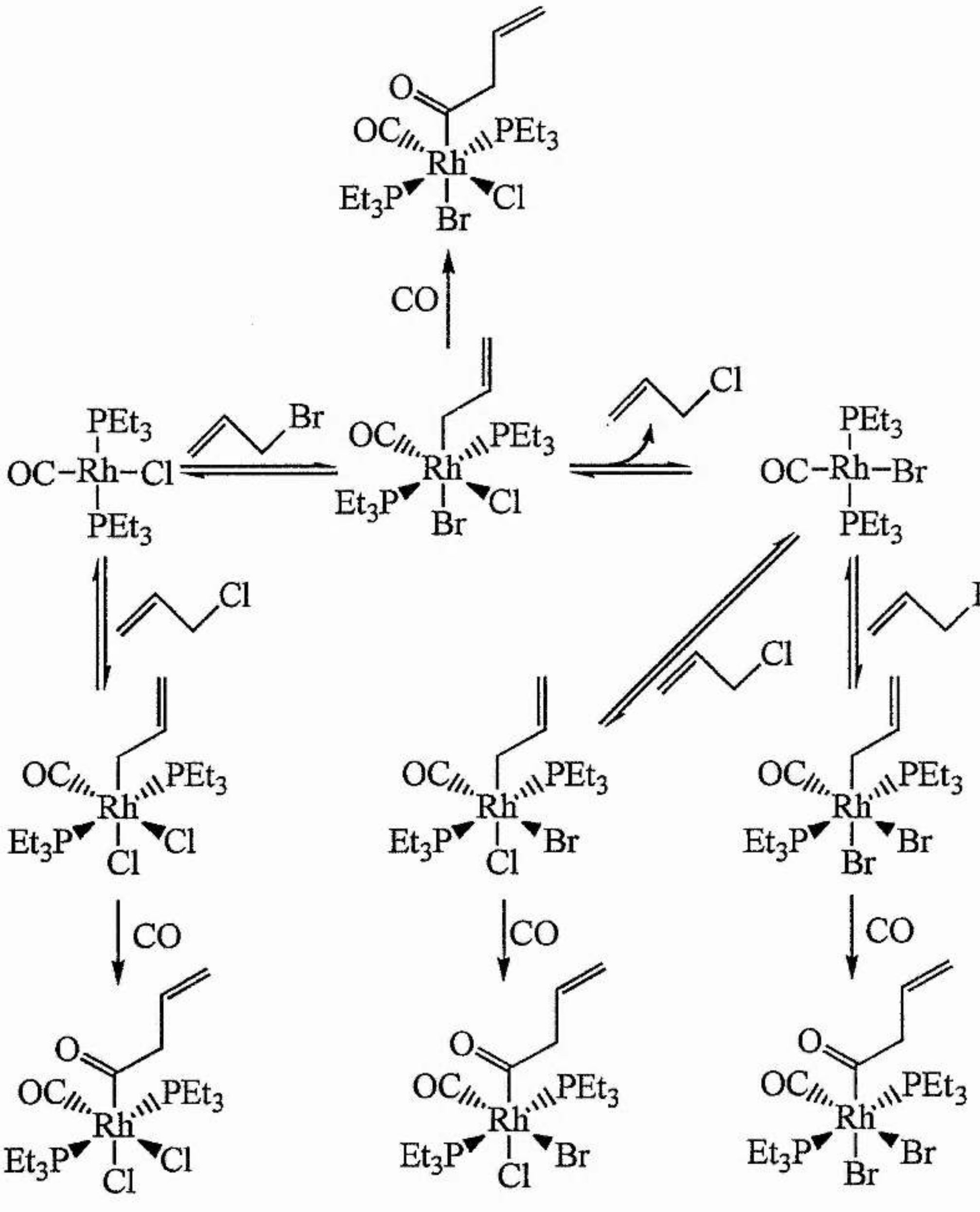
Spectra 4.3a-e
^{31}P NMR Spectra of the Oxidative Addition and Migratory Insertion Products of 1-bromoprop-2-ene and [RhCl(CO)(PEt$_3$)$_2$]

Table 4.3 Products from the Migratory Insertion Reactions in the [RhCl(CO)(PEt$_3$)$_2$]/1-bromoprop-2-ene System at 90 °C

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment	Rel. Int.
24.1	d	118	[RhCl(CO)$_2$(PEt$_3$)$_2$]	48
22.5	d	120	[RhBr(CO)$_2$(PEt$_3$)$_2$]	46
19.1	d	73		9.4
16.9	d	74	Possibly 	42.0
14.1	d	71	Possibly 	31.2
13.0	d	73	Unidentified Rh(III) complex	18.5
9.7	d	73		12.4

Both the dibromo oxidative addition complex and the insertion complex assignments have been confirmed by carrying out a reaction between 1-bromoprop-2-ene and [RhBr(CO)(PEt$_3$)$_2$] under an atmosphere of carbon monoxide (Spectrum 4.3 e).

The ^{1}H NMR spectrum contained four, possibly five, doublets between δ 3.10 and 3.33 ppm. As before these doublets were assigned to the methylene protons of the acyl products with coupling to the adjacent vinylic proton. From the NMR evidence the following species were formed on heating 1-bromoprop-2-ene with [$RhCl(CO)(PEt_3)_2$] under carbon monoxide (figure 4.11).



(fig. 4.11)

The most abundant species in the solution were the two isomers of [$RhClBr(CO)(COCH_2CHCH_2)(PEt_3)_2$].

4.4 Migratory Insertion Reactions Followed by HPIR

The migratory insertion reactions could also be studied using infrared techniques because of the nature of the ligands and products from the reaction. The carbon monoxide ligands that were present on the metal complexes occurred in the region between 2200 and 1800 cm^{-1} and the carbonyls on the products occurred between 1800 and 1650 cm^{-1}. These regions are free of peaks due to other functional groups so the system was quite readily studied by IR spectroscopy.

Background spectra were recorded using the solvents and substrates under carbon monoxide in the absence of the metal complex. This ensured only the peaks that were present from the catalytic intermediates were seen in the spectra. Initially the HPIR cell was placed in an optical bench but because of the long path-length for the IR beam the spectra had very noisy baselines. To get around this problem the cell and the focusing mirrors were placed directly into the instrument. This greatly improved the quality of the spectra.

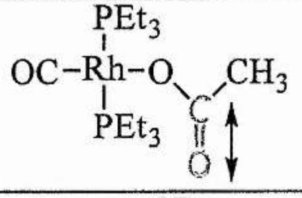
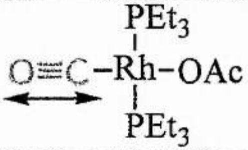
The positions of the peaks due to the stretches of the carbon monoxide ligands on the rhodium centres allowed the oxidation state of the complexes to be determined. Generally peaks between 2200 and 2000 cm^{-1} were from Rh(III) complexes whilst those between 2000 and 1800 cm^{-1} were due to Rh(I) complexes.

4.4.1 Carbonylation of 1-Chlorobut-2-ene using [$Rh_2(OAc)_4.2EtOH$], PEt_3 and Carbon Monoxide

The reaction between [$Rh_2(OAc)_4.2EtOH$], PEt_3 and carbon monoxide in ethanol without 1-chloroprop-2-ene was carried out to monitor the formation of [$Rh(OAc)(CO)(PEt_3)_2$] *in situ* and to identify the peaks due to the unreacted catalyst. At 20 °C peaks at 1963 cm^{-1} and 1710 cm^{-1} were assigned to $\tilde{\nu}_{C\equiv O}$ of the carbon monoxide ligand and $\tilde{\nu}_{C=O}$ of the ethanoato group in [$Rh(OAc)(CO)(PEt_3)_2$] respectively (table 4.4).

It was hoped that intermediates during the formation of [$Rh(OAc)(CO)(PEt_3)_2$] would be observed; however, only the end product was observed in the IR. The complex can be synthesised by bubbling carbon monoxide through an ethanolic solution of [$Rh_2(OAc)_4.2EtOH$] and PEt_3 at atmospheric pressure. The reaction normally goes to completion in approximately two minutes; under 40 bar pressure the reaction would be more rapid so by the time the HPIR cell was placed in the FTIR the reaction would have been over. As the temperature was increased another two very weak peaks appeared in the spectrum. It was possible that these were due to Rh(I) dicarbonyl species (table 4.4).

Table 4.4 IR Data for the Formation of [Rh(OAc)(CO)(PEt$_3$)$_2$]

Wavenumber (cm^{-1})	Intensity	Assignment
1710 (at 15 and 75 °C)	s/m	
1963 (at 15 and 75 °C)	m	
1990 (at 75 °C)	vw	[Rh(OAc)(CO)$_2$(PEt$_3$)$_2$]
2050 (at 75 °C)	vw	[Rh(OAc)(CO)$_2$(PEt$_3$)$_2$]

The carbonylation of 1-chlorobut-2-ene was carried out in ethanol using the catalytic precursors to investigate the formation of the intermediates and products produced in a typical catalytic run. 1-chlorobut-2-ene was used as the substrate because of the good conversion to products observed in the catalytic reactions.

All the reactants were added to the HPIR cell which was pressurised with carbon monoxide to 40 bar. At 12 °C a peak at 1962 cm^{-1} was observed which corresponded to [Rh(OAc)(CO)(PEt$_3$)$_2$]. On heating to 100 °C the peak at 1962 cm^{-1} disappeared and was replaced by a peak at 1953 cm^{-1}. This new peak was attributed to the formation of [RhCl(CO)(PEt$_3$)$_2$] which was confirmed by running an IR of an authentic sample of the compound in ethanol. Approximately 20 minutes after the formation of [RhCl(CO)(PEt$_3$)$_2$] was observed, a peak at 1726 cm^{-1} appeared and started to increase in intensity. This peak corresponded to ethyl pent-3-eneoate. The C=O stretch in an authentic sample of ethyl pent-3-enoate occurred at 1721 cm^{-1} (thin film at room temperature).

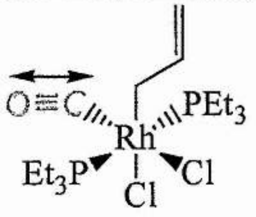
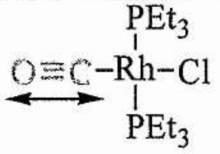
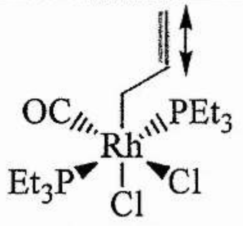
When the temperature was increased to 120 °C the baseline of the spectrum became very noisy thus no further information could be gained from the reaction. This reaction was carried out using the stainless steel 316 autoclave body. On inspection of the rod on completion of the reaction it was found that a thin film of metal had plated out onto the surface of the rod thus cutting down the transmission of infrared radiation into the solution. This was thought to cause the degradation of the baseline.

4.4.2 Reaction of $[RhCl(CO)(PEt_3)_2]$ with 1-Chloroprop-2-ene and Carbon Monoxide in CH_2Cl_2

The reaction of $[RhCl(CO)(PEt_3)_2]$ with 1-chloroprop-2-ene and carbon monoxide was carried out in CH_2Cl_2 so that the formation of the migratory insertion product could be observed. This reaction was carried out with the HPIR cell in the spectrometer. The use of $[RhCl(CO)(PEt_3)_2]$ instead of $[Rh(OAc)(CO)(PEt_3)_2]$ made the IR spectra less complicated, as with the NMR spectra.

A spectrum was taken before the cell was pressurised with carbon monoxide. The results are shown in table 4.5.

Table 4.5 IR Data from Reaction of [RhCl(CO)(PEt$_3$)$_2$] with 1-Chloroprop-2-ene at 12 °C

Wavenumber (cm^{-1})	Intensity	Assignment
2049	s	
1955	m	
1639	m	

This spectrum showed that there was a large amount of oxidative addition product present in the reaction solution compared with [RhCl(CO)(PEt$_3$)$_2$]. This experiment was carried out with approximately fifty times excess of 1-chloroprop-2-ene which would have pushed the equilibrium over towards the oxidative addition product. The analogous NMR experiment at this temperature had less oxidative addition product present in the solution. This was because the [RhCl(CO)(PEt$_3$)$_2$] and 1-chloroprop-2-ene were present in a ratio of approximately 1:1.

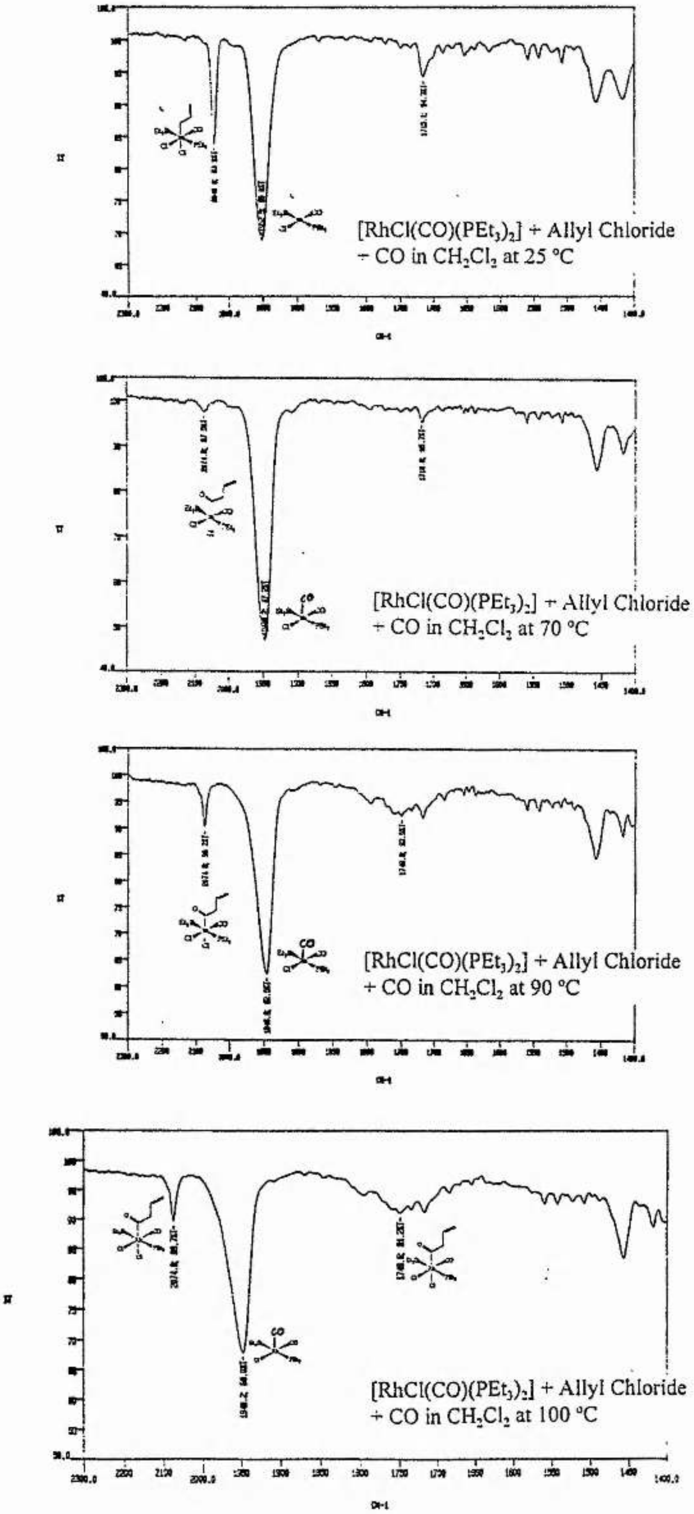
When the cell was pressurised with carbon monoxide (40 bar) at 12 °C the peak due to [RhCl(CO)(PEt$_3$)$_2$] decreased in intensity and two other peaks of unequal intensity appeared at 1992 cm^{-1} and 1936 cm^{-1}. The assignments for these peaks are given in table 4.6. The peaks at 2049 and 1639 cm^{-1} remained but had decreased in intensity.

Table 4.6 IR Data from Reaction of [RhCl(CO)(PEt$_3$)$_2$] with 1-Chloroprop-2-ene and Carbon Monoxide at 12 °C

Wavenumber (cm^{-1})	Intensity	Assignment
2049	m	$[RhCl_2(CO)(CH_2CHCH_2)(PEt_3)_2]$
1992	w	$[RhCl(CO)_2(PEt_3)_2]$
1955	m	$[RhCl(CO)(PEt_3)_2]$
1936	s	$[RhCl(CO)_2(PEt_3)_2]$
1639	vw	$[RhCl_2(CO)(CH_2CHCH_2)(PEt_3)_2]$

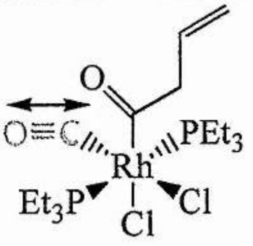
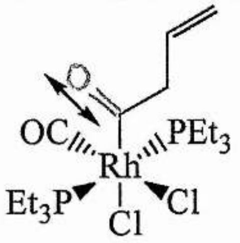
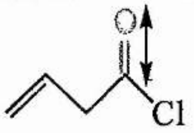
At this temperature no peak was present that could have been assigned to the migratory insertion product. As in the NMR experiments it would seem that [RhCl(CO)(PEt$_3$)$_2$] coordinated another molecule of carbon monoxide to become a pentacoordinated, 18 electron species. This reaction will be discussed later.

When the solution was heated up to 120 °C a strong peak at 2074 cm^{-1} appeared which was assigned to the migratory insertion product. Strong peaks were also present at 1764 and 1798 cm^{-1} which were due to the $\tilde{\nu}_{C=O}$ of the insertion product and but-3-enoyl chloride respectively (table 4.7). The IR spectra of authentic samples of ethyl but-3-enoate and but-3-enoyl chloride contained peaks due to carbonyl stretches at 1738 and 1802 cm^{-1} respectively. The peak at 2049 cm^{-1} from the oxidative addition product had disappeared because of the increase in temperature as had the peaks from the Rh(I) dicarbonyl species. A weak peak was present at 1955 cm^{-1} due to [RhCl(CO)(PEt$_3$)$_2$] (Spectrum 4.4).



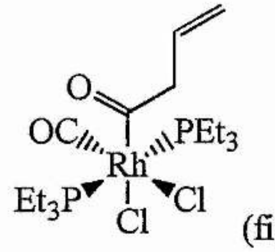
Spectra 4.4a-d
Variable Temperature IR Spectra of the Oxidative Addition and Migratory Insertion Products of 1-chloroprop-2-ene, Carbon Monoxide and [RhCl(CO)(PEt$_3$)$_2$]

Table 4.7 IR Data from Reaction of [$RhCl(CO)(PEt_3)_2$] with 1-Chloroprop-2-ene and Carbon Monoxide at 120 °C

Wavenumber (cm^{-1})	Intensity	Assignment
2074	s	
1955	w	[$RhCl(CO)(PEt_3)_2$]
1764	vs	
1798	s	
1633	m	[$RhCl_2(CO)(COCH_2CHCH_2)(PEt_3)_2$]

4.5 Attempted Isolation and Crystallisation of Migratory Insertion Intermediates

It was seen in both the HPNMR and HPIR experiments carried out on the migratory insertion products that once formed, in the absence of a protic solvent, they were stable. Therefore, it should have been possible to isolate the Rh(III) migratory insertion complex and attempt to crystallise it (figure 4.12).



(fig. 4.12)

The synthesis of the above complex was straight forward. 1-chloroprop-2-ene and [RhCl(CO)(PEt_3)$_2$] were placed in a Torion bottle which was pressurised with carbon monoxide (3-4 bar). No solvent was used for this reaction. The solution was heated to 100 °C in a water bath for four hours during which time the migratory insertion complex came out of solution in the form of a thick, dark orange oil. The oil was transferred to a Schlenk tube and freed of excess 1-chloroprop-2-ene *in vacuo*. ^{31}P NMR showed the complex (δ 19.3 ppm, $^1J_{Rh-P}$= 67 Hz) was the same as had been formed in the HPNMR experiments, however, attempts to crystallise the oil were unsuccessful. A wide variety of solvents were tried but the oil would only dissolve in the more polar solvents, even when heated. When cooled the oil would either come out of solution or remain there unchanged. Adding ethanol to the oil resulted in the reductive elimination of ethyl but-3-enoate giving [RhCl(CO)(PEt_3)$_2$]. If the oil was exposed to the air but-3-enoic acid was produced *via* reaction with water vapour, so this was avoided if at all possible because of its smell!

A different synthesis of the complex was attempted using but-3-enoyl chloride and [RhCl(CO)(PEt_3)$_2$] dissolved in CH_2Cl_2. When the acid chloride was added to the solution containing the Rh(I) complex the solution immediately turned from bright yellow to a deep purple colour. The colour remained for approximately three minutes before the solution turned dark orange. Analysis of the ^{31}P NMR spectrum of the reaction mixture showed that instead of only the one product, as in the previous reaction, there was a mixture of Rh(I), Rh(III) and many phosphorous containing compounds not bonded to a metal centre. The compound formed in the greatest yield was the one shown in figure 4.12. Attempts were made to isolate the purple species at low temperature but they were unsuccessful.

The synthesis of the insertion complex of benzyl chloride was attempted using the same technique as initially used with the 1-chloroprop-2-ene. However, this failed to produce the Rh(III) insertion complex.

When neat phenylacetoyl chloride was added to $[RhCl(CO)(PEt_3)_2]$ a creamy white solution was obtained. There was no intermediate purple colour seen in this reaction. The solution was stored at 4 °C for three weeks during which time very light yellow crystals formed (tables 4.8 and 4.9). These were washed with a little diethyl ether and submitted for single crystal X-ray analysis. Unfortunately this was unsuccessful because the crystals were very air sensitive and could not be mounted on the glass support before going off.

Table 4.8 ^{31}P NMR Data for $[RhCl_2(CO)(PhCH_2)(PEt_3)_2]$

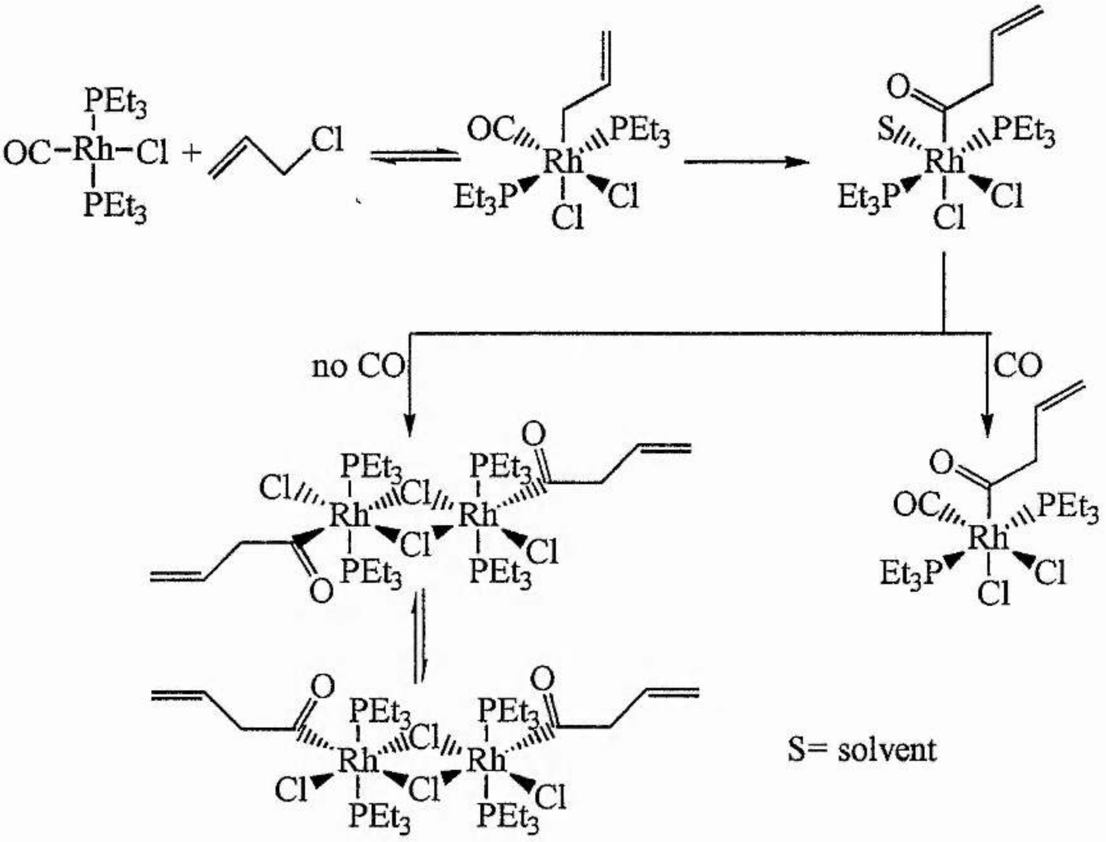
Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment
15.99	d	89	$[RhCl_2(CO)(PhCH_2)(PEt_3)_2]$

Table 4.9 ^{1}H NMR Data for [$RhCl_2(CO)(PhCH_2)(PEt_3)_2$]

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment
1.20	pentet	8.5	[$RhCl_2(CO)(COCH_2Ph)(P(CH_2CH_3)_3)_2$]
2.19	multiplet	5.1	[$RhCl_2(CO)(COCH_2Ph)(P(CH_2CH_3)_3)_2$]
4.36	s	-	[$RhCl_2(CO)(COCH_2Ph)(P(CH_2CH_3)_3)_2$]
7.09	multiplet	-	Aromatic protons
7.25	broad multiplet	-	Aromatic protons

4.6 Conclusions on the Migratory Insertion Reactions

The reaction of 1-chloroprop-2-ene with [$RhCl(CO)(PEt_3)_2$] under carbon monoxide in an inert solvent gave the kinetically stable migratory insertion complex. However, when the pressure of carbon monoxide in the HPNMR tube dropped the formation of Rh(III) dimers was suspected (figure 4.13).



(fig. 4.13)

$[RhCl(CO)(PEt_3)_2]$ could react with carbon monoxide to produce a pentacoordinate dicarbonyl rhodium species. This was stable under high pressures of carbon monoxide and at low temperatures; on heating the complex lost a molecule of carbon monoxide and reverted to $[RhCl(CO)(PEt_3)_2]$. Therefore, at the temperatures of the catalytic reactions (120 °C) none of the pentacoordinated complex would have been present to hinder the oxidative addition.

The migratory insertion of the allylic or benzylic species in this system shows some major differences from the reaction that occurs to produce the acyl species in the BP-Monsanto process. The oxidative addition product $[RhMeI_3(CO)_2]^-$ is unstable with respect to both reductive elimination and methyl migration at 35 °C in CH_2Cl_2. However, the oxidative addition product in this system, $[RhCl_2(CH_2CHCH_2)(CO)(PEt_3)_2]$ is only unstable to reductive elimination at 35 °C in the same solvent. The migratory insertion reaction only occurs above 70 °C with this complex.

Once formed, $[Rh(COMe)I_3(CO)]^-$ is only stable in the presence of carbon monoxide. Once the dicarbonyl complex is formed the complex reductively eliminates ethanoyl iodide thus regenerating the catalyst. In the absence of carbon monoxide the complex reductively eliminates iodomethane. In comparison, once $[RhCl_2(COCH_2CHCH_2)(CO)(PEt_3)_2]$ has been formed it is stable in the absence of protic solvents. Reductive elimination of but-3-enoyl chloride does not appear to occur as readily as the analogous reaction in the BP-Monsanto system; thus the complex can be isolated. The reductive elimination of but-3-enoyl chloride is dependent upon the presence of a protic solvent to convert the acid chloride to an ester thus pulling the equilibrium of the reaction over to the side of the products. It was suspected that in the absence of carbon monoxide and above 70 °C migratory insertion produced stable chloro-bridged rhodium dimers ($[RhCl_2(COCH_2CHCH_2)(PEt_3)_2]_2$) in this system; these complexes were not isolated.

Though the same number of steps are involved in the carbonylation of allylic and benzylic halides as in the carbonylation of iodomethane the thermodynamic and the kinetic parameters of the reactions are quite different.

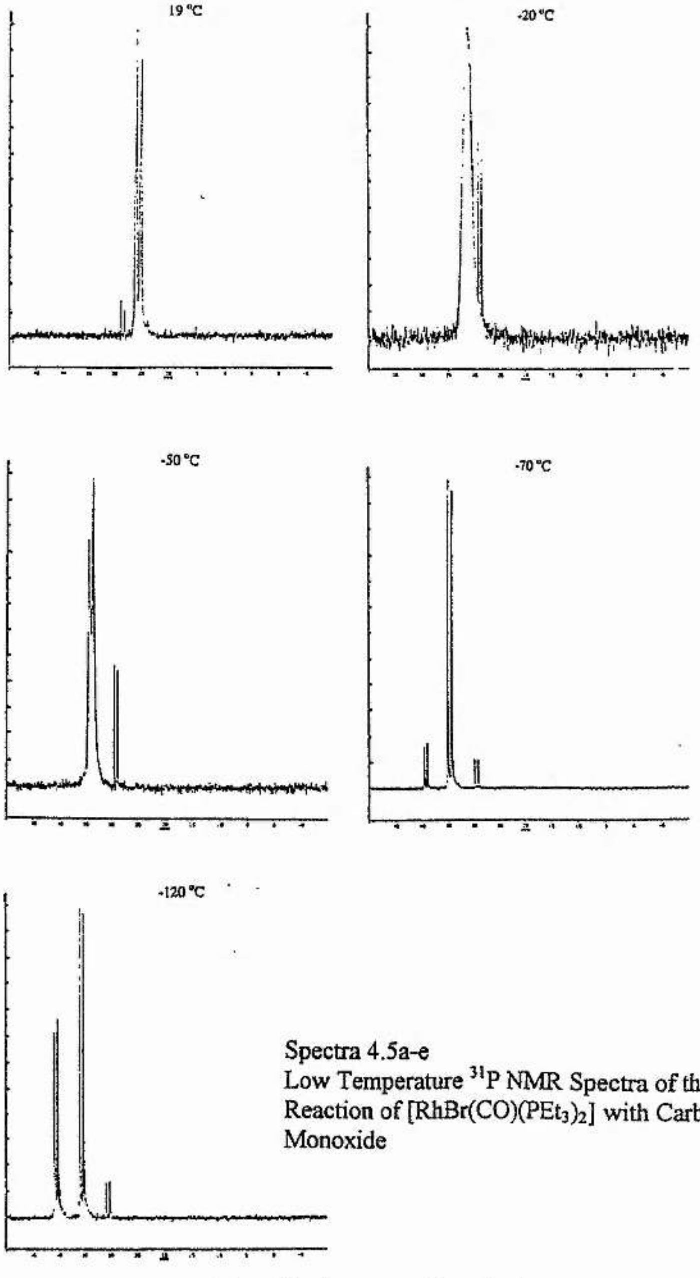
4.7 Reaction of [RhX(CO)(PEt$_3$)$_2$] with Carbon Monoxide

The reaction of the catalyst with carbon monoxide was first noticed in the reaction of [RhCl(CO)(PEt$_3$)$_2$] with 1-chloroprop-2-ene under an atmosphere of carbon monoxide monitored by ^{31}P NMR. At 19 °C the doublet at δ 24.5 ppm corresponding to [RhCl(CO)(PEt$_3$)$_2$] broadened and shifted down field by approximately 1 ppm. A similar reaction occurred with [RhBr(CO)(PEt$_3$)$_2$] but the downfield shift was approximately 2 ppm. The broad peaks suggested that carbon monoxide was exchanging on the NMR timescale with the Rh(I) complexes at 19 °C. In order to confirm that the reaction was one of [RhX(CO)(PEt$_3$)$_2$] with carbon monoxide, and slow this exchange down, 1-chloroprop-2-ene was omitted from the system and the temperature was dropped.

When [RhBr(CO)(PEt$_3$)$_2$] was dissolved in CD_2Cl_2 and placed under 40 bar carbon monoxide the following events were observed in the ^{31}P NMR spectra (table 4.10) (Spectrum 4.5a-e).

Table 4.10 ^{31}P NMR Data for the Reaction Between $[RhBr(CO)(PEt_3)_2]$ and Carbon Monoxide at Low Temperatures

Temperature (°C)	Chemical Shift (ppm)	Multiplicity	Coupling (Hz)	Rel. Int.
19	25.38	broad doublet	108	-
-10 to -30	28.34 - 32.76	v. broad singlet	-	-
-50	34.14	broad doublet	85	-
-70	39.12	sharp doublet	68	6.8
	34.54	sharp doublet	84	50.0
-120	40.38	sharp doublet	69	30.8
	35.42	sharp doublet	84	47.8



Spectra 4.5a-e
Low Temperature ^{31}P NMR Spectra of the Reaction of $[RhBr(CO)(PEt_3)_2]$ with Carbon Monoxide

Throughout the cooling there was a downfield shift of all the peaks. At -50 °C there seemed to be only one dicarbonyl species present in the solution which was exchanging with $[RhBr(CO)(PEt_3)_2]$. On cooling down to -70 °C a new doublet appeared at δ 39.12 ppm and the peaks sharpened. On further cooling the doublet further down field increased in intensity indicating that this species was more stable at lower temperatures. These results suggested that two dicarbonyl complexes were present that contained equivalent phosphine ligands.

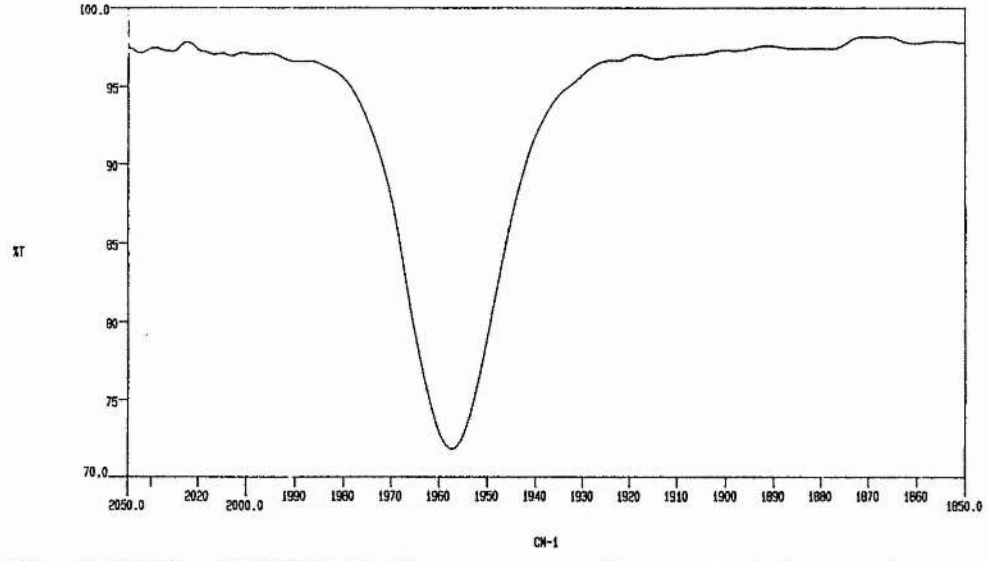
The IR spectrum of $[RhBr(CO)(PEt_3)_2]$ run in CH_2Cl_2 showed a peak at 1958 cm^{-1} corresponding to the $\tilde{\nu}_{C\equiv O}$ stretch of the carbon monoxide ligand. When the HPIR cell containing this solution was pressurised with carbon monoxide to 40 bar the peak at 1958 cm^{-1} was replaced by two peaks (table 4.11) (Spectrum 4.6a and b).

Table 4.11 IR Data for the Reaction Between $[RhBr(CO)(PEt_3)_2]$ and Carbon Monoxide (40 bar) at 19 °C

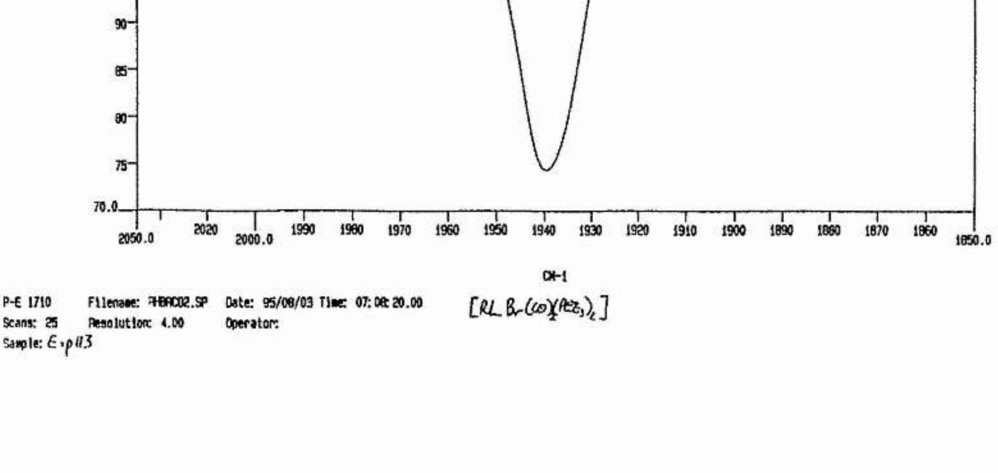
Wavenumber (cm^{-1})	Intensity	Assignment
1958	s	$[RhBr(CO)(PEt_3)_2]$
1998	s	$[RhBr(CO)_2(PEt_3)_2]$
1939	w	$[RhBr(CO)_2(PEt_3)_2]$

The ^{31}P NMR data suggests that at room temperature only one species (doublet at δ 35.4 ppm) other than $[RhBr(CO)(PEt_3)_2]$ is present in solution so that the peaks at 1998 and 1939 cm^{-1} must both arise from this species. This suggests a structure in which the two carbon monoxide ligands of $[RhBr(CO)_2(PEt_3)_2]$ are not mutually *trans* and the doublet resonance in the

^{31}P NMR spectrum -80 °C shows that this species has equivalent phosphorous atoms. Two possibilities exist for the structures of the pentacoordinate Rh(I) complexes though these could not be distinguished from these experiments. These were either square pyramidal or trigonal bipyramidal structures containing *trans* phosphines.

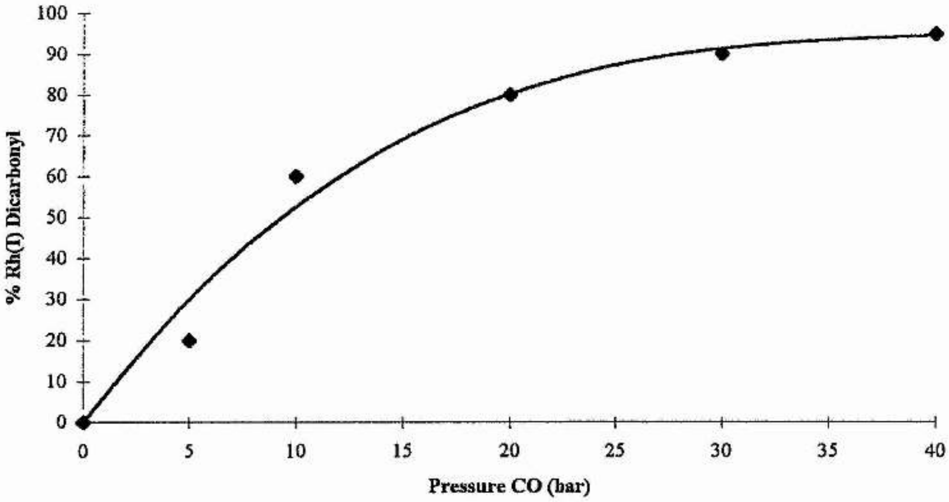


Spectrum 4.6 a and b
IR Spectra of the Reaction of $[RhBr(CO)(PEt_3)_2]$ with Carbon Monoxide at 19 °C

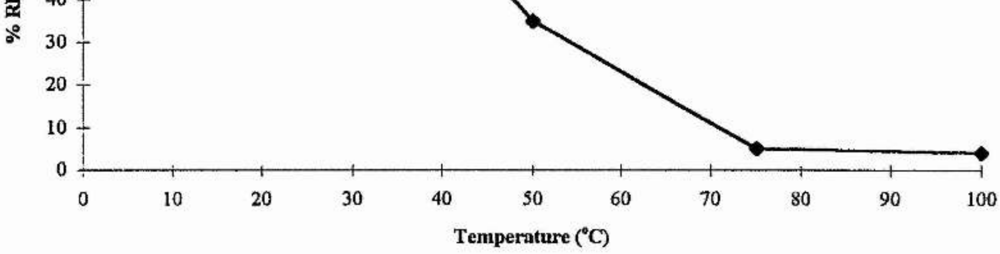


A reaction was carried out between [RhCl(CO)(PEt$_3$)$_2$] and CO to determine the dependence on the formation of the Rh(I) dicarbonyl species on pressure and temperature. The results of the experiments are shown in graphs 4.1 and 4.2.

Graph 4.1 % Rh(I) Dicarbonyl Present at 25 °C as a Function of CO Pressure



Graph 4.2 % Rh(I) Dicarbonyl Present Under 40 bar Carbon Monoxide as a Function of Temperature



The graphs were produced by measuring the peaks areas of the IR spectra with the assumption that both complexes would give the same response. From graph 4.1 it can be seen that on increasing the pressure of carbon monoxide the proportion of $[RhCl(CO)_2(PEt_3)_2]$ in the solution increased. This reaction was reversible so on reducing the pressure less of the dicarbonyl species was present in the solution. Increasing the temperature had a similar effect to reducing the pressure. Both of these results are consistent with the dominant equilibrium being that shown in figure 4.14. The temperature dependence of the equilibrium could arise because of the expected negative ΔS^o value for the reaction as written. Under the usual conditions for a catalytic run (i.e. 120 °C, 40 bar CO) only a very small proportion of $[RhCl(CO)_2(PEt_3)_2]$ would be present in the solution. Thus, the oxidative addition of the substrates to the Rh(I) complex would not have been dependent upon the dissociation of a carbon monoxide ligand to produce a vacant site under normal reaction conditions.

$$[RhCl(CO)(PEt_3)_2] + CO \rightleftharpoons [RhCl(CO)_2(PEt_3)_2 \quad \text{(fig. 4.14)}$$

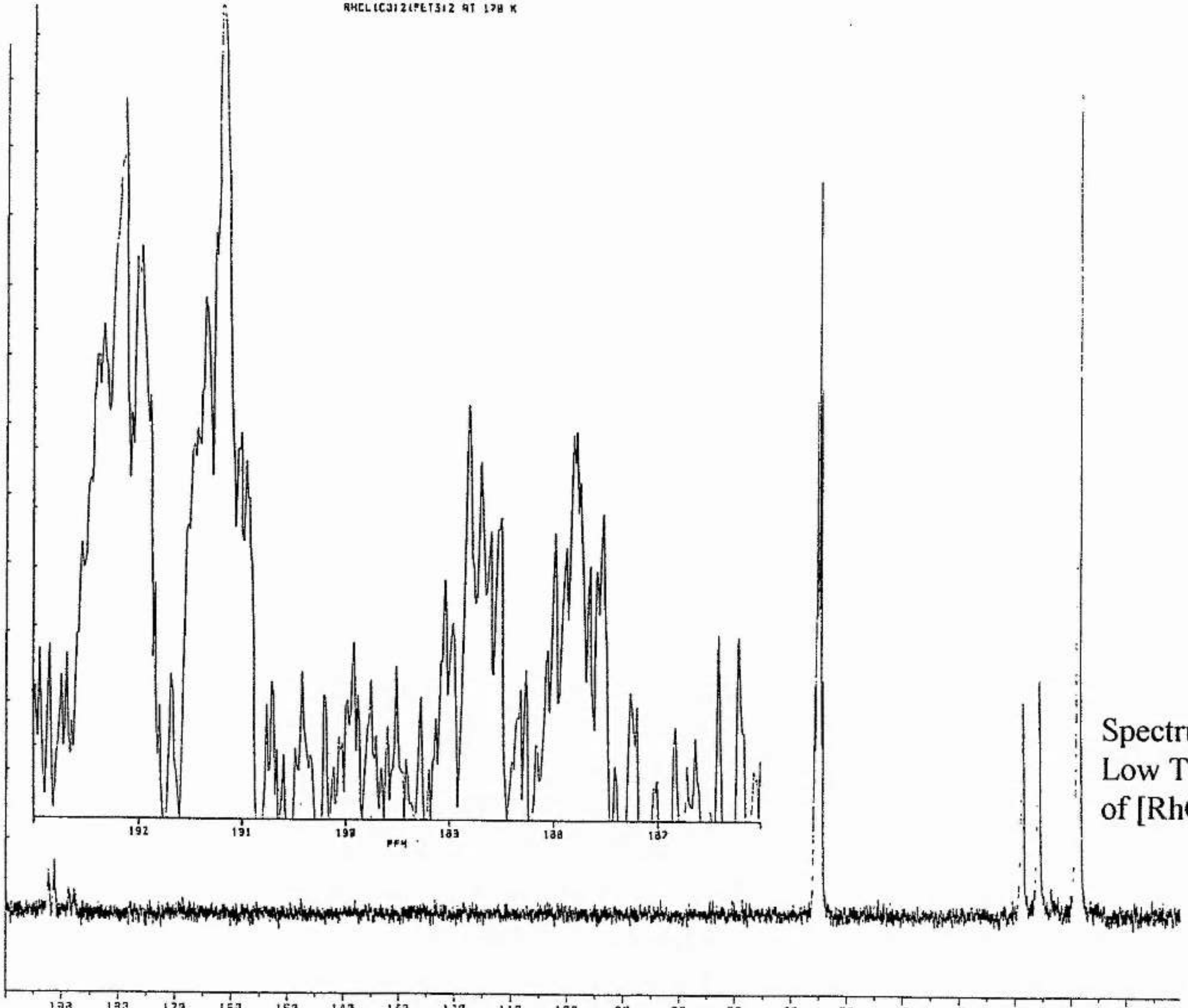
In order to obtain information on the structure of the Rh(I) dicarbonyl species a low temperature ^{13}C NMR experiment was carried out. The carbonyl region was of interest in the spectra because this would give information about the nature of the pentacoordinate Rh(I) complexes. The T_1 relaxation time was increased to 5 seconds to allow the ^{13}C nuclei of the carbon monoxide ligands time to relax fully.

The ^{13}C NMR spectrum of $[RhCl(CO)(PEt_3)_2]$ contained the expected doublet of triplets in the carbonyl region (table 4.12)

Table 4.12 ^{13}C NMR Data for $[RhCl(CO)(PEt_3)_2]$ at 25 °C

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment
8.7	s	-	$[RhCl(CO)(P(CH_2CH_3)_3)_2]$
17.0	t	14	$[RhCl(CO)(P(CH_2CH_3)_3)_2]$
188.5	d of t	74 ($^1J_{Rh\text{-}C}$) 13 ($^2J_{P\text{-}Rh\text{-}C}$)	$[RhCl(CO)(P(CH_2CH_3)_3)_2]$

When the HPNMR tube was pressurised at 25 °C with carbon monoxide (40 bar) the doublet of triplets were replaced by a singlet at δ 189.7 ppm. At -30 °C a new doublet of triplets appeared centred on δ 186 ppm along with a new triplet at δ 20.8 ppm. The singlet at δ 189.7 ppm was still present but the triplet at δ 17.0 ppm had been replaced by a broad singlet. This meant that one of the $[RhCl(CO)_2(PEt_3)_2]$ isomers was stable and not exchanging carbon monoxide. The amount of this stable isomer increased as the temperature decreased. At -103 °C there were two distinct doublets of triplets present in the ^{13}C NMR spectrum (table 4.13) (Spectrum 4.7). This meant that the exchange between the second isomer of $[RhCl(CO)_2(PEt_3)_2]$ and carbon monoxide had stopped.



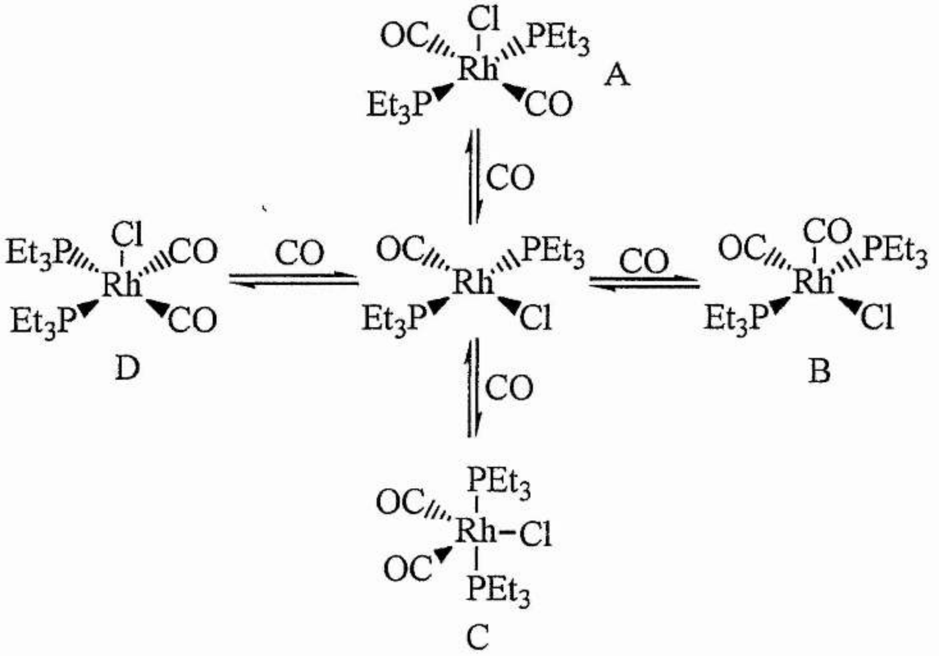
Spectrum 4.7
Low Temperature ^{13}C NMR Spectrum
of $[RhCl(CO)_2(PEt_3)_2]$

Table 4.13 ^{13}C NMR Data for $[RhCl(CO)_2(PEt_3)_2]$ at -103 °C

Chem.Shift (ppm)	Multiplicity	Coupling (Hz)	Assignment
8.7	broad singlet	-	$[RhCl(CO)_2(P(CH_2CH_3)_3)_2]$
15.8	broad singlet	-	$[RhCl(CO)_2(P(CH_2CH_3)_3)_2]$ (A)
18.7	broad singlet	-	$[RhCl(CO)_2(P(CH_2CH_3)_3)_2]$ (B)
188.3	d of t	74 ($^1J_{Rh\text{-}C}$) 14 ($^2J_{P\text{-}Rh\text{-}C}$)	$[RhCl(CO)_2(P(CH_2CH_3)_3)_2]$ (A)
191.7	d of t	74 ($^1J_{Rh\text{-}C}$) 14 ($^2J_{P\text{-}Rh\text{-}C}$)	$[RhCl(CO)_2(P(CH_2CH_3)_3)_2]$ (B)

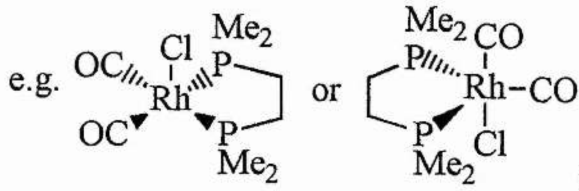
All the signals were broad at this temperature because the solution would have been very viscous; thus some resolution was lost.

Any two of the four isomers of $[RhCl(CO)_2(PEt_3)_2]$ shown in figure 4.15 are possible. The only way to solve the structures of these complexes would be to use single crystal X-ray diffraction. However, crystals could not be obtained from these complexes because they lost one of the carbon monoxide ligands as soon as the pressure was released. The most likely structure for the dicarbonyl complexes are C and D because they contain equivalent phosphines and carbon monoxide ligands and thus are consistent with the spectroscopic data. Structure A would have a weak $\tilde{\nu}_{C\equiv O}$ (sym) thus is also consistent with the IR data. Structure B contains inequivalent carbon monoxide ligands and would, therefore, give two doublets of triplets in the ^{13}C NMR. Other structures containing equivalent phosphines are also possible and cannot be excluded on the available evidence.



(fig. 4.15)

Interestingly, a related pentacoordinate Rh(I) dicarbonyl rather than the expected [RhCl(CO)(dmpe)] was obtained when $[RhCl(CO)_2]_2$ was reacted with dimethylphosphinoethane.[112] The chelating ligand ensured that the phosphines remained in the *cis* position on the metal centre (figure 4.16). The resulting complexes were dicarbonyl pentacoordinate rather than the tetracoordinate complexes with mutually *trans* phosphorus atoms obtained with the unidentate phosphines. The reasons for these complexes preferring to be in the dicarbonyl pentacoordinate configuration rather than tetracoordinate are unclear at the present time.



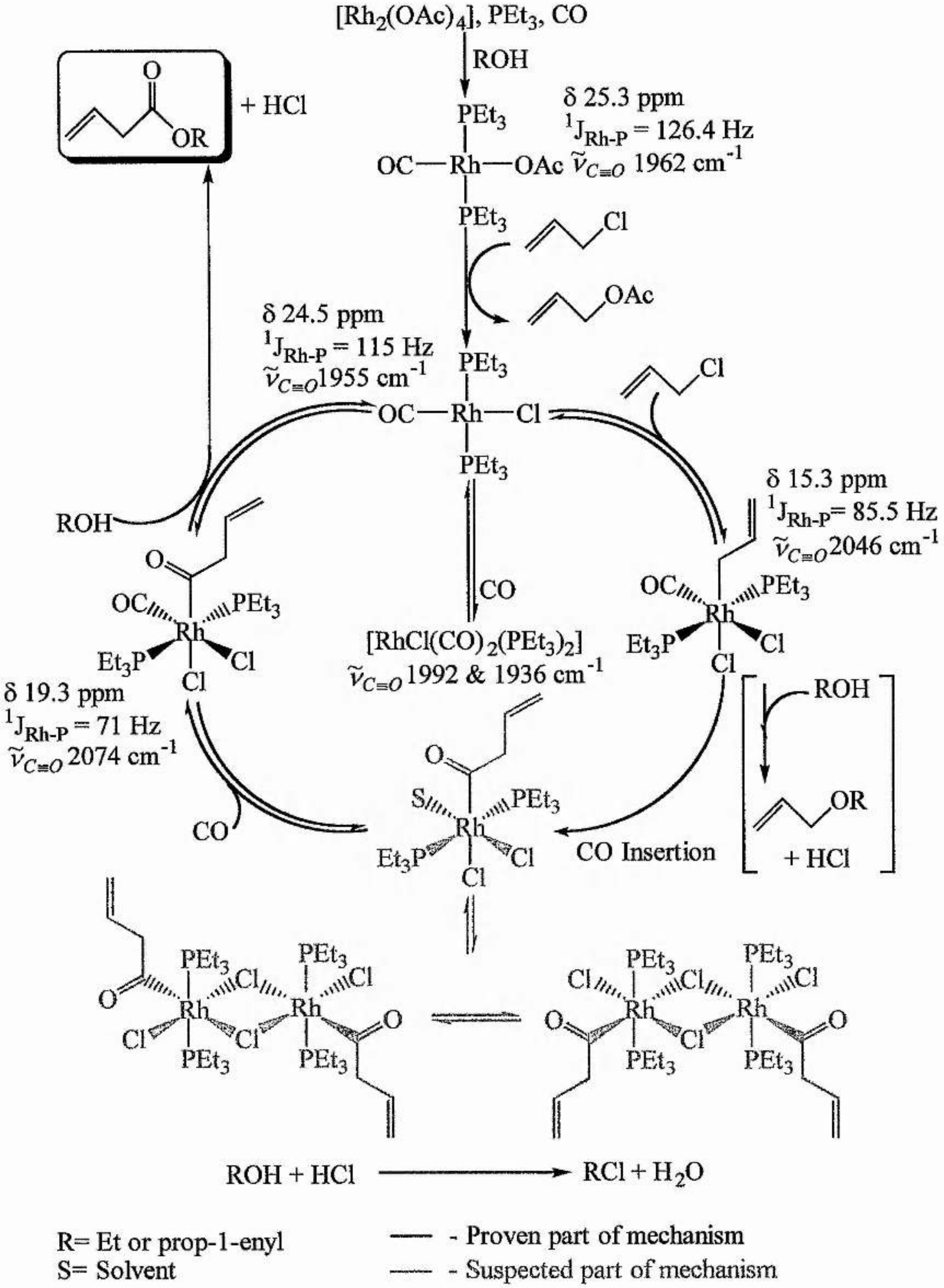
(fig. 4.16)

CHAPTER 5

5. MECHANISM FOR THE CARBONYLATION OF ALLYLIC AND BENZYLIC HALIDES

The results described in Chapters 3 and 4 have enabled the mechanism for the catalytic production of esters from allylic and benzylic halides in ethanol to be elucidated. Unlike most of the other carbonylation reactions involving alkyl, alkenyl or aryl halides the system utilising $[RhCl(CO)(PEt_3)_2]$ as the catalyst did not require any base to neutralise the acid produced in the reaction; thus there was no wasteful production of salts. However, ethyl chloride was produced in this reaction and because this compound could not oxidatively add to the rhodium centre it would build up and could cause problems if the reaction were to be scaled up. In order to solve this problem the reaction was carried out in prop-2-en-1-ol. This meant that the solvent could be converted to the substrate upon reaction with HCl thus preventing the formation of any wasteful products.

This is one of few catalytic systems that can activate a carbon-chlorine bond using a rhodium based catalyst. There are several advantages for using chlorides rather than bromides or iodides in catalytic systems. The first is that the organochlorides are considerably cheaper than the bromides and the iodides. They are also less toxic and less carcinogenic than the corresponding bromides and iodides, though only slightly. The reaction proceeds under relatively mild conditions, ideally at 120 °C and 40 bar, though carbonylation can occur at temperatures as low as 70 °C and 4 bar albeit very slowly. The overall mechanism for the reaction is shown in figure 5.1.


[Rh2(OAc)4], PEt3, CO
ROH
+ HCl
δ 25.3 ppm
1JRh-P = 126.4 Hz
ṽC≡O 1962 cm-1
δ 24.5 ppm
1JRh-P = 115 Hz
ṽC≡O 1955 cm-1
δ 15.3 ppm
1JRh-P = 85.5 Hz
ṽC≡O 2046 cm-1
CO
[RhCl(CO)2(PEt3)2]
ṽC≡O 1992 & 1936 cm-1
δ 19.3 ppm
1JRh-P = 71 Hz
ṽC≡O 2074 cm-1
ROH
CO
CO Insertion
ROH
+ HCl
ROH + HCl → RCl + H2O
R= Et or prop-1-enyl
S= Solvent
- Proven part of mechanism
- Suspected part of mechanism

(fig. 5.1)

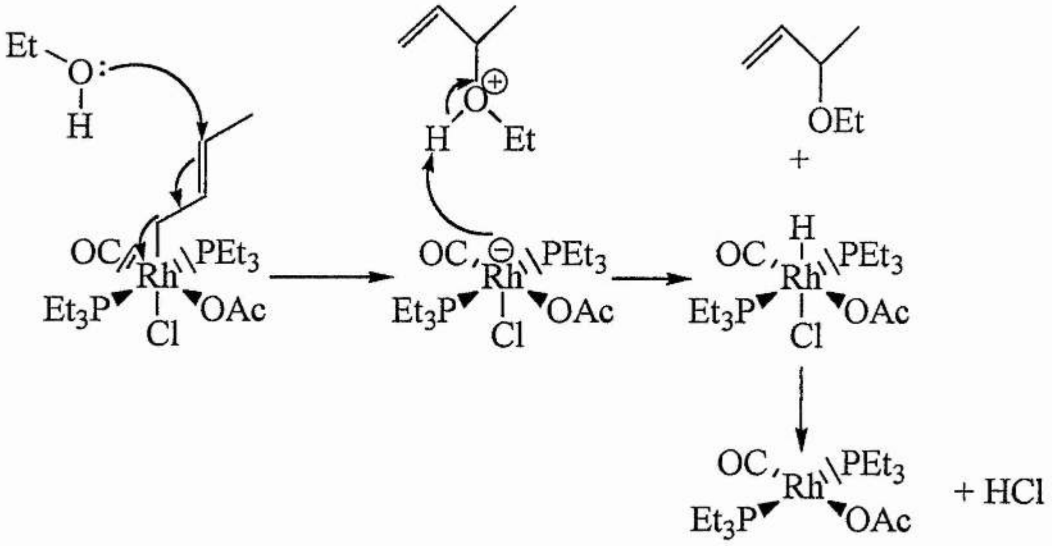
The catalytic cycle proceeds as follows. The $[Rh_2(OAc)_4]$ is reduced by the alcoholic solvent and the triethylphosphine giving $[Rh(OAc)(CO)(PEt_3)_2]$. This complex can oxidatively add 1-chloroprop-2-ene then reductively eliminate prop-1-enyl ethanoate to give the active catalytic species $[RhCl(CO)(PEt_3)_2]$. It was found that greater yields could be achieved by using preformed $[RhCl(CO)(PEt_3)_2]$ instead of preparing the catalyst *in situ*. The Rh(I) complex can then oxidatively add another molecule of 1-chloroprop-2-ene to give the Rh(III) dichloro complex. Experiments involving unsymmetrical substrates, namely 1-chlorobut-2-ene and 3-chlorobut-1-ene, have shown that the oxidative addition reaction proceeds *via* an S_N2 mechanism when unhindered substrates are used. However, if the α-carbon is hindered by, for example, a methyl group then the reaction goes *via* the slightly different S_N2' mechanism which involves isomerisation of the double bond.

The migratory insertion reaction proceeds rapidly at temperatures above 70 °C giving the Rh(III) acetyl complex. If the pressure is very low then chloro-bridged Rh(III) dimers are thought to form otherwise carbon monoxide is rapidly inserted into the vacant site. This complex can then undergo reductive elimination of but-3-enoyl chloride and in so doing regenerate the catalyst. This reaction is reversible. However, the alcoholic solvent instantly reacts with the acid chloride giving an ester and a molecule of HCl. The ester cannot oxidatively add to $[RhCl(CO)(PEt_3)_2]$; thus the equilibrium shown in figure 5.2 is pulled over to the right-hand-side.

$$[RhCl_2(COCH_2CHCH_2)(CO)(PEt_3)_2] \rightleftharpoons \begin{array}{c} [RhCl(CO)(PEt_3)_2 \\ + \\ CH_2CHCH_2COCl \end{array}$$

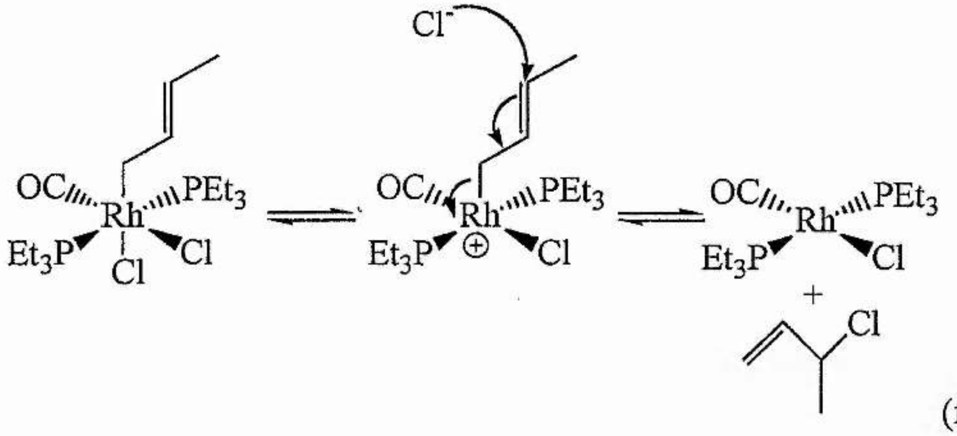
(fig. 5.2)

The production of the same ether from the carbonylation reactions of both 1-chlorobut-2-ene and 3-chlorobut-1-ene suggests that the reaction occurs on the Rh(III) oxidative addition complex (figure 5.3). This reaction also shows that a π-allylic intermediate is unlikely as the ethanol would attack the least hindered end of the double bond giving the straight chain ether.



(fig. 5.3)

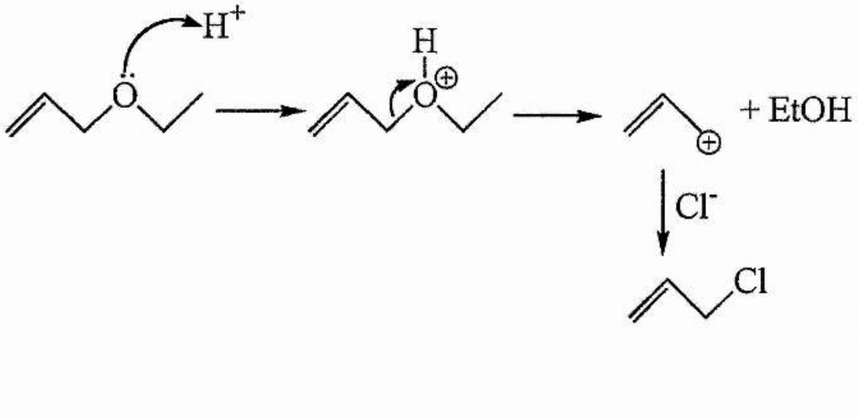
This process can also account for the observed isomerisation of 1-chlorobut-2-ene to 3-chlorobut-1-ene but not vice-versa (figure 5.4).



(fig. 5.4)

Two isomers of [RhCl(CO)$_2$(PEt$_3$)$_2$] were produced at low temperatures from [RhCl(CO)(PEt$_3$)$_2$] under pressure of carbon monoxide. However, on heating the solution one of the carbon monoxide ligands was liberated reforming [RhCl(CO)(PEt$_3$)$_2$]. Thus it was unlikely that the Rh(III) dicarbonyl species would hinder the oxidative addition of the substrates at 120 °C.

The ethers produced in the carbonylation reactions are also substrates (see graph 2.2, chapter 2). After approximately two hours the amount of ether present in the reaction drops. A possible explanation for this is that the HCl produced in the reaction reacts with the ether to produce 1-chloroprop-2-ene and ethanol (figure 5.3).



(fig. 5.3)

As the concentration of ether builds up in the solution the equilibrium in figure 5.4 is pushed over to the left hand side.

(fig. 5.4)

This can readily be compared to a similar process that occurs during the production of ethanoic acid from methanol *via* the BP-Monsanto process. Dimethyl ether is produced by the reaction of iodomethane with methanol generating HI in the process (figure 5.5).

$$\mathrm{MeI} + \mathrm{MeOH} \rightleftharpoons \mathrm{Me{-}O{-}Me} + \mathrm{HI} \quad \text{(fig 5.5)}$$

It has been shown that dimethyl ether can be used as a substrate for this process because of the above equilibrium. The HI reacts with the ether to produce the iodomethane thus generating the required substrate.

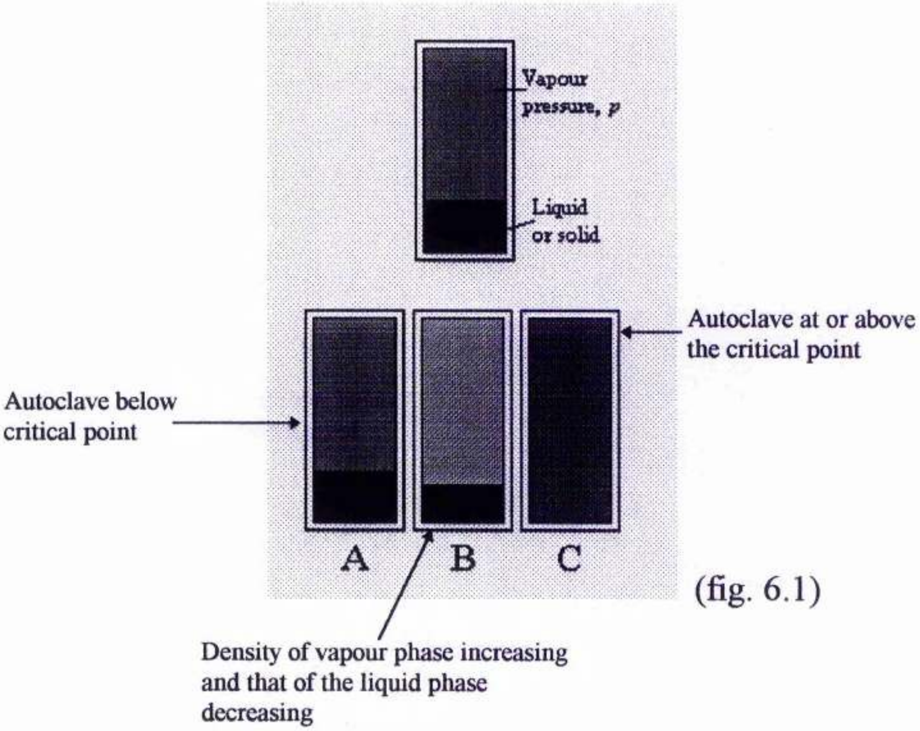
In order to increase the selectivity towards the ester a way would have to found to increase the rate of the migratory insertion reaction. This could possibly be achieved by increasing the concentration of carbon monoxide in the solution.

CHAPTER 6

6. CARBONYLATION IN SUPERCRITICAL CARBON DIOXIDE

6.1 Introduction[5, 113, 114]

When a liquid is heated in a sealed vessel, e.g. an autoclave, it cannot boil. The density of the vapour phase increases along with the pressure and temperature. Simultaneously, the density of the liquid phase decreases. The volume of the liquid phase also decreases but this is because of vaporisation. As the density of the vapour increases and that of the liquid decreases there comes a point when the two densities are equal. This is called the critical point. At this point the interface between the phases disappears resulting in the formation of a single fluid. The temperature at which this occurs is called the critical temperature, T_c. The corresponding pressure is called the critical pressure, P_c. This process is shown in figure 6.1.



(fig. 6.1)

The most commonly used fluid for supercritical reactions is carbon dioxide. The critical conditions for this substance are near ambient; thus it is convenient to use compared with many of the other available fluids (see table 2.1).

Table 2.1 Critical Properties of Some Common Fluids[67]

Fluid	T_c (°C)	P_c (bar)
Carbon dioxide	31.05	73.76
Methanol	239.45	80.96
Ethanol	243.05	63.83
Water	374.15	220.48
Acetone	234.95	47.01
Xenon	16.55	58.36
Carbon monoxide	-140.24	34.99

As can be seen from the table the critical temperatures for the substances that are liquid under standard conditions are all above 200 °C though the critical pressures for all but water are very similar to those of the gases. Xenon is a good supercritical solvent but is very expensive. Ethene and ethane can also be used as supercritical solvents but they exhibit poor solvating power and are highly flammable. Chloro-fluoro carbons also have good supercritical properties but are environmentally unacceptable. Carbon dioxide seems to be ideal for most uses. It is cheap, non-flammable, non-toxic and has the ability to dissolve polar molecules.

The solvating power of a supercritical fluid is related to the critical density. To act as a solvent the fluid must be able totally to encapsulate the molecules in the solution. Although the supercritical fluids have very high densities for gases their gaseous nature can prevent the formation of stable solvation shells. Thus they are poor solvents for ionic species. However, the ability of the supercritical fluid to dissolve substances can be controlled by altering the pressure. As the pressure is increased the fluid contracts and its density increases thus solutions become more stable. The reverse is true when the pressure is decreased.

There are now many processes that operate in supercritical fluids because of their unique properties. Some of the more colourful examples depend on the enhanced rates of diffusion that can be achieved in the fluids. The dyeing of artificial fibres using s.c. CO_2 is now an established technique. Fingerprints on paper can be dyed purple with a solution of ninhydrin, water and acetic acid in s.c. CO_2 at 40 °C and 125 bar. Esterification and transesterification reactions catalysed by lipase that are important in the processing of oils can also be carried out in supercritical fluids. The rates of the reactions increase because of better diffusion in both the bulk fluid and within the pores that contain the enzyme.

The products from reactions can be controlled by both diffusion and preferential stabilisation of a particular transition state in supercritical fluids. The effects rely on changes in density in the critical region. Hence reactions with two products can be made to favour one particular product simply by adjusting the pressure.

One of the largest areas of growth in the area of supercritical fluids involves the use water to oxidise organic compounds. Many organic compounds can be rapidly and almost completely oxidised by molecular oxygen in supercritical water. The end products are species like CO_2, H_2O, N_2, Cl^- and SO_4^-. There are no oxides of nitrogen produced in the reaction because of the low combustion temperatures and chloride rather than chlorine volatiles are produced. Reactor residence times are approximately one minute compared with 60 minutes for the analogous wet oxidation process carried out below 300 °C.

Supercritical fluids are now also involved in the extraction of natural materials. One of the best known examples is the extraction of caffeine from coffee using s.c. CO_2. New techniques involve the *in situ* derivitisation of compounds before extraction to make them soluble in the fluid. Metal ions e.g. lanthanides and actinides may also be extracted into s.c. CO_2 containing a complexing agent.

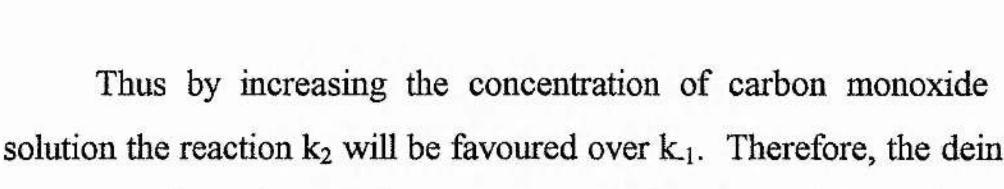
One of the most innovative uses of supercritical carbon dioxide is the preservation of waterlogged archaeological wood (e.g. from sunken wooden ships).[115] However, water does not dissolve very well in supercritical carbon dioxide, therefore, it must be substituted for methanol. This is carried out by simply immersing the sample of wood in methanol. Once this process is complete the methanol impregnated wood is placed in an autoclave which is charged with carbon dioxide. Once the critical point is reached the methanol dissolves in the supercritical carbon dioxide and thus is extracted from the wooden sample. The methanol is removed from the supercritical fluid by dropping the pressure causing the methanol to drop out of solution. The carbon dioxide can then be repressurised and fed back into the autoclave. This technique allows both the methanol and the carbon dioxide to be recycled. If the wood were to be dried naturally it would split and crack because the surface tension generated within the cell walls would cause them to collapse. However, in the supercritical carbon dioxide this does not occur because there is no phase change; thus no change in surface tension when the methanol is removed from within the cell wall. This allows the methanol to be removed from the wood without causing the cell walls to collapse in on themselves, thus damaging the artefact.

One of the most useful features of a supercritical fluid is that it has the ability to dissolve large quantities of light gases such as hydrogen, oxygen and carbon monoxide with which they are totally miscible. Thus in homogeneously catalysed reactions involving metal catalysts to activate the small molecules there is no liquid-gas interface. The reaction, therefore, takes place in a truly homogeneous medium possibly increasing the rate of the reaction because the gases do not have to cross an interface.

One of the most interesting examples of this phenomenon is the homogeneously catalysed hydrogenation of supercritical carbon dioxide to produce methanoic acid.[116] The process is catalysed by either *cis*-$[RuH_2(PMe_3)_4]$ or *trans*-$[RuCl_2(PMe_3)_4]$. It uses the ability of the s.c. CO_2 to solubilise the hydrogen, catalyst and the base (triethylamine). The methanoic acid is precipitated out as the formate which drives the equilibrium forwards. The reaction takes place at 50 °C under a pressure of 200 bar and is an order of magnitude faster than the analogous liquid phase reaction.

6.2 Carbonylation of 1-Chloroprop-2-ene in Supercritical Carbon Dioxide

The selectivity towards the ester in the carbonylation of 1-chloroprop-2-ene was limited by the amount of ether produced in the reaction. As discussed previously (chapter 5) the majority of the ether was produced *via* a reaction between the solvent and the oxidative addition product containing an allylic group. The only way to increase the selectivity towards the ester would be to increase the rate of migratory insertion. Common ways of doing this are to increase the polarity of the solvent and to add a Lewis acid to the reaction (chapter 4). However, increasing the concentration of carbon monoxide in the solution may also increase the rate of the insertion reaction thus the rate of formation of the ester (figure 6.2).



(fig. 6.2)

Thus by increasing the concentration of carbon monoxide in the solution the reaction k_2 will be favoured over k_{-1}. Therefore, the deinsertion reaction will be less likely to occur reducing the residence time of the oxidative addition product in the reaction. This in turn would make the ether forming reaction less likely to occur.

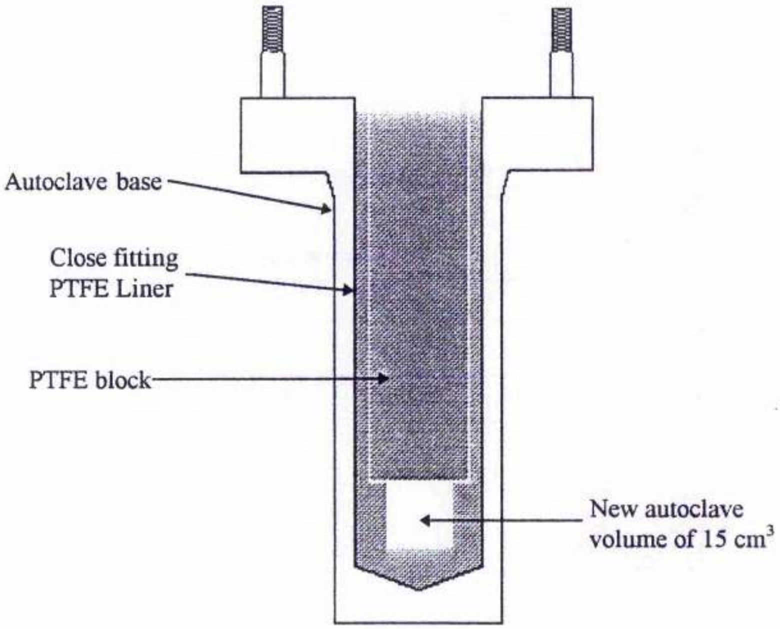
One way of increasing the concentration of carbon monoxide in the solution would be to carry out the reaction in a supercritical fluid. Carbon dioxide was chosen as the fluid because it was readily obtainable, non-flammable and easy to weigh. The reactions were carried out in a 150 cm^3 autoclave rated at 352 bar at 200 °C.

However, the reactions were unsuccessful. The possible reasons for this are as follows. The first was reaction of $[RhCl(CO)(PEt_3)_2]$ with carbon monoxide to produce $[RhCl(CO)_2(PEt_3)_2]$. This reason was discounted because it had been shown that the 16 electron, tetracoordinated complex was favoured at 120 °C. Secondly, $[RhCl(CO)(PEt_3)_2]$ could have been insoluble in the supercritical fluid. Thirdly, the increase in the volume of the reaction solution could have contributed to a reduction in the rate of the reaction by reducing the catalyst concentration. Finally, the ionic intermediates in the oxidative addition reaction may not have been stabilised in the supercritical fluid, thus increasing the activation energy for the oxidative addition step. Increasing the pressure of the system could have increased the solvating power of the s.c. CO_2 possibly stabilising the ionic intermediates. However, the volume of the autoclave was limited and the maximum pressure obtainable was 260 bar because of the amount of $CO_{2\,(s)}$ that could be fitted into the autoclave (the CO_2 was introduced into the autoclave by packing it full of powdered $CO_{2\,(s)}$. Even at this pressure only ~1% yield of ethyl but-3-enoate was obtained.

For the autoclave the volume of the s.c. solution was 150 cm^3 compared with a reaction volume of 5 cm^3 for reactions carried out in ethanol. Therefore, the concentrations of both $[RhCl(CO)(PEt_3)_2]$ and

1-chloroprop-2-ene were reduced by a factor of 150/5= 30. If the rate is assumed to be ∝ [RhCl(CO)(PEt$_3$)$_2$][1-chloroprop-2-ene][CO] then it will be reduced by a factor of 30 x 30 x 1= 900! However this will be partially compensated for by an increase of [CO] by a factor of ~30 and by the diffusion controlled reaction being faster in the s.c. CO$_2$ by ~3x. This leaves a reduction in rate simply as a result of the change in volume of approximately 900/(30 x 3)= 10 times.

In view of this, the autoclave was modified by placing a tight fitting PTFE block containing suitable channels for the dip tube and venting (figure 6.3).



(fig. 6.3)

For the modified autoclave the volume of the s.c. solution was 30 cm^3 compared with the 5 cm^3 solution for the reaction in ethanol. Therefore, both [RhCl(CO)(PEt$_3$)$_2$] and [1-chloroprop-2-ene] are reduced by a factor of

30/5 = 6. Again, if the rate is assumed to be $\propto$ $[RhCl(CO)(PEt_3)_2]$[1-chloroprop-2-ene][CO] then it will be reduced by a factor of 6 x 6 x 1= 36. Again because of compensation for the increase in [CO] and diffusion the reaction rate should be reduced by 36/(30 x 3)= 0.4. This means the reaction rate should increase by ~2.5 times.

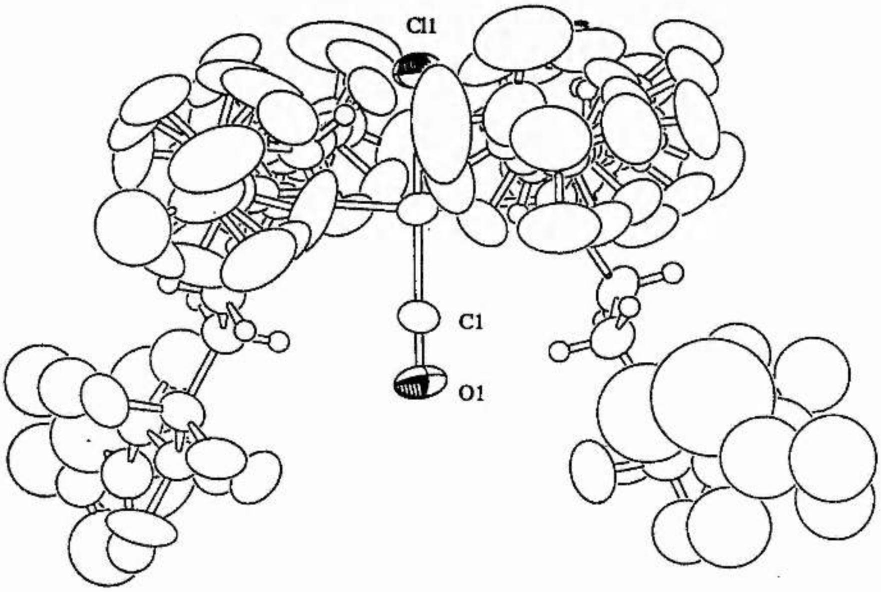
When 1-chloroprop-2-ene was carbonylated using the reduced volume autoclave ethyl but-3-enoate was obtained in a yield of approximately 5%. Ethyl prop-2-enyl ether was obtained in a yield of less than 1%. This was an improvement over the unmodified autoclave but not over the standard autoclave reactions.

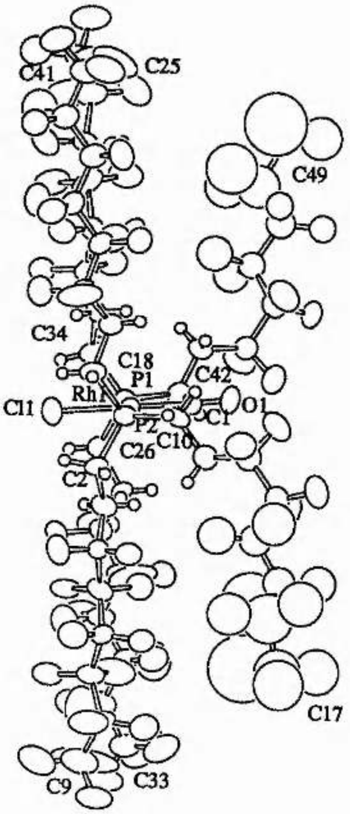
In a further attempt to improve the yield of ester the catalyst was modified. The easiest way to modify $[RhCl(CO)(PEt_3)_2]$ would be to replace the triethylphosphine ligands with phosphines that would render the catalyst more soluble in the supercritical fluid. Fluorinated compounds are very soluble in supercritical carbon dioxide; therefore, fluorinated phosphines seemed to be the ideal compounds for the task. It was important to preserve the electronic properties of the catalyst; attempts were made to synthesise fluorinated phosphines which contained an ethylene group between the phosphorus atom and the perfluorinated groups.

Finally, a catalyst was made using a 'ponytail' phosphine. The phosphine used was tri-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorophosphine ($P(CH_2CH_2(CF_2)_5CF_3)_3$). Five grammes of the phosphine was kindly donated by Exxon Chemical Ltd. The synthesis of $[RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2]$ was carried out by simply adding the phosphine to an ethanolic solution of $[Rh(CO)_2Cl]_2$. The Rh(I) complex precipitated from solution and was crystallised from a perfluorinated solvent (e.g. perfluorodecalin). The ^{31}P NMR spectrum of the complex showed a doublet at δ 22.95 ppm ($^1J_{Rh-P}$ = 122 Hz). This was very similar to the ^{31}P NMR resonance of $[RhCl(CO)(PEt_3)_2]$ (δ 24.5 ppm, $^1J_{Rh-P}$= 117 Hz) showing that the electronic properties of the two complexes were very similar to each other. Thus the ethylene group between the phosphorus atom and the perfluorinated part of the carbon chain had effectively isolated the metal centre from any of the effects of the electron withdrawing fluorine atoms. The stretching frequency of the carbon monoxide ligand for the complex ($\tilde{\nu}_{C\equiv O}$) occurred at 1987 cm^{-1} in the IR spectrum. This was slightly higher than the corresponding stretch for $[RhCl(CO)(PEt_3)_2]$ ($\tilde{\nu}_{C\equiv O}$ = 1956 cm^{-1}).

The structure of this complex was solved by single crystal X-ray diffraction (figure 6.4, Appendix 1).

Figure 6.4 Crystal Structure of [$RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2$]





Fluorine atoms are labelled sequentially as are the carbon atoms.

The carbonylation reaction carried out in supercritical carbon dioxide using this complex was unsuccessful. The most likely reason for this is that the supercritical solution did not stabilise the ionic oxidative addition intermediates. This would have effectively prevented the oxidative addition reaction from occurring. Increasing the solvating power of the supercritical carbon dioxide may have enabled these intermediates to be stabilised. To increase the solvating power of the supercritical solution the pressure would have to be increased thus increasing the density of the fluid. This would mean that the carbon dioxide molecules would be able to form better solvation spheres around the ionic intermediates thus stabilising them.

Attempts at carbonylating 1-chloroprop-2-ene using $[RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2]$ in a biphasic system were also unsuccessful. In this system the rhodium complex was dissolved in perfluordecalin and the substrate was dissolved in ethanol. At the end of the reaction both phases were recovered. No carbonylation products were present in either phase. It was shown in Chapter 3 that the oxidative addition was hindered by non-polar solvents. Thus, as was the case above, the ionic intermediates would not have been stabilised by the non-polar perfluordecalin.

6.3 Conclusions

The carbonylation of 1-chloroprop-2-ene in supercritical carbon dioxide gave much reduced yields of ethyl but-3-enoate compared with a standard autoclave run. The reasons for this were thought to be due to either catalyst insolubility or the failure of the supercritical carbon dioxide to stabilise the ionic oxidative addition intermediates.

A rhodium complex containing shorter fluorinated phosphines with an ethylene group separating the fluorinated part of the chain from the phosphorus atom (e.g. $P(CH_2CH_2CF_3)_3$) may be more suitable for use as a catalyst in this system. It may also be possible to use this rhodium complex in a biphasic system where the catalyst would remain dissolved in a perfluorinated solvent and the substrates and products in the ethanol. In general these reactions occur in a monophasic system but phase separation occurs on cooling to room temperature.

EXPERIMENTAL

7. EXPERIMENTAL

All the solvents used for the reactions were freshly distilled and dried. THF, petroleum ether (boiling range 40-60 °C) and diethyl ether were distilled over sodium diphenyl ketyl; toluene was distilled over sodium; ethanol was dried over magnesium ethoxide and distilled using a 30 cm Vigreux column; acetone was dried and distilled over calcium sulphate; dichloromethane was distilled over calcium hydride; DMF was dried over calcium hydride and distilled *in vacuo* using a 30 cm Vigreux column discarding the first and last fractions. All the solvents were deoxygenated using dry argon.

All manipulations of air sensitive compounds were carried out using standard Schlenk line and catheter tubing techniques. All of the compounds were handled under argon. All traces of water and oxygen were removed from the argon by passing it through a column of Cr^{II} absorbed onto silica gel. The column was activated by passing carbon monoxide through it at 500 °C reducing CrO_3 to Cr^{II}.

All NMR spectra were recorded on a Brucker AM 300 spectrometer. The ^1H spectra were recorded at 300 MHz, the ^{13}C at 74.76 MHz and the ^{31}P at 121.49 MHz, the last two with broad band proton decoupling. Unless otherwise stated the spectra were run at 24 °C. The NMR solvents used were d^6-benzene at 24 °C and d^8-toluene and d^2-dichloromethane for the variable temperature experiments.

All gas chromatographs (GC) were run on a Phillips PU 4500 GC using Chrompac software. The column used was a 25 m SGE BP-1 (non-polar). The GC was calibrated before each run using 1 cm^3 solutions containing known amounts of ester, ether and alkenyl halide of which 0.1 μl was injected into the GC. Toluene (50 μl) was added to each of the solutions as an internal standard. The trends in peak area were shown to be linear over the range of concentrations for each of the compounds. After an autoclave run 1 cm^3 of the solution was pipetted into a sample vial and toluene (50 μl) added before injecting 0.1 μl into the GC. The peak areas were reproducible to within 5% on each injection of a sample. Samples were injected three times and an average peak area taken.

The GCMS spectra were recorded using a Hewlett-Packard 5890 GC fitted to an Incos 50 electric quadrupole mass spectrometer. The GC was fitted with a 25 m SGE BP-1 column.

The $[RhCl(CO)(PEt_3)_2]$ and $[RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2]$ were checked for purity by ^1H, ^{13}C and ^{31}P NMR and by microanalysis after the initial preparation. Subsequent preparations were checked by for purity by ^1H and ^{31}P NMR. The complexes were recrystallised before use under an argon atmosphere.

7.1 Metal Complex Preparation

Synthesis of μ-tetrakisacetatodirhodium(II) ($[Rh_2(OAc)_4.2MeOH]$)[117]

$RhCl_3.3H_2O$ (1.04 g, 0.0039 mol), NaOAc (2 g, 0.024 mol) and glacial acetic acid (20 cm^3) were dissolved in ethanol (20 cm^3) and refluxed for one hour in a 100 cm^3 round bottomed flask. The flask was cooled for 30 minutes and stored at 3 °C for 12 hours. The resulting green solid was filtered and the residue was dissolved in hot methanol (~ 350 cm^3). More NaOAc and glacial acetic acid could be added to the filtrate. Refluxing for a further hour produced more of the green solid. This could be repeated twice. The methanol solution was stored at 3 °C for one week to yield very dark green cubic crystals. These were filtered and dried *in vacuo* for two hours at 20 °C. Yield: 1.25 g (73%).

Synthesis of acetatocarbonylbis(triethylphosphine)rhodium(I) ($[Rh(OAc)(CO)(PEt_3)_2]$)[100]

$[Rh_2(OAc_4).2MeOH]$ (0.2 g, 0.00045 mol) was dissolved in ethanol (20 cm^3). Triethylphosphine (0.321 g, 0.40 cm^3, 0.0027 mol) was added to the solution turning it dark orange. This was stirred for one hour. Carbon monoxide was bubbled through the solution for 15 minutes, turning it bright yellow. The solution was filtered and the ethanol removed *in vacuo* to leave a bright yellow oil to which petroleum ether (2.5 cm^3) was added. The solution was cooled to -100 °C in an ethanol/liquid nitrogen bath forming yellow micro-crystals. These were filtered, washed with petroleum ether

(2x 1 cm^3) and dried *in vacuo* for 1 hour. The oil was stored under argon at -30 °C. Yield: 0.27g (70%).

Synthesis of μ-chlorobis[(biscyclooctene)rhodium(I)] ([RhCl(C_8H_{14})$_2$]$_2$)[118]

$RhCl_3.3H_2O$ (0.5 g, 0.0019 mol) was dissolved in deoxygenated propan-1-ol (10 cm^3). Cyclooctene (1.29 g, 1.52 cm^3, 0.01 mol) was added and the solution was stirred under argon for 15 minutes. The solution was stored under argon at 20 °C for one week. The resulting brown crystals were filtered and washed with cold water (4 cm^3) and cold methanol (2x 1cm^3) and dried *in vacuo* at 20 °C for three hours. The crystals were stored under argon at 3 °C. Yield: 1.07 g (78%).

Synthesis of chlorocarbonylbis(triethylphosphine)rhodium(I) ([RhCl(CO)(PEt_3)$_2$])

[RhCl(C_8H_{14})$_2$]$_2$ (0.92 g, 0.0013 mol) was suspended in petroleum ether (15 cm^3) with PEt_3 (0.68 g, 0.85 cm^3, 0.0058 mol) and stirred at 20 °C for 20 hours. The solvent volume was reduced *in vacuo* to ~1 cm^3 and the product was dissolved in diethyl ether (5 cm^3). Carbon monoxide was bubbled through the solution for 5 minutes during which there was a colour change from deep red/orange to bright yellow. The volume of the solution was reduced to ~1 cm^3 and the product was allowed to crystallise overnight at -30 °C. The product was filtered cold (-50 °C) and washed with cold diethyl ether (2x 1cm^3) before drying *in vacuo* at 20 °C for 2 hours. Yield: 0.42g (80%).

Improved synthesis of chlorocarbonylbis(triethylphosphine)rhodium(I) ([RhCl(CO)(PEt$_3$)$_2$])[119]

RhCl$_3$.3H$_2$O (2.0 g, 0.0076 mol) was dissolved in ethanol (40 cm^3) and water (1.5 cm^3). The resulting solution was heated under reflux for three hours under a continuous stream of carbon monoxide to yield a bright yellow solution. After filtration, PEt$_3$ (2.82 g, 3.53 cm^3, 0.024 mol) was slowly added to the solution. A gas, possibly carbon monoxide, was evolved during the addition of PEt$_3$. The solution was heated under reflux for a further 30 minutes under a stream of carbon monoxide. The solution was filtered and the ethanol removed *in vacuo* to yield a bright green sticky solid. The solid was washed with diethyl ether (5x 15 cm^3) to leave a dull green sticky oil. The ethereal washings were combined and reduced in volume to ~5 cm^3 and stored at 3 °C for four days to yield large (5-6 mm^3) bright yellow prisms. These were collected and dried *in vacuo* at 20 °C for 2 hours. Yield: 3.0 g (98%).

^{1}H NMR δ (ppm), multiplicity, integral: 1.05, b. mult, 3; 1.80, b. mult, 2.
^{31}P NMR δ (ppm), multiplicity, $^1J_{Rh-P}$ (Hz): 24.4, d, 117.
Found: C 38.95%, H 7.68%; C$_{13}$H$_{30}$ClOP$_2$Rh requires C 38.8%, H 7.5%.

Synthesis of chlorocarbonylbis(tri-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-*n*-octylphosphine)rhodium(I) ([RhCl(CO)(P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$)$_2$])

RhCl$_3$.3H$_2$O (1.0 g, 0.0038 mol) was dissolved in ethanol (20 cm^3) and water (0.75 cm^3). The resulting solution was heated under reflux for three hours under a continuous stream of carbon monoxide to yield a bright yellow solution. After filtration, the aqueous ethanol was removed *in vacuo* to yield bright red needles of [RhCl(CO)$_2$]$_2$. [RhCl(CO)$_2$]$_2$ (0.17 g, 0.00044 mol) was redissolved in dry ethanol (4 cm^3) yielding a

yellow solution. $P(CH_2CH_2(CF_2)_5CF_3)_3$ (0.93 g, 0.00088 mol) was added dropwise to the solution whilst venting the Schlenk tube because of release of carbon monoxide. The solution was stirred rapidly for three hours during which time a light yellow sticky solid precipitated. The ethanol became colourless. The solid was filtered, washed with ethanol (3x 2 cm^3) and dried *in vacuo* for two hours. The solid was dissolved in perfluorodecalin (1.5 cm^3) and crystallised at 3 °C for two days to yield pale yellow micro needles. A portion of these were recrystallised from perfluorobenzene (0.5 cm^3) to yield pale yellow cubic crystals suitable for single crystal X-ray diffraction. Both sets of crystals were filtered and dried *in vacuo* for 2 hours at 20 °C. Yield: 2.01 g (99%). NMR spectra were obtained in perfluorobenzene with a D_2O capillary to provide the lock signal.
^1H NMR δ (ppm), multiplicity, integral: 2.30, b. mult, 2; 2.51, b. mult, 2.
^{31}P NMR δ (ppm), multiplicity, $^1J_{Rh-P}$ (Hz): 22.95, d, 122.
^{19}F NMR δ (ppm), multiplicity, coupling (Hz): -80.65, t, 10; -114.08, p, 16; -121.27, bs; -122.29, bs; -122.59, bs; -125.70, hex, 7.
Found: C 25.5%, H 0.9%; $C_{49}H_{24}ClF_{78}OP_2Rh$ requires C 25.5%, H 1.1%.

Synthesis of dichlorocarbonylphenylacetylbis(triethylphosphine) rhodium(III) ($[RhCl_2(CO)(COCH_2Ph)(PEt_3)_2]$)

$[RhCl(CO)(PEt_3)_2]$ (0.5 g, 0.0012 mol) was dried *in vacuo* at 150 °C and dissolved in dichloromethane (5 cm^3) in a flame dried flask. The solution was cooled to -78 °C. Precooled (-10 °C) phenylacetyl chloride (0.31 g, 0.27 cm^3, 0.002 mol) was added to the solution with stirring. The solution was allowed to warm slowly to room temperature. The solvent volume was reduced to ~1 cm^3 and the solution was stored at 3 °C for 2 weeks to crystallise. Pale yellow crystals were collected and freed of solvent *in vacuo* and stored under argon. Yield: 0.63 g (94%).

Synthesis of dichlorocarbonylbut-3-enoylbis(triethylphosphine) rhodium(III) ($[RhCl_2(CO)(COCH_2CHCH_2)(PEt_3)_2]$)

$[RhCl(CO)(PEt_3)_2]$ (0.5 g, 0.0012 mol) was dried *in vacuo* at 150 °C and dissolved in 1-chloroprop-2-ene (2.9 g, 3 cm^3, 0.037 mol) in a flame dried Torion bottle (thick walled glass pressure vessel). The bottle was pressurised with carbon monoxide (4 bar) and heated to 100 °C in a water bath for four hours during which time a dark orange separated. The flask was cooled and the excess 1-chloroprop-2-ene was decanted off. The oil was dried *in vacuo* for 15 minutes at 20 °C. Yield: 0.5 g (82%). Numerous attempts were made to crystallise the oil but they were unsuccessful.

Attempted isolation and crystallisation of Rh(III) oxidative addition complexes: General procedure

$[RhCl(CO)(PEt_3)_2]$ (~0.15 g, ~0.00038 mol) was dissolved in CD_2Cl_2 (0.5 cm^3). The alkenyl halides (~0.2 cm^3, ~0.0025 mol) were added to the solution before cooling to between -20 and -40 °C. The reaction was monitored by ^{31}P NMR spectroscopy. When the reaction was complete the NMR tube was placed in a $CO_{2\,(s)}$/acetone bath at -78 °C and the contents transferred to a precooled Schlenk tube. The solution was then left to crystallise at -30 °C. Any solids obtained were extremely thermally sensitive, so they were characterised by NMR spectroscopy.

7.2 Preparation of Authentic Samples of Products of Catalytic Reactions

Preparation of Esters

Ethyl but-3-enoate (5 cm^3) and ethyl pent-3-enoate (5 cm^3) were prepared by dissolving but-3-enoic acid or pent-3-enoic acid in an excess of ethanol (10 cm^3) and adding two drops of concentrated sulphuric acid to each of the solutions. These were left overnight and distilled using an Ace microscale spinning band distillation apparatus. The esters were shown to be pure by GC analysis.

Preparation of Ethers[120]

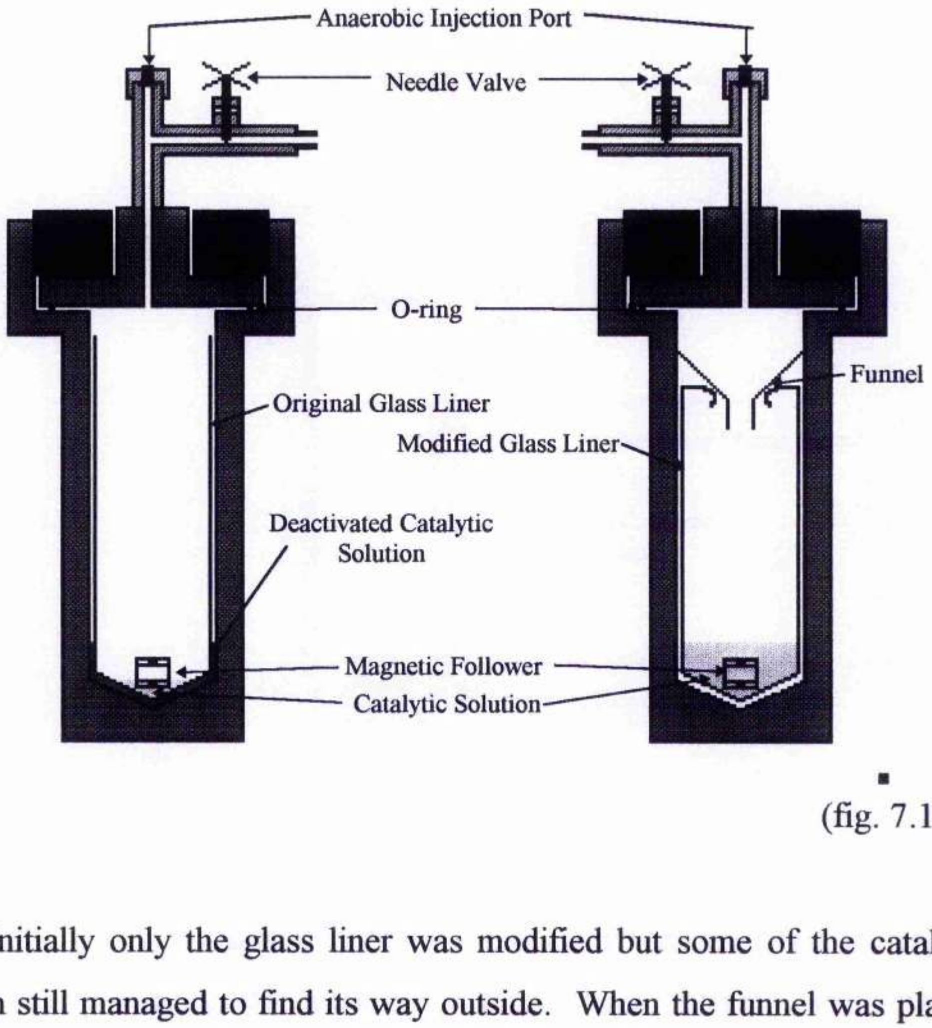
Ethyl 1-methylprop-2-enyl ether and but-2-enyl ethyl ether were both prepared by the Williamson ether synthesis.

Sodium (3 g, 0.13 mol) was added to dry ethanol (30 cm^3) in small pieces to produce sodium ethanoate. 1-chlorobut-2-ene or 3-chlorobut-1-ene (11.77 g, 0.13 mol) were added dropwise to the solution whilst stirring vigorously. After the addition was completed the solution was heated on a water bath for 1 hour and then cooled to room temperature. The sodium chloride produced in the reaction was removed by a trap-to-trap distillation *in vacuo*. The resulting solutions were distilled using a 10 cm Vigreux column. The resulting ethers, ethyl 1-methylprop-2-enyl ether and but-2-enyl ethyl ether respectively, were shown to be pure by GC analysis.

7.3 Autoclave Reactions: General Procedure

The catalyst (0.00005-0.0001 mol) was dissolved in a protic solvent (4 cm^3), usually ethanol, with the substrate (1 cm^3) in a degassed Schlenk tube. A glass liner containing a magnetic follower was placed in the autoclave and sealed (see figure 7.1). The autoclave was then deoxygenated with argon and loaded with the catalytic solution *via* the anaerobic injection port using a syringe. It was then pressurised, heating bands were fitted, and the autoclave was heated at a rate of 20 °C min^{-1} to the required temperature. After the run was complete the autoclave was cooled in a water bath for 1 hour and slowly vented in a fume cupboard. The solutions were analysed by GC and GCMS or distilled to obtain the products. The autoclaves, Schlenk tubes and syringes were all precooled to -20 °C when 1-fluoroprop-2-ene was used as a substrate.

It was noticed at the end of the autoclave reactions that more than half of the solution was outside the glass liner and in contact with the stainless steel wall of the autoclave. The colour of these solutions was dependent upon the allylic halide used. With chlorides the solutions in contact with the metal were green, with bromides they were orange and with iodides they were dark red. To quote Simpson, "the colours were reminiscent of traffic lights." The solutions remaining in the glass liner were still bright yellow, the colour of the original catalytic solution. This change in colour was thought to be due to dissolution of the autoclave wall by the reaction solution which led to catalyst degradation. It was known that the reaction solution was quite corrosive because of the slight degradation of the autoclave walls after a carbonylation reaction. This was undoubtedly due to the HCl produced in the reaction. In an attempt to prevent the solution from coming into contact with the autoclave wall the glass liners were redesigned[121] (figure 7.1) and the method of pressurising the autoclave was also revised.



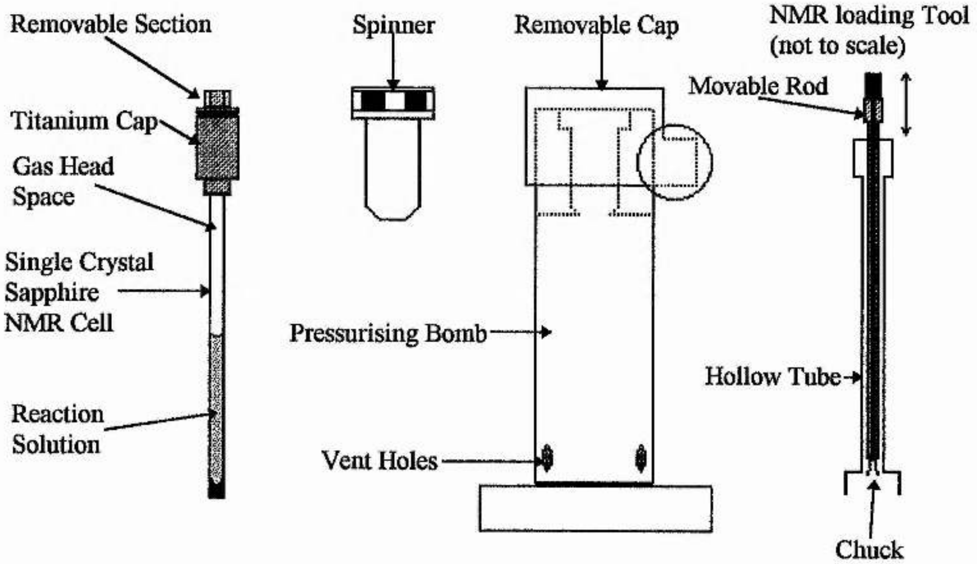
(fig. 7.1)

Initially only the glass liner was modified but some of the catalytic solution still managed to find its way outside. When the funnel was placed in the top this prevented all but approximately 0.25 cm^3 from escaping the glass liner. The method of pressurising the autoclave was also modified. Instead of taking the autoclave up to 40 bar within a few seconds, it was pressurised over a period of 15 minutes at approximately 3 bar a minute.

Again this only allowed ~ 0.25 cm^3 of the solutions to escape from the glass liner.

7.4 High Pressure NMR Reactions: General Procedure

The catalyst (0.0004-0.0005 mol) was dissolved in an NMR solvent (0.4 cm^3) with the substrate in a degassed Schlenk tube. The HPNMR cell was placed in its spinner without its cap and deoxygenated with argon in a specially designed Schlenk tube. The reaction solution was transferred into the HPNMR cell *via* catheter and the cap replaced by holding the cell at the mouth of the Schlenk tube under a fast stream of argon. The spinner was removed and the cell transferred to its steel casing and pressurised with carbon monoxide using a high pressure line. The spinner was replaced and the cell lowered into the NMR using a long rod. The HPNMR equipment is shown in figure 7.2.



(fig. 7.2)

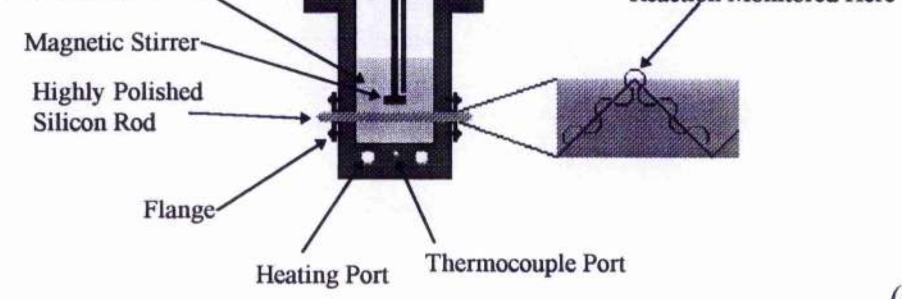
7.5 High Pressure IR Reactions: General Procedure

The HPIR cell used to study these reactions was a circle internal reflectance (CIR) cell produced by SpectraTech. The rod material that was initially used was zinc selenide because of its large window for the transmission of IR radiation. However, this rod was easily etched by the reaction solutions and was very brittle thus it was replaced by a silicon rod which was very resistant to the extreme reaction conditions and was much less brittle. The IR transmission window for the silicon rod cut off at 1500 cm^{-1} so it was still suitable to study the catalytic reactions.

Problems were initially encountered with the autoclave body. The original base was made out of stainless steel 316 (SS 316); it was found that it was etched by the reaction solutions. Intense peaks at 2045 cm^{-1} appeared at higher temperatures which swamped the spectra. These were thought to be due to the presence of $[Ni(CO)_4]$. This could have been formed because SS 316 contained nickel which would quite readily react with carbon monoxide. This problem was solved by the use of a new base made out of a chemically resistant alloy Hastelloy C.

The rods have conical ends with angles of 30° for a silicon rod and 45° for a zinc selenide rod (the angles depend on the refractive index of the material). For most of this work the silicon rod was used because of the corrosive nature of the solutions. A diagram of the HPIR cell is shown in figure 7.3.

The catalyst (~0.0009 mol) was dissolved in a solvent (8 cm^3) with the substrate (2 cm^3) in a degassed Schlenk tube. The HPIR cell was deoxygenated by passing argon through it for 15 minutes before injecting the reaction solution *via* the anaerobic injection port. The cell was pressurised with carbon monoxide at approximately 2 bar min^{-1}. Heating rods were inserted into the ports before the cell was mounted into the focusing mirror stage and the whole assembly was placed directly into the path of the IR beam. A thermocouple was placed into the thermocouple port and the cell heated to the required temperature. On completion of the reaction the cell was allowed to cool down to room temperature before being slowly vented in a fume cupboard.



(fig. 7.3)

The blown up section of the silicon rod shows how the reaction is monitored at the surface. The direction of propagation of the IR beam is along the black line. The IR beam is transmitted through the rod *via* internal reflection. The internal reflections from the rod-solution interface lead to a modulation of the IR intensity by absorbtions from the solution. The resulting IR is almost identical to that obtained from a conventional transmission cell. The pathlength for the CIR cell is approximately 350-525 μm depending on how many reflections occur inside the rod.

7.6 Carbonylation in supercritical carbon dioxide: General procedure

$[RhCl(CO)(PEt_3)_2]$ (0.05 g, 0.00012 mol) and 1-chloroprop-2-ene (0.935 g, 1cm^3, 0.012 mol) were dissolved in ethanol (4 cm^3) and cooled to -78 °C using external $CO_{2(s)}$. Alternatively, $[RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2]$ (0.1 g, 0.000043 mol) was dissolved in hexafluorobenzene (1 cm^3) whilst 1-chloroprop-2-ene (1 cm^3) was dissolved in ethanol (4 cm^3) and the solutions cooled to -78 °C. The autoclave was also cooled before adding the $CO_{2\,(s)}$ and reaction solutions. $CO_{2\,(s)}$ (20 g) was weighed out and placed in the cooled autoclave along with the cooled reaction solutions. The autoclave was quickly sealed and pressurised to the required pressure with carbon monoxide. A heating band was fitted to the autoclave which was then lagged with glass wool and aluminium foil to ensure proper heating. On completion of the reaction the autoclave was cooled in a cold water bath and then ice and vented in a fume hood. The results were analysed by GC and GCMS.

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APPENDIX

Space Group for $[RhCl(CO)(P(CH_2CH_2(CF_2)_5CF_3)_3)_2]$: P1 triclinic

Unit cell dimensions:

$a = 15.131(4)$
$b = 22.624(8)$
$c = 11.323(6)$

$\alpha = 94.27(4)^\circ$
$\beta = 99.62(3)^\circ$
$\gamma = 84.89(3)^\circ$

$R = 11.5\%$

A large cavity exists around the carbon monoxide ligand, therefore, this would be the most likely area for a substrate (e.g. 1-chloroprop-2-ene) to oxidatively add to the complex. The area around the chloride ligand is too sterically crowded due to the fluorinated 'ponytail' ligands for there to be much chance of oxidative addition occurring at that side of the complex.

The error in the intramolecular bond angles and distances is high at the ends of the fluorinated 'ponytails' due to molecular motion of the crystal. The greatest errors occur in the fluorine atoms attached to the carbon atoms labelled C_{16}, C_{17}, C_{48} and C_{49}.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Rh(1)	P(1)	85.3(3)	F(2)	C(4)	C(3)	110(2)
Cl(1)	Rh(1)	P(2)	86.9(3)	F(2)	C(4)	C(5)	108(2)
Cl(1)	Rh(1)	C(1)	179.4(9)	C(3)	C(4)	C(5)	115(2)
P(1)	Rh(1)	P(2)	172.2(3)	F(3)	C(5)	F(4)	110(2)
P(1)	Rh(1)	C(1)	94.8(8)	F(3)	C(5)	C(4)	107(2)
P(2)	Rh(1)	C(1)	93.0(8)	F(3)	C(5)	C(6)	111(2)
Rh(1)	P(1)	C(2)	113.9(9)	F(4)	C(5)	C(4)	106(2)
Rh(1)	P(1)	C(10)	120(1)	F(4)	C(5)	C(6)	107(2)
Rh(1)	P(1)	C(18)	113(1)	C(4)	C(5)	C(6)	115(2)
C(2)	P(1)	C(10)	102(1)	F(5)	C(6)	F(6)	107(3)
C(2)	P(1)	C(18)	103(1)	F(5)	C(6)	C(5)	109(2)
C(10)	P(1)	C(18)	103(1)	F(5)	C(6)	C(7)	108(3)
Rh(1)	P(2)	C(26)	113.3(9)	F(6)	C(6)	C(5)	110(2)
Rh(1)	P(2)	C(34)	112.9(9)	F(6)	C(6)	C(7)	111(2)
Rh(1)	P(2)	C(42)	118.7(9)	C(5)	C(6)	C(7)	112(3)
C(26)	P(2)	C(34)	102(1)	F(7)	C(7)	F(8)	109(3)
C(26)	P(2)	C(42)	102(1)	F(7)	C(7)	C(6)	110(3)
C(34)	P(2)	C(42)	106(1)	F(7)	C(7)	C(8)	108(3)
C(14)	F(20)	C(15)	51(2)	F(8)	C(7)	C(6)	110(3)
C(16)	F(24)	C(17)	77(5)	F(8)	C(7)	C(8)	110(3)
Rh(1)	C(1)	O(1)	178(2)	C(6)	C(7)	C(8)	109(3)
P(1)	C(2)	C(3)	114(2)	F(9)	C(8)	F(10)	109(3)
C(2)	C(3)	C(4)	113(2)	F(9)	C(8)	C(7)	115(3)
F(1)	C(4)	F(2)	105(2)	F(9)	C(8)	C(9)	110(3)
F(1)	C(4)	C(3)	110(2)	F(10)	C(8)	C(7)	105(3)
F(1)	C(4)	C(5)	108(2)	F(10)	C(8)	C(9)	107(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
C(7)	C(8)	C(9)	110(3)	F(19)	C(14)	C(13)	93(3)
F(11)	C(9)	F(12)	108(4)	F(19)	C(14)	C(15)	97(3)
F(11)	C(9)	F(13)	106(4)	F(20)	C(14)	C(13)	109(3)
F(11)	C(9)	C(8)	109(4)	F(20)	C(14)	C(15)	62(3)
F(12)	C(9)	F(13)	113(4)	C(13)	C(14)	C(15)	120(3)
F(12)	C(9)	C(8)	114(4)	F(20)	C(15)	F(21)	109(4)
F(13)	C(9)	C(8)	106(3)	F(20)	C(15)	C(14)	67(3)
P(1)	C(10)	C(11)	115(2)	F(20)	C(15)	C(16)	102(4)
C(10)	C(11)	C(12)	114(2)	F(21)	C(15)	C(14)	117(3)
F(14)	C(12)	F(15)	108(2)	F(21)	C(15)	C(16)	112(4)
F(14)	C(12)	C(11)	110(2)	C(14)	C(15)	C(16)	131(5)
F(14)	C(12)	C(13)	103(2)	F(22)	C(16)	F(23)	84(5)
F(15)	C(12)	C(11)	111(3)	F(22)	C(16)	F(24)	99(6)
F(15)	C(12)	C(13)	105(2)	F(22)	C(16)	C(15)	101(6)
C(11)	C(12)	C(13)	119(3)	F(23)	C(16)	F(24)	161(7)
F(16)	C(13)	F(17)	105(3)	F(23)	C(16)	C(15)	80(5)
F(16)	C(13)	C(12)	108(3)	F(24)	C(16)	C(15)	118(6)
F(16)	C(13)	C(14)	105(3)	F(24)	C(17)	F(25)	134(8)
F(17)	C(13)	C(12)	112(3)	F(24)	C(17)	F(26)	88(5)
F(17)	C(13)	C(14)	109(3)	F(25)	C(17)	F(26)	92(6)
C(12)	C(13)	C(14)	116(3)	P(1)	C(18)	C(19)	112(2)
F(18)	C(14)	F(19)	89(3)	C(18)	C(19)	C(20)	112(2)
F(18)	C(14)	F(20)	93(3)	F(27)	C(20)	F(28)	106(3)
F(18)	C(14)	C(13)	116(3)	F(27)	C(20)	C(19)	111(2)
F(18)	C(14)	C(15)	123(3)	F(27)	C(20)	C(21)	105(2)
F(19)	C(14)	F(20)	154(3)	F(28)	C(20)	C(19)	113(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
F(28)	C(20)	C(21)	109(2)	F(37)	C(25)	F(38)	109(4)
C(19)	C(20)	C(21)	113(3)	F(37)	C(25)	F(39)	101(3)
F(29)	C(21)	F(30)	108(2)	F(37)	C(25)	C(24)	114(3)
F(29)	C(21)	C(20)	110(2)	F(38)	C(25)	F(39)	113(3)
F(29)	C(21)	C(22)	109(2)	F(38)	C(25)	C(24)	114(4)
F(30)	C(21)	C(20)	104(2)	F(39)	C(25)	C(24)	106(3)
F(30)	C(21)	C(22)	105(2)	P(2)	C(26)	C(27)	111(2)
C(20)	C(21)	C(22)	120(3)	C(26)	C(27)	C(28)	111(2)
F(31)	C(22)	F(32)	104(2)	F(40)	C(28)	F(41)	104(2)
F(31)	C(22)	C(21)	110(2)	F(40)	C(28)	C(27)	111(2)
F(31)	C(22)	C(23)	113(2)	F(40)	C(28)	C(29)	106(2)
F(32)	C(22)	C(21)	105(2)	F(41)	C(28)	C(27)	110(2)
F(32)	C(22)	C(23)	103(2)	F(41)	C(28)	C(29)	109(2)
C(21)	C(22)	C(23)	121(3)	C(27)	C(28)	C(29)	115(2)
F(33)	C(23)	F(34)	104(2)	F(42)	C(29)	F(43)	103(3)
F(33)	C(23)	C(22)	111(3)	F(42)	C(29)	C(28)	110(2)
F(33)	C(23)	C(24)	111(3)	F(42)	C(29)	C(30)	111(3)
F(34)	C(23)	C(22)	105(2)	F(43)	C(29)	C(28)	105(2)
F(34)	C(23)	C(24)	104(2)	F(43)	C(29)	C(30)	102(3)
C(22)	C(23)	C(24)	121(3)	C(28)	C(29)	C(30)	123(3)
F(35)	C(24)	F(36)	109(3)	F(44)	C(30)	F(45)	99(3)
F(35)	C(24)	C(23)	111(3)	F(44)	C(30)	C(29)	100(3)
F(35)	C(24)	C(25)	97(3)	F(44)	C(30)	C(31)	104(3)
F(36)	C(24)	C(23)	111(3)	F(45)	C(30)	C(29)	113(2)
F(36)	C(24)	C(25)	108(3)	F(45)	C(30)	C(31)	112(3)
C(23)	C(24)	C(25)	120(3)	C(29)	C(30)	C(31)	123(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
F(46)	C(31)	F(47)	104(3)	F(55)	C(37)	F(56)	108(2)
F(46)	C(31)	C(30)	109(3)	F(55)	C(37)	C(36)	110(2)
F(46)	C(31)	C(32)	110(3)	F(55)	C(37)	C(38)	109(2)
F(47)	C(31)	C(30)	106(3)	F(56)	C(37)	C(36)	107(2)
F(47)	C(31)	C(32)	103(3)	F(56)	C(37)	C(38)	108(2)
C(30)	C(31)	C(32)	123(3)	C(36)	C(37)	C(38)	115(2)
F(48)	C(32)	F(49)	107(3)	F(57)	C(38)	F(58)	110(3)
F(48)	C(32)	C(31)	103(3)	F(57)	C(38)	C(37)	111(3)
F(48)	C(32)	C(33)	105(3)	F(57)	C(38)	C(39)	107(2)
F(49)	C(32)	C(31)	107(3)	F(58)	C(38)	C(37)	109(2)
F(49)	C(32)	C(33)	110(3)	F(58)	C(38)	C(39)	103(3)
C(31)	C(32)	C(33)	124(3)	C(37)	C(38)	C(39)	116(3)
F(50)	C(33)	F(51)	104(3)	F(59)	C(39)	F(60)	104(3)
F(50)	C(33)	F(52)	106(3)	F(59)	C(39)	C(38)	109(2)
F(50)	C(33)	C(32)	113(3)	F(59)	C(39)	C(40)	108(3)
F(51)	C(33)	F(52)	105(4)	F(60)	C(39)	C(38)	108(2)
F(51)	C(33)	C(32)	108(4)	F(60)	C(39)	C(40)	108(2)
F(52)	C(33)	C(32)	119(4)	C(38)	C(39)	C(40)	119(3)
P(2)	C(34)	C(35)	112(2)	F(61)	C(40)	F(62)	109(3)
C(34)	C(35)	C(36)	113(2)	F(61)	C(40)	C(39)	108(3)
F(53)	C(36)	F(54)	109(2)	F(61)	C(40)	C(41)	107(3)
F(53)	C(36)	C(35)	112(2)	F(62)	C(40)	C(39)	107(3)
F(53)	C(36)	C(37)	105(2)	F(62)	C(40)	C(41)	109(3)
F(54)	C(36)	C(35)	109(2)	C(39)	C(40)	C(41)	116(3)
F(54)	C(36)	C(37)	109(2)	F(63)	C(41)	F(64)	110(4)
C(35)	C(36)	C(37)	112(2)	F(63)	C(41)	F(65)	109(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
F(63)	C(41)	C(40)	111(3)				
F(64)	C(41)	F(65)	101(3)				
F(64)	C(41)	C(40)	114(3)				
F(65)	C(41)	C(40)	112(3)				
P(2)	C(42)	C(43)	116(2)				
C(42)	C(43)	C(44)	111(2)				
F(66)	C(44)	F(67)	107(2)				
F(66)	C(44)	C(43)	112(2)				
F(66)	C(44)	C(45)	103(2)				
F(67)	C(44)	C(43)	109(2)				
F(67)	C(44)	C(45)	105(2)				
C(43)	C(44)	C(45)	119(2)				
F(68)	C(45)	F(69)	109(2)				
F(68)	C(45)	C(44)	111(2)				
F(68)	C(45)	C(46)	106(2)				
F(69)	C(45)	C(44)	107(2)				
F(69)	C(45)	C(46)	104(2)				
C(44)	C(45)	C(46)	119(2)				
F(70)	C(46)	F(71)	96(2)				
F(70)	C(46)	C(45)	108(3)				
F(71)	C(46)	C(45)	107(3)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
Rh(1)	Cl(1)	2.348(7)	F(17)	C(13)	1.31(3)
Rh(1)	P(1)	2.307(8)	F(18)	C(14)	1.21(4)
Rh(1)	P(2)	2.296(8)	F(19)	C(14)	1.61(5)
Rh(1)	C(1)	1.81(3)	F(20)	C(14)	1.74(6)
P(1)	C(2)	1.81(3)	F(20)	C(15)	1.66(6)
P(1)	C(10)	1.85(3)	F(21)	C(15)	1.29(4)
P(1)	C(18)	1.81(3)	F(22)	C(16)	1.43(8)
P(2)	C(26)	1.84(3)	F(23)	C(16)	1.68(8)
P(2)	C(34)	1.83(3)	F(24)	C(16)	1.54(9)
P(2)	C(42)	1.83(3)	F(24)	C(17)	1.50(9)
F(1)	C(4)	1.36(3)	F(25)	C(17)	1.17(8)
F(2)	C(4)	1.34(3)	F(26)	C(17)	1.70(8)
F(3)	C(5)	1.34(3)	F(27)	C(20)	1.39(3)
F(4)	C(5)	1.36(3)	F(28)	C(20)	1.32(3)
F(5)	C(6)	1.33(3)	F(29)	C(21)	1.32(3)
F(6)	C(6)	1.29(3)	F(30)	C(21)	1.37(3)
F(7)	C(7)	1.25(3)	F(31)	C(22)	1.33(3)
F(8)	C(7)	1.32(4)	F(32)	C(22)	1.42(3)
F(9)	C(8)	1.27(4)	F(33)	C(23)	1.34(3)
F(10)	C(8)	1.33(4)	F(34)	C(23)	1.40(3)
F(11)	C(9)	1.24(5)	F(35)	C(24)	1.38(4)
F(12)	C(9)	1.25(5)	F(36)	C(24)	1.34(4)
F(13)	C(9)	1.29(5)	F(37)	C(25)	1.25(4)
F(14)	C(12)	1.33(3)	F(38)	C(25)	1.23(5)
F(15)	C(12)	1.36(3)	F(39)	C(25)	1.38(4)
F(16)	C(13)	1.32(4)	F(40)	C(28)	1.38(3)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	atom	atom	distance
F(41)	C(28)	1.37(3)	F(67)	C(44)	1.36(3)
F(42)	C(29)	1.31(3)	F(68)	C(45)	1.29(3)
F(43)	C(29)	1.44(4)	F(69)	C(45)	1.36(3)
F(44)	C(30)	1.45(4)	F(70)	C(46)	1.38(4)
F(45)	C(30)	1.31(4)	F(71)	C(46)	1.37(4)
F(46)	C(31)	1.35(3)	O(1)	C(1)	1.14(3)
F(47)	C(31)	1.37(4)	C(2)	C(3)	1.51(4)
F(48)	C(32)	1.42(4)	C(3)	C(4)	1.46(4)
F(49)	C(32)	1.37(4)	C(4)	C(5)	1.56(4)
F(50)	C(33)	1.33(4)	C(5)	C(6)	1.56(4)
F(51)	C(33)	1.37(5)	C(6)	C(7)	1.55(4)
F(52)	C(33)	1.24(4)	C(7)	C(8)	1.63(4)
F(53)	C(36)	1.33(3)	C(8)	C(9)	1.60(5)
F(54)	C(36)	1.36(3)	C(10)	C(11)	1.46(4)
F(55)	C(37)	1.29(3)	C(11)	C(12)	1.48(4)
F(56)	C(37)	1.36(3)	C(12)	C(13)	1.55(4)
F(57)	C(38)	1.33(4)	C(13)	C(14)	1.60(4)
F(58)	C(38)	1.39(4)	C(14)	C(15)	1.46(5)
F(59)	C(39)	1.35(3)	C(15)	C(16)	1.55(8)
F(60)	C(39)	1.35(3)	C(18)	C(19)	1.56(4)
F(61)	C(40)	1.33(4)	C(19)	C(20)	1.46(4)
F(62)	C(40)	1.31(4)	C(20)	C(21)	1.53(4)
F(63)	C(41)	1.30(4)	C(21)	C(22)	1.54(4)
F(64)	C(41)	1.33(4)	C(22)	C(23)	1.46(4)
F(65)	C(41)	1.34(4)	C(23)	C(24)	1.45(4)
F(66)	C(44)	1.33(3)	C(24)	C(25)	1.60(5)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	atom	atom	distance
C(26)	C(27)	1.56(3)			
C(27)	C(28)	1.51(4)			
C(28)	C(29)	1.49(4)			
C(29)	C(30)	1.48(4)			
C(30)	C(31)	1.48(4)			
C(31)	C(32)	1.52(4)			
C(32)	C(33)	1.41(5)			
C(34)	C(35)	1.54(4)			
C(35)	C(36)	1.49(4)			
C(36)	C(37)	1.57(4)			
C(37)	C(38)	1.52(4)			
C(38)	C(39)	1.55(4)			
C(39)	C(40)	1.54(4)			
C(40)	C(41)	1.51(5)			
C(42)	C(43)	1.54(4)			
C(43)	C(44)	1.48(4)			
C(44)	C(45)	1.56(4)			
C(45)	C(46)	1.58(4)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.