Nafion as a support for transition metal catalysis

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Dedication

This book is dedicated to the memory of my mother who helped me through its inception but didn't make it to the last chapter....

Acknowledgements

I would like to thank Dr Mel Kilner for his continued faith in me, the denizens of lab 101 past and present, namely, Graham, Nicky, Pete and Derek for their help and good company. I am grateful to EPSRC for their funding and to ICI for two scholarships and to all the support staff within the department who have helped me achieve my goals.

In particular I would like to thank my wife Victoria for her patience and inspiration.

The material in this thesis has not been submitted for examination for any other degree or part thereof, at the University of Durham or any other institution. The material contained herein is the sole work of the author except where formally acknowledged by reference.

Abstract

The properties of the perfluoropolymer sulphonic acid resin, sold under the trade name of Nafion have been examined. The use of Nafion as a support for transition metal catalysts has been studied in the context of alternative support systems. It has been demonstrated that transition metal complexes are readily incorporated into Nafion, provided they are either ionic in nature or contain ligands which are organic acid anions or ligands which can be protonated. Nafion used as a support has been successfully recycled and forms of Nafion with modified functional groups have been successfully synthesised.

In order to explore the scope of Nafion as a catalyst support, a range of reactions has been investigated, the main purpose being comparison between the performance of a catalyst used homogeneously to its performance supported in Nafion. The hydroesterification of ethene to methyl propanoate was studied using several palladium complexes as catalysts. The effects of temperature, CO pressure, catalyst loading and ligand to metal ratio on yields of product were recorded, using the most effective of the supported palladium catalyst systems. Yields of methyl propanoate using Nafion supported complex as catalyst were higher than the same catalyst used unsupported under comparable conditions. The hydrogenation of cyclohexene, dimethyl maleate and nitrotoluene was accomplished using the complexes, $[Ir(COD)(PPh_2Me)]PF_6$, $[Rh(NBD)\{Fe(C_5H_4PPr_2)_2\}]BF_4$ and $[RhCl(Ph_2P\text{-}NC_5H_{10})_3]$. Yields of hydrogenation products using Nafion supported complexes were comparable or higher than yields obtained homogeneously.

The hydroformylation of hexene was carried out using a series of complexes of the form $[Rh(NBD)L_2]BF_4$ where L represents a phosphine. Yields of aldehydes and normal to branched ratios were slightly lower using Nafion supported complexes in comparison to the homogeneous case. The production of substituted pyridines from propyne and acetonitrile was attempted using cobalt complexes coordinated to modified cyclopentadiene rings without success.

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Chapter 4 Hydrogenation

Chapter 5 Hydroformylation

Abbreviations

Å	Ängstrom
acac	acetylacetonate
BINAP	2,2'-bis(diphenylphosphinyl)-1,1'-binapthyl
COD	cyclo-octadiene
Cp	cyclopentadiene
dba	dibenzylideneacetone
diphos	any chelating diphosphine
dmf	dimethylformamide
dmso	dimethylsulphoxide
DPPB	diphenylphosphinobutane
DPPE	diphenylphosphinoethane
DPPM	diphenylphosphinomethane
DPPP	diphenylphosphinopropane
Et	ethyl
FID	flame ionisation detector
GC	gas chromatograph
GC-MS	gas chromatograph-mass spectrometer
IR	infra red
Me	methyl
MMA	methyl methacrylate
MPt.	melting point
NBD	norbornadiene
NMR	nuclear magnetic resonance
ODS	octadecyl silane
PFSA	perfluorosulphonic acid
Ph	phenyl
phen	phenanthroline
pip	piperidine

PPh_2py	diphenylphosphinopyridine
PPh_2Q	diphenylphosphinoquinoline
PTFE	polytetrafluoroethane
py	pyridine
THF	tetrahydrofuran
TMEDA	tetramethyl ethylenediamine
TOF	turnover frequency
TON	turnover number
Tol	toluene
UV	ultra violet

Chapter 1

Introduction

This study is an investigation into the suitability and scope of Nafion perfluorosulphonic acid resin to act as a support for transition metal complexes used to catalyse a range of reactions. The reasons for supporting homogeneous catalysts are discussed, together with an appraisal of the relative merits of Nafion compared to alternative approaches. Nafion itself is discussed in detail in Chapter 2 then the following four chapters are each dedicated to a particular class of reactions studied, namely, hydroesterification, hydrogenation, hydroformylation and cyclisation. Finally, in chapter 7 issues are discussed which relate to ligands containing both phosphorus and nitrogen that have featured heavily in the research programme.

1.1 Supported Catalysis

Transition metal homogeneous catalysts have several advantages over heterogeneous catalysts. They can achieve high selectivity under moderate reaction conditions and as a group are more diverse in the number of reactions they can catalyse. A serious drawback with homogeneous catalysts which, until comparatively recently, has limited their wider adoption by industry, is the need for at least one extra process step, the separation of the catalyst from the product stream. Several approaches have been adopted to circumvent this problem, most involving the anchoring in some way of the catalyst onto a solid support, thus mimicking a heterogeneous catalyst. The ability to tailor the catalyst to the needs of the reaction is therefore retained without the difficulties of recovery. Additionally, the reactivity of supported catalysts is less dependent on choice of solvent.

A notable exception to the anchoring techniques for ease of separation of catalyst from the product is the use of a two-phase liquid system in which the catalyst is soluble in one phase and the products are soluble in the other phase.

Transition metals and their complexes have been supported on silica and other refractory oxides, in clays, in siloxanes, exchanged onto ion-exchange resins and have been polymerised through their ligands.

This study concentrates on the use of the ionomeric perfluorosulphonic acid resin traded by Du Pont under the name "Nafion".

1.2 Catalysed reactions useful to industry

The industrial use of catalysts often involves the large scale production of intermediates from cheap, readily available feedstocks, often products from the coal and petrochemical industries. Examples of this include alkene hydrogenation, oxidation (Wacker process), hydroformylation, hydrocyanation, methoxycarbonylation and the Monsanto carbonylation of methanol. The Shell Higher Olefin Process (SHOP) combines several catalysed steps to obtain long chain alcohols. The oligomerisation and hydroformylation steps are catalysed homogeneously using a nickel phosphine and cobalt carbonyl phosphine respectively. Production of polymer can also be a transition metal catalysed process, for example the palladium catalysed polyketone synthesis.

Homogeneous catalysts are being increasingly used in the fine chemicals industry for the production of pharmaceuticals, flavours, fragrances and additives. The use of chiral ligands has allowed the commercial production of pure optical isomers, a notable example of this being the production of L-dopa by Monsanto in 1971 involving enantioselective hydrogenation. L-phenylaniline is also produced by enantioselective hydrogenation and L-menthol by isomerisation of an allylic amine.

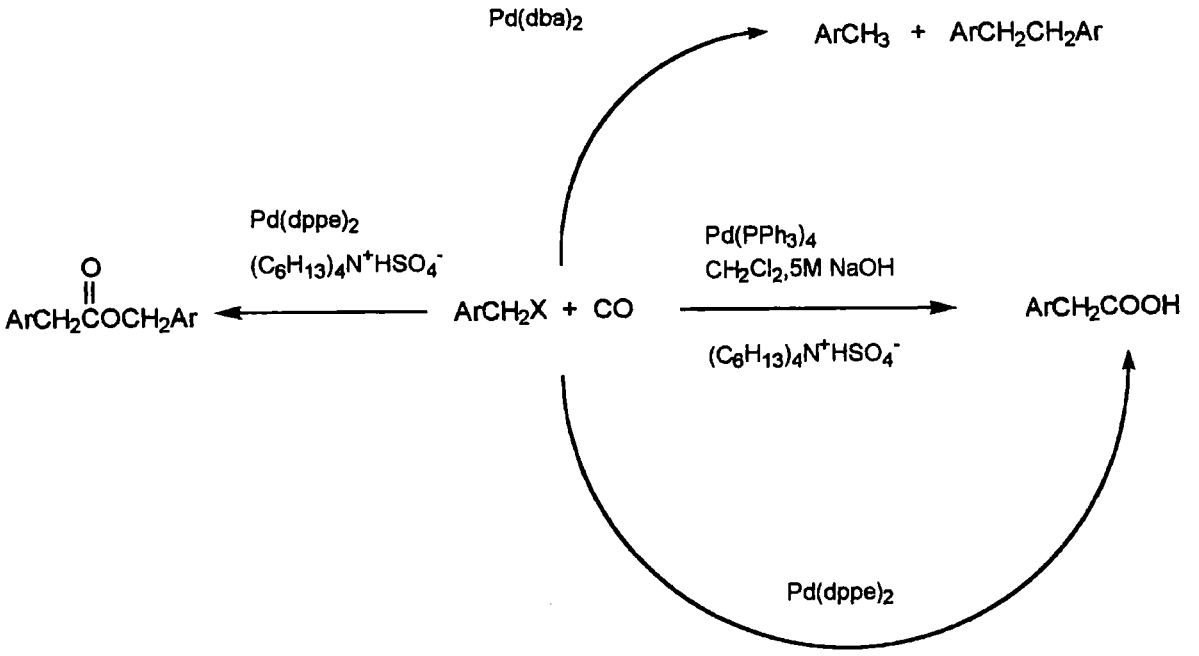
1.3 Methods of Catalyst Retention.

1.3.1 Biphasic systems

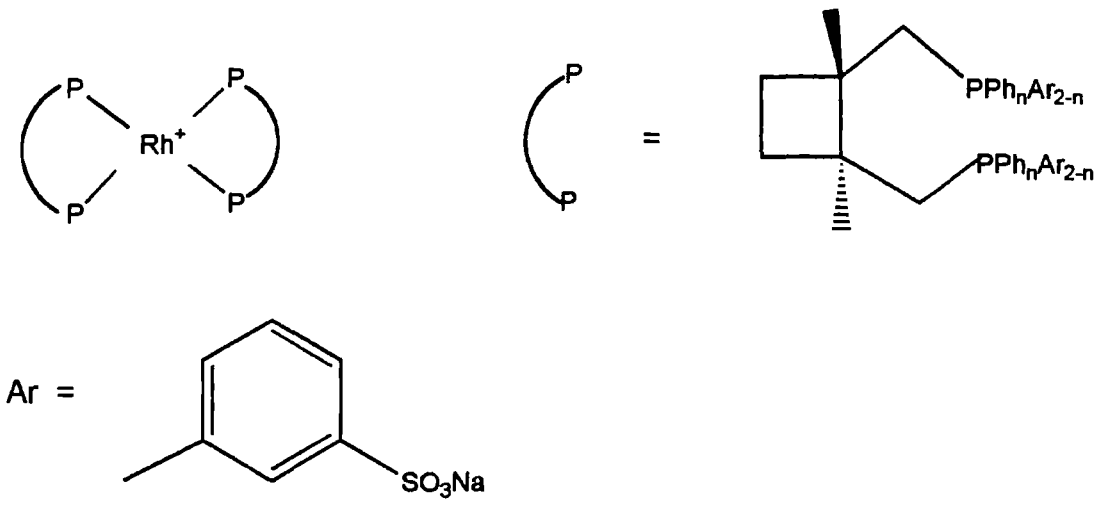
These systems rely on the catalyst and products being soluble in the different phases of a pair of immiscible solvents, usually an organic and an aqueous phase. It is not intended here to give a comprehensive review of the subject but to show a few interesting examples which demonstrate the scope of the approach. Alper and Des Abbeyes[1] used cobalt carbonyl to carbonylate benzylic halides in the organic phase into carboxylic acids which pass into a basic (5M NaOH) aqueous phase with tertiary ammonium salts providing the anion phase transfer. This was one of many reactions effected using similar systems.

Alper *et al.*[2] also examined the phase transfer catalysed carbonylation of benzylic halides using $Pd(PPh_3)_4$ as the metal catalyst and found not only that the reaction took place under mild conditions but that no phase transfer agent was required, since the yields of carboxylic acids obtained were only marginally increased in the presence of a quaternary ammonium salt. In other words this particular reaction takes place at the interface of the aqueous and organic phases. If bis(dibenzylideneacetone)palladium(0) was used then coupling and dehalogenation took place, affording hydrocarbon products. Here, no reaction takes place in the absence of quaternary ammonium halides. While bis[bis(1,2-diphenylphosphino)ethane]palladium (0),$\{Pd(dppe)_2\}$, which also has bidentate ligands, exhibits the same behaviour as $Pd(PPh_3)_4$ in the absence of a phase transfer agent (i.e. halides are carbonylated to acids), carbalkoxylation occurs in the presence of tetrahexylammonium sulphate. (Scheme 1.1 below gives an overview). Thus the results with $Pd(dppe)_2$ are an unusual example of a change in reaction pathway depending on whether a phase transfer catalyst is used or not.

Scheme 1.1: carbonylation reactions of benzylic halides



Amrani and co-workers[3] describe the synthesis of chiral sulphonated phosphines as ligands for the construction of rhodium based catalysts for asymmetric hydrogenation under phase transfer conditions. The catalysts were variations of the one depicted below in Scheme 1.2 with n being 0-2.



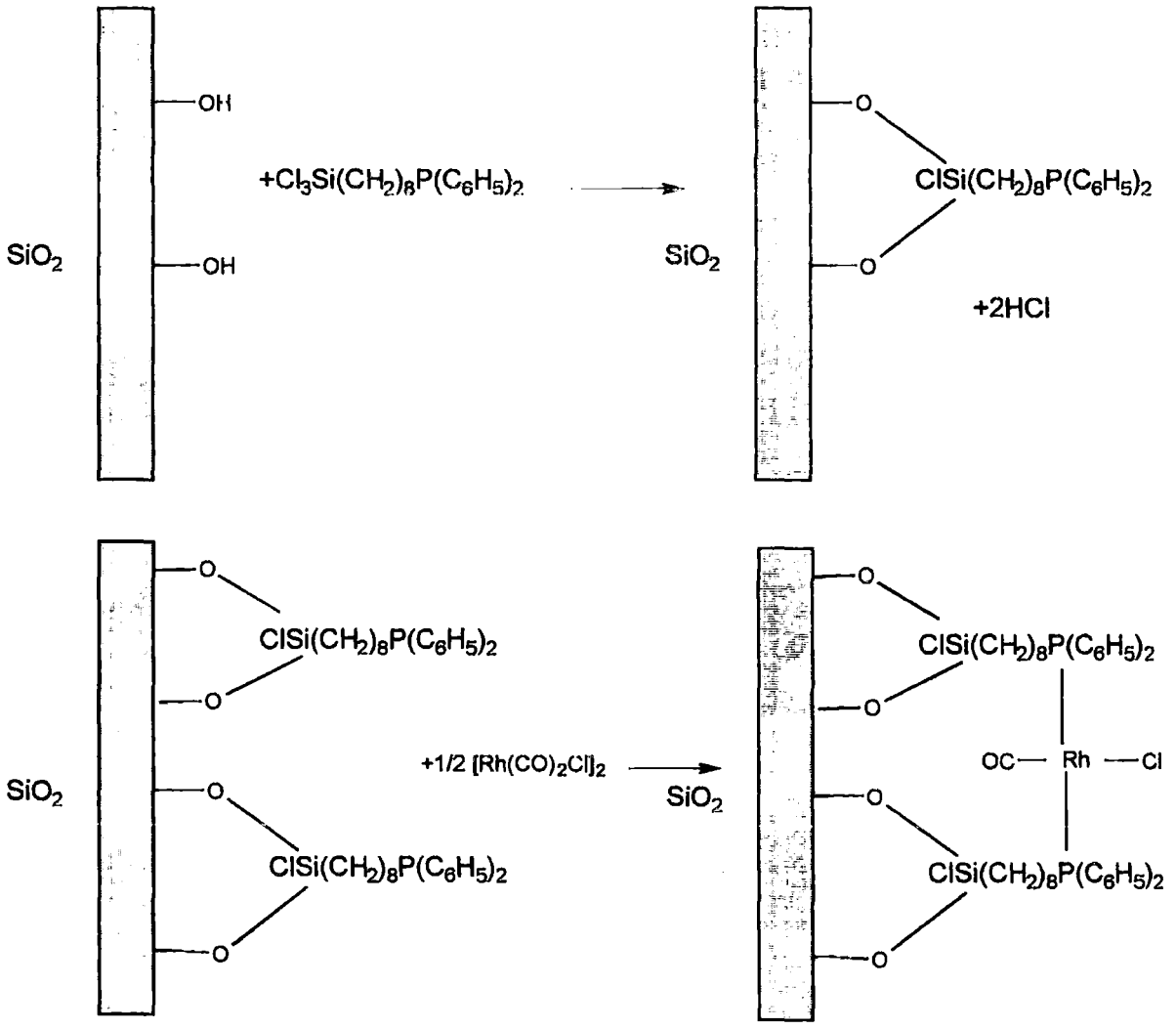
Scheme 1.2: chiral sulphonated phosphine ligands

The rhodium catalyst was prepared *in situ* by the addition of the chiral ligand to $[Rh(COD)Cl]_2$ and was used to hydrogenate various enamides in a dichloromethane/water solvent system, achieving enantiomeric excesses up to 88%.

1.3.2 Catalyst supports

1.3.2.1 Inorganic Oxides

Leaving aside the special case of Nafion (PFSA) which will be discussed in more detail later, catalyst supports comprise of three main groups: inorganic materials, ion-exchange polymers and those with polymerisation through the ligands. Murrell provides a good review of catalysts supported on silica[4]. Silica has surface hydroxyl groups which can be reacted with a bifunctional molecule having a ligand function (e.g. phosphine) and an anchoring function (e.g. silyl halide), see scheme 1.3.



Scheme 1.3: Reaction scheme for the formation of a silica supported rhodium catalyst

Catalysts manufactured in this way were found to be resistant to leaching, surviving 16hr Soxhlet extraction with benzene at 80°C, 2hr at 150°C in acetic acid and standard methanol carbonylation or propylene hydroformylation conditions at 175°C. Activity of the catalyst was comparable to homogeneous analogues for hydrogenation of cyclohexene and for hydroformylation of propene. However, in general, anchored catalysts may be active for one type of reaction but not another, while the

corresponding homogeneous catalyst is active for both types since the support influences the nature of the catalyst.

Inorganic anchored catalysts can suffer the same problems as those encountered by heterogeneous catalysts, e.g. poisoning by trace metals such as mercury. In addition the ligands themselves may react whilst on the support leading to increased leaching, e.g. oxidation of a phosphine ligand to a phosphine oxide, leading to a more labile phosphine oxide-metal complex. Polymer anchored catalysts have the same problems except that poisoning by metals is far less likely due to the lipophilic nature of the polymer and the active sites are distributed over three-dimensions *vs.* the two-dimensional inorganic surface. Of course, it is possible to render the inorganic surface more polymer-like by lengthening the anchoring chains.

An alternative to silica as an inorganic support is montmorillonite, a form of silicate clay. Lee and Alper[5] examined the hydroesterification of various alkenes using palladium acetate with excess triphenylphosphine introduced into montmorillonite. Transition metal complexes immobilised on montmorillonite show enhanced reactivity and better selectivity in hydrogenation, hydroformylation and carbonylation reactions. The enhanced selectivities are due to the lamellar, swelled structure, large surface area, availability of both Brønsted and Lewis acid sites and favourable redox properties. The authors concluded that the supported catalyst was an effective system for the hydroesterification reaction with similar regiochemistry to homogeneous analogues, but the work did not explicitly compare relative reaction rates.

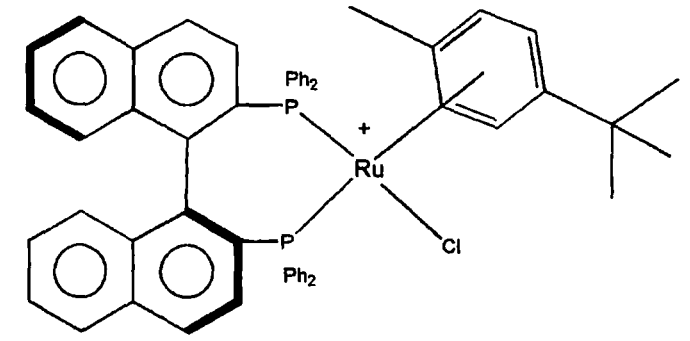
An interesting application of inorganic supported catalysis was reported recently[6]. A ruthenium dichloride complex containing three $PPh_2(CH_2)_2Si(OEt)_3$ ligands was incorporated into a silica gel structure by acid hydrolysis of the silyl groups. The resulting catalyst was effective in converting supercritical CO_2 with hydrogen and methylamine into DMF, achieving turnovers of >1800/hr. with 100% selectivity.

1.3.2.2 Ligand polymerisation

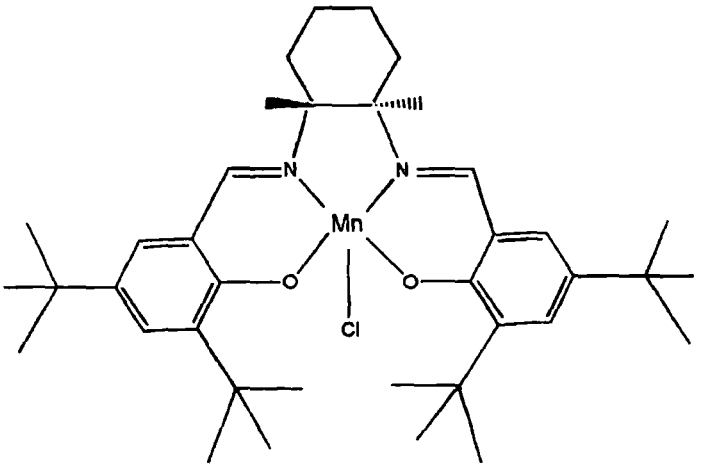
One of the first reports of polymerisation of ligands concerned the anchoring of transition metal catalysts used subsequently for the hydrogenation of alkenes[7]. Polystyrene beads, crosslinked through divinylbenzene were chloromethylated on 10% of the aromatic rings (this polymeric intermediate is sold commercially and known as Merrifield polymer). The polymer was then treated with a THF solution of lithiodiphenylphosphine to replace 80% of the chlorines with diphenylphosphine groups. These beads were equilibrated with chloro-[tris(triphenylphosphine)rhodium(I)]. The beads proved to be effective catalysts for the hydrogenation of various alkenes, comparable in rate to $RhCl(PPh_3)_3$ alone for smaller alkenes, but slightly slower when applied to bulkier alkenes. This effect was attributed to the restrictions of pore size for the bulkier substrates. Multiple use of the catalyst was possible without loss of performance and the beads were easily recovered.

Cai-Yuan Pan[8] reports the synthesis of polymer phosphine ligands from diphenylvinylphosphine, styrene and divinylbenzene. The resulting polymeric ligands were reacted with $PdCl_2$-$SnCl_2$ and used for the hydroesterification of α-olefins. Generally yields were higher for the anchored system than for the comparable homogeneous system $PdCl_2(PPh_3)_2$-$SnCl_2$.

An example of asymmetric catalysis is given by Vankelecom *et al.*[9],who describe the hydrogenation of methyl acetate using a Ru-BINAP complex, (**1**) and the epoxidation of olefins using a Jacobsen catalyst (**2**), immobilised in both cases on polymethylsiloxane elastomers, (scheme 1.4). Results compared favourably for yield and enantiomeric excess with the same complexes used homogeneously.



(1)



(2)

Scheme 1.4 Asymmetric catalysts

1.4 Nafion as an acid catalyst

Nafion is a perfluoropolymer sulphonic acid (PFSA). Its physical properties are reported in detail in Chapter 2. The electron withdrawing properties of the fluorinated backbone make PFSA a super-acid with a Hammett acidity of 12 (equivalent to 100% sulphuric acid); therefore it can also act as an acid catalyst. Olah[11] demonstrates the use of PFSA for the chlorination of methane in comparison with various alumina/ transition metal fluorides at 185°C.

Olah *et al.*[10] review the uses of PFSA as an acid catalyst. PFSA catalyses, in the gas phase, reactions between olefins and aromatic rings, e.g. propene and naphthalene react over Nafion-H to give 90% 2-isopropylnaphthalene[10]. At temperatures of 150°C, methanol condenses to form dimethyl ether and water.

Olefins have been polymerised by Nafion-H. At 145°C, 2-methylpropene formed dimers, trimers and tetramers, and the addition of 1% by weight of Nafion-H to 1-decene at 150°C gave, after 5 hours, a 65% conversion to oligomeric products.

Of particular interest to this study is the comment by Olah[10] that in using methanol (as a methylating agent), the reactivity of the catalyst was found to decrease with time probably due to the increased esterification of the acid sites of the solid catalyst.

The review indicates that, generally, the temperatures used in these reactions are above 140°C though oligomerisation of olefins was reported as low as 100°C, albeit at a slower rate. Using the acid form of Nafion below 140°C, or using salt forms of Nafion at higher temperatures, will not lead to acid catalysis. When studying Nafion as a support for transition metal catalysts it is important to remember that the Nafion support may acid catalyse unwanted side reactions between the substrate and solvent

Nafion is also available as a thin film supplied by Du Pont, which can act as a diffusion membrane, and use has been made of this physical property in conjunction with its chemical nature. Bagnell and co-workers[12] describe the use of Nafion in pellets enclosed in a Nafion membrane as an acid catalyst for the gas phase esterification of acetic acid with methanol and with n-butanol. The reaction takes place in a gas stream with water diffusing through the membrane, the overall loss of water from the equilibrium driving it in favour of the products. Improvements over equilibrium conditions were greater for butanol since this diffuses more slowly than methanol.

Nafion is also available in a propan-2-ol solution enabling it to be deposited on a solid support. Frusteri et al.[13] describe the partial oxidation of light alkanes in a continuous flow reactor using hydrogen peroxide. The catalysts were made by depositing carbon and PTFE pastes on carbon paper and impregnating this with Nafion solution. The authors postulate the active catalytic species as $H_3O_2^+$ formed by the protonation of H_2O_2 by Nafion.

Industrial interest has also been shown in the conversion of methanol and isobutanol, both derived initially from synthesis gas, into methyl isobutyl ether.[14]

1,2-diols can be transformed in a pinacol type rearrangement to form aldehydes[15]. In the case of 1,2-propanediol similar conversions are achieved with either Nafion-H or NaHX zeolite as acid catalyst. If the substrate is 1,2-ethanediol however, the major product with Nafion is 1,4-dioxane as opposed to acetaldehyde obtained from the zeolite catalysed reaction. 2-butanone is the major product in both cases starting from 2,3-butanediol.

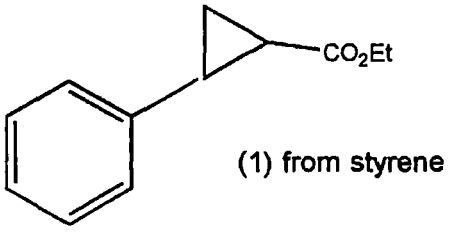
1.5 Transition metals supported in Nafion as catalysts.

Ion exchange resins including PFSA can be used to incorporate transition metal ions by exchange from their salt solutions. Kanemoto et al.[16] describe a procedure for the preparation of Cr(III)-Nafion and Ce(IV)-Nafion from Nafion-K and their subsequent use for oxidation of alcohols. The authors obtained fair to good yields of carbonyl compounds, secondary alcohols being transformed into the corresponding ketones, but primary alcohols gave a mixture of products. The catalysts could be used again with only minor loss of performance. If the catalysts were prepared from Nafion-H instead of Nafion-K then products were contaminated with acetals due to the further acid catalysis of the ketones. Metals such as Cu(II), Ni(II), and Mn(II) proved to be less effective under the same reaction conditions.

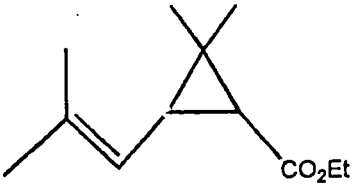
Mattera *et al.*[17] prepared Rh-PFSA and Ru-PFSA from centimolar aqueous solutions of the chlorides and Pt-PFSA from a centimolar aqueous solution of $Pt(NH_3)_4Cl_2$ and employed them for the catalytic oxidation of CO to CO_2. The metals are constrained within the polymer cluster network during the reduction process, leading to a narrow distribution of particle sizes. Transition electron micrographs of the catalyst allowed particle size distributions to be made. The Gaussian distributions peaked on a particle size of 2.5nm diameter, roughly in accord with Gierke's estimates of the cluster diameters (discussed in Chapter 2). The Nafion in this case acts to limit the size of particle growth effectively forming many microscopic heterogeneous catalysts. The authors report comparable turnover frequencies to silica supported rhodium. Temperature increase up to 473K led to an increase in turnover but further

increase in temperature led to a fall off. At temperatures above 400K the catalyst became deactivated at a rate proportional to the temperature increase. Turnover frequencies for the three metals were in the sequence Ru>Rh>Pt which is the same as found for silica supported catalysts.

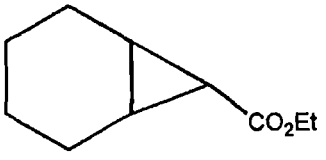
Nugent and Waller[18] looked for a cost effective way of catalysing the decomposition of α-diazocarbonyl compounds, used in the synthesis of cyclopropane-carboxylate esters, themselves useful organic intermediates.
Rhodium acetate and copper(II)trifluoromethanesulphonate are the standard catalysts used to date. These same compounds were immobilised by ion-exchange in the potassium form of PFSA. They were used to prepare the compounds shown in scheme 1.5 below. Yields of (1) were higher using supported copper(II) than the homogeneous reaction but in other cases the yields were reduced. The copper catalyst was used successfully more than ten times without leaching. In contrast the rhodium catalyst suffered from leaching after repeated use.



(1) from styrene



(2) from
1,1-dichloro-4-methylpentadiene



(3) from cyclohexene

Scheme 1.5: Cyclopropane-carboxylate ester products from the reaction with ethyl diazoacetate

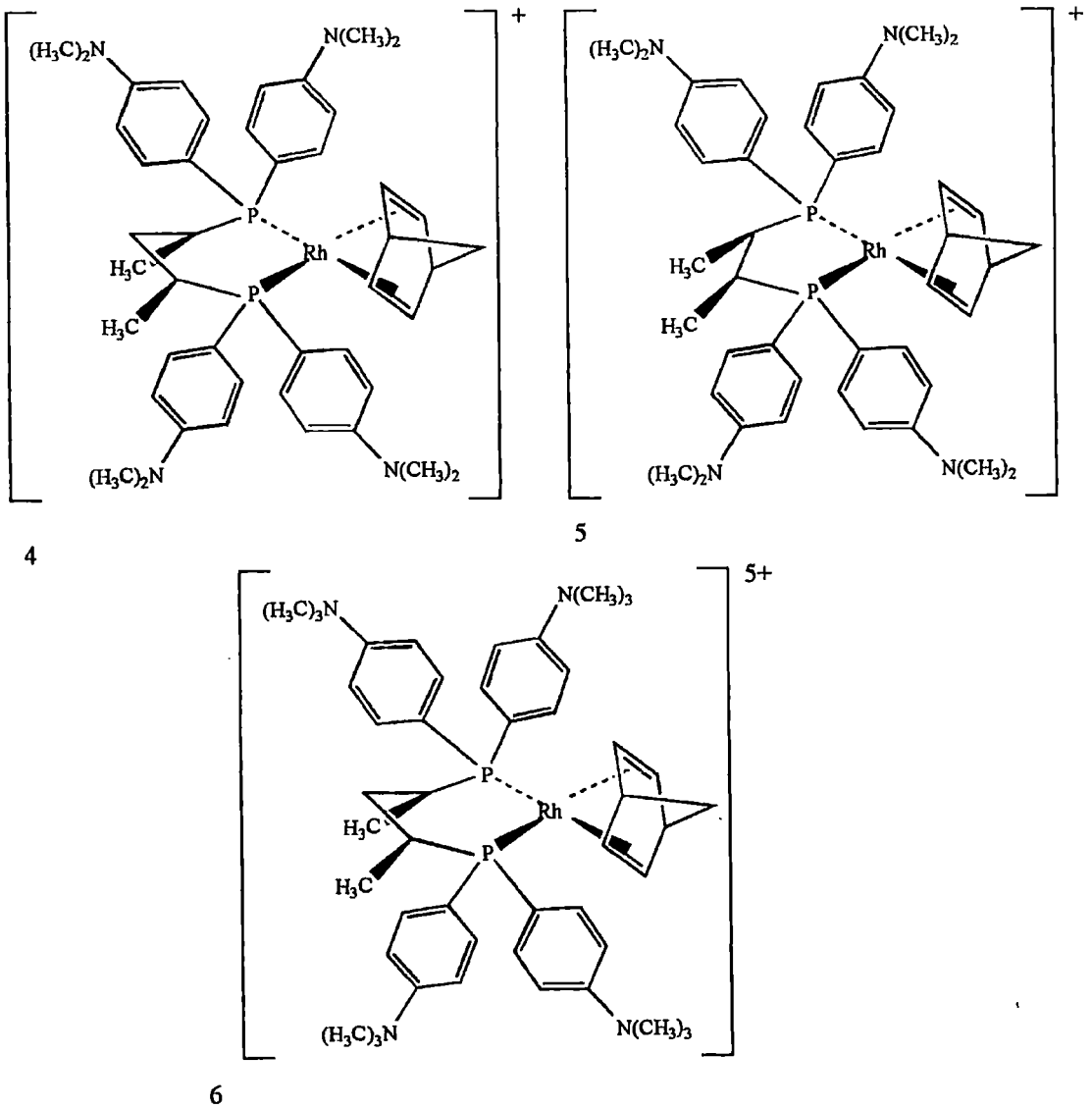
Significantly lower yields were obtained for the electron-deficient diene to form (2) than the other substrates.

Kanno et al.[19] followed the example of Mattera in first introducing rhodium(III) into PFSA as the nitrate by ion-exchange, and then reducing the ion to metal particles *in situ* using hydrogen gas at 135°C. This they used for ethene hydroformylation. They estimate the activation energy for propanal formation to be 63±3 kJ mol^{-1} and for ethane 53±4 kJ mol^{-1}. The kinetic data were similar to those obtained for rhodium on zeolite.

1.6 Transition metal complexes supported on PFSA as catalysts.

The use of chiral, sulphonated, water soluble phosphines as ligands for the construction of rhodium based catalysts for asymmetric hydrogenation was described earlier in section 1.3.1 on biphasic systems. Toth, Hanson and Davies[20] use Nafion as a support to immobilise other chiral phosphine rhodium complexes. Scheme 1.6 depicts the complexes introduced, all with tetrafluoroborate counterions.
When methanol solutions of **4,5** and **6** were stirred in the presence of a stoichiometric amount of Nafion the quantitative removal from solution of the rhodium complexes was measured using atomic absorption spectrophotometry. Even in acid solution or in concentrated HBF_4, the complexes were absorbed by the Nafion. However the addition of a Lewis base stronger than dimethylaniline resulted in the quantitative removal of the exchanged complexes from the resins.

Conversion > 95% was achieved for the asymmetric hydrogenation of unsaturated amino acid derivatives in methanol. Enantioselectivities achieved using supported catalyst were sometimes inferior and sometimes superior to the homogeneous reaction depending on the substrate. However, in all cases, the reaction time of the supported catalyst was two orders of magnitude slower than the homogeneous case. The catalysts were proven for up to six cycles without significant deterioration.



Scheme 1.6: chiral water-soluble catalysts exchanged into Nafion

4 is known as [(*S,S*)-2,4-bis[-bis(-*p*-*N,N*-dimethylammoniumphenyl)phosphino]-pentanenorbornadienerhodium(I) or $[BDPP(NMe_2)_4Rh(NBD)]^+$ for short.

5 is [(*S,S*)-2,3-bis[-bis(-*p*-*N,N*-dimethylammoniumphenyl)phosphino]-butanenorbornadienerhodium(I) or $[Rh(NBD)(chiraphos\text{-}(pNMe_2)_4)]^+$ and

6 is [(*S,S*)-2,4-bis[-bis(-*p*-*N,N,N*-trimethylammoniumphenyl)phosphino]-pentanenorbornadienerhodium(I)

. The authors noted no activity when THF was used as solvent as this did not swell Nafion. The swelling of Nafion is maximised in aqueous/alcoholic solvents and the authors note that the degree of swelling may influence the observed selectivities.

The same authors subsequently published findings using the soluble form of Nafion[21]. When a 5% Nafion solution was added dropwise to a solution of $[BDPP(NMe_2)_4Rh(NBD)]^+$ (**4** above) or $[Rh(NBD)(chiraphos\text{-}(pNMe_2)_4)]BF_4$ (**5** above) (both 0.125 mmol in methanol), a gel-like mixture was formed. In this form rates of hydrogenation were found to be significantly improved over the previous study using Nafion beads and rates were comparable to those for the homogenous reaction. The gel suffered irreversible loss of activity if it was vacuum dried.

Olefin double bond shift isomerisation can be carried out in Nafion using a nickel phosphite catalyst $[Ni\{P(OEt)_3\}_4]$, the active species, $[HNi\{P(OEt)_3\}_3]^+$ forming slowly by protonation and loss of ligand in the Nafion-H support[22]. Rates of isomerisation of 1-octene using the supported catalyst were of the order of one third of that shown by the homogeneous systems, but were improved by partially neutralising the Nafion by exchanging some of the acid sites by Na^+. C_8 isomers produced were predominately *trans*-oct-2-ene and *cis*-oct-2-ene in the ratio of 4:1 and 3.2:1 in the homogeneous and supported cases respectively. The ratio found in equilibrium distribution is 5.5:1, thus the support marginally increases the selectivity for the *cis* form. The decrease in isomerisation rates is attributed by the authors to diffusion limitation of the olefins into and out of the Nafion.

Seen *et al.*[23] later describe the dimerisation of ethene using a Nafion supported nickel(II) complex. Nickel was introduced as $[Ni(o\text{-tolyl})Br(PPh_3)_2]$ in a pyridine/methanol solution containing Nafion. The Nafion assisted in the formation of $[Ni(o\text{-tolyl})(py)_2(PPh_3)]^+$ and subsequently supported the complex. The use of Nafion to effect the transformation obviated the need for thallium salts. In common with other studies it was found that the supported catalysts had lower turnover numbers per hour but continued to be active for much longer than the comparable homogeneous system. Eventually the yields in mol/mol of catalyst were higher using the supported system.

Next the same team turned its attention to palladium catalysts[24] for ethene dimerisation. It was known from Drent that $[Pd(1,10\text{-phen})_2][p\text{-tolyl-}SO_3]_2$ was an efficient catalyst for olefin oligomerisation and carbonylation. These Pd(II) species are suited to immobilisation in PFSA as they are cationic and it is believed that their catalytic activity is enhanced by non-coordinating anions. The RSO_3^- ion in PFSA is very weakly co-ordinating with co-ordination ability between PF_6^- or BF_4^- and ClO_4^-. The authors reported the immobilisation of three Pd(II) species in Nafion, namely $[Pd(1,10\text{-phen})_2]^{2+}$, $[Pd(1,10\text{-phen})(py)_2]^{2+}$ and $[Pd(2,2'\text{-bipy})_2]^{2+}$. It was found that the catalyst activity and stability were dependent on the basicity of the N donor ligand, and on the nature of the counter ion (H^+ or Na^+) in the Nafion. The conditions for maximum activity were optimised using the $[Pd(1,10\text{-phen})_2]^{2+}$ system. One significant finding was the importance of catalyst loading. Initially loadings of 2 wt.% of Pd were used, which corresponds to about one Pd atom per five SO_3 ion-exchange sites. At this loading, activities of around 1500 turnovers/hr were obtained at 80°C. Decreasing the catalyst loading steadily increased the activity reaching a maximum of 16,000 turnovers/hr with a loading of 0.065% Pd. The exercise was repeated in water with even more dramatic improvement. At a loading of 0.025% an activity of 80,000 turnovers/hr was obtained. Several explanations were put forward for these results. Firstly higher loadings would limit the diffusion of ethene to the centre of the beads; secondly it is known that exchange of larger cations (than H^+) limits the swelling of PFSA, necessary for efficient diffusion of reactants and products to and from the catalytic sites. Finally the swelling of PFSA may reduce steric hindrance in one or more of the catalytic steps of the reaction. Also the effect of ethene pressure was studied and it was observed that a linear increase in activity resulted from an increase in pressure, as is also the case in homogeneous catalysis.

Tests were undertaken at a catalyst loading of 0.065 wt.%Pd, in water and methanol at various temperatures between 40° and 100°C. Activation energies of 73 and 121 kJ mol^{-1} were reported for the homogeneous species and 122 and 88 kJ mol^{-1} for the supported species in methanol and water respectively. These figures are greater than would be expected for a diffusion limited process and hence support the notion

that diffusion is not rate limiting at these low loadings. Another explanation for the improvement in turnover found at low loadings would result from the decrease in catalyst deactivation at low catalyst loadings. It is known that a common cause of catalyst deactivation is the interaction between intermediates to form dimers and clusters. Yagi et al[25] found a higher activity for the oxidation of water by $(NH_4)_2Ce(NO_3)_6$ using a $[Ru(NH_3)_5Cl]^{2+}$ catalyst when the catalyst was supported in a Nafion membrane. By measuring the evolution of O_2 they could compare rates of oxidation. They measured rates of evolution of N_2 and inferred from these the rates of catalyst decomposition. The initial N_2 evolution rate, was second order with respect to the catalyst concentration, indicating bimolecular decomposition of the catalyst. The rate of oxygen evolution decreased at higher concentrations due to this decomposition. Although no nitrogen evolution was detected in the absence of catalyst, this is not proof that the nitrogen originates only from catalyst decomposition.

Premkumar and Ramaraj[26] report the immobilisation of metal phthallocyanines onto Nafion to make a photocatalyst for CO_2 reduction. Cobalt(II)phthallocyanine and zinc(II)phthallocyanine were dissolved in dmf and a Nafion membrane (0.13 mm thick, 1 cm^2 area) was immersed in this solution. After absorption of the complexes the membrane was washed with water and immersed in the photolysis cell containing an aqueous solution of triethanolamine and $HClO_4$ saturated with CO_2. The membrane was exposed to visible light from a tungsten filament source and the sole product was found to be formic acid. In the absence of any of the components (light, phthallocyanine, triethanolamine, H^+ or CO_2) no product was formed. The results were reproducible and the membrane re-usable and stable for weeks. Turnovers of the order of 10^4 /hour were reported. The reaction scheme is as follows: (MPC = metallo-phthallocyanine, TEA is triethanolamine, h represents a hole, CB and VB are conduction band and valence band respectively)

$$MPC + h\nu \rightarrow MPC^* (e^-_{CB} + h^+_{VB})$$

$$2\,TEA + 2\,h^+_{VB} \rightarrow 2\,(TEA)_{OX} + 2\,H^+$$

$$CO_2 + 2\,e^-_{CB} + 2\,H^+ \rightarrow HCOOH$$

The exact nature of the triethanolamine in its oxidised state is not discussed, however it is not regenerated in the cycle and therefore formic acid is produced at the cost of loss of triethanolamine.

1.7 Electrochemical and other uses of Nafion membranes

Although not of direct relevance to this study, a review of the uses of Nafion cannot exclude its use in electrochemical cells which forms the bulk of the research pertaining to PFSA. In a study of water electrolysis using a Nafion membrane as the electrolyte and plating the faces with metal as the electrodes it was found[27] that iridium was the most effective electrode material overtaking the initially superior ruthenium due to the latter's corrosion by nascent oxygen. Cells were capable of operating for hundreds of hours at 50°C.

The reverse reaction can also be employed in a fuel cell[28]. Platinum was deposited on the surface of a Nafion membrane by reduction of $Pt(NH_3)_4Cl_2$ by $NaBH_4$. The resulting membrane was used in a fuel cell to catalyse the production of water and electricity under near ambient conditions from hydrogen and air.

Electrodes have also been prepared by syringing 0.5% Nafion solution in alcohol onto pyrolytic graphite[29] and allowing the solvent to evaporate. These electrodes were subsequently used in the reduction of CO_2. To this end the authors measured redox potentials of a series of ionic ruthenium complexes in Nafion. The potentials provide information about ΔS for the electrochemical reduction of the complex, which in turn gives insight into the environment within the membrane. The authors conclude that the redox potentials differed markedly from that in solution in line with comments by Falk (Chapter 2) about the nature of hydrogen bonding within the cavities. Taguchi et al[30] also produced electrodes using Nafion solution. In this case the solution contained metallo-porphyrins for H_2 production. Rates of production were greatly increased by the presence of Nafion but the authors are unclear of the role Nafion plays in the process.

Separation of olefin mixtures, dienes from mono-enes, or styrene from ethylbenzene, can be achieved using a Nafion membrane and improved dramatically by exchanging silver ions into that membrane.[31] Finally Nafion has also found a use as a pervaporation membrane in which separation of vapour mixtures is accomplished on the basis of their differing diffusion rates through a Nafion membrane. Sometimes this is accompanied by acid catalysis of the vapours by the membrane,[12] for example the rate of esterification of n-butanol by acetic acid is enhanced by both the selective removal of the water by-product and the acid catalysis due to the membrane.

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Chapter 2

Nafion: Its properties, handling and treatment.

2.1 Introduction

This chapter contains information concerning the physical properties of Nafion itself and describes experiments designed to demonstrate the potential of Nafion as a catalyst support in general terms. In addition, procedures are described in which the sulphonic acid functional group is modified with the aim of generating a new form of polymeric catalyst support.

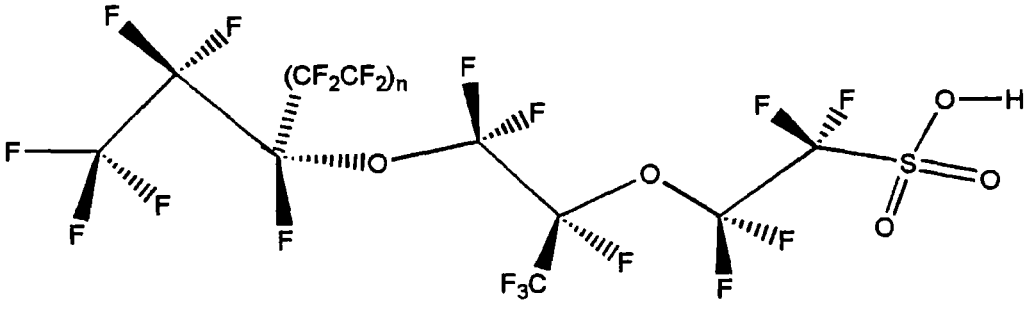
Nafion can be obtained commercially in a number of physical forms. It is supplied by the Aldrich Chemical company as pellets, chopped from extruded fibre, between 10 and 35 mesh, or as a transparent film of thickness 0.007 inch, or as a reinforced film 0.017 inch thick. They will also supply Nafion as a 5 wt.% solution in a mixture of low boiling alcohols. The Du Pont company, who own the copyright to the name Nafion will supply beads of *ca.* 1mm diameter and a variety of reinforced films. Nafion can be obtained in the strong (sulphonic) acid form, or weak (carboxylic) acid form, or with sodium or potassium counter ions. Each of these is obtainable in various equivalent weights, typically 900,1100 or 1200 Daltons. The Asahi Glass company of Japan market a form of Nafion with amide groups.

2.2 The morphology of Nafion

Nafion is an example of a perfluorosulphonic acid resin (PFSA), consisting of a hydrophobic, fluorinated backbone interspersed with ether linkages and with pendant sulphonic acid groups. The precursor polymer has $-SO_3F$ functional groups which are easily hydrolysed to the sulphonic acid derivatives.

The seminal work for studying the structure of PFSA at microscopic level comes from X-ray studies performed by Gierke, Munn and Wilson[1]. Based on this study, Hsu and Gierke propose a cluster network model[2], in which phase-separated domains take the form of spherical inverted micelles connected by short narrow channels. The two phases are the hydrophobic polymer backbone phase and the hydrophilic sulphonic ion phase.

Scheme 2.1: The structure of PFSA



The model considers the change in free energy in a hypothetical cluster, containing a fixed number of ion-exchange sites, as it hydrates. The diameter of the cluster is therefore that which will minimise this free energy. The cluster diameters so obtained increase linearly with the equivalent weight of the polymer, decrease with increasing cation size and increase with increasing water uptake. In all cases the cluster diameters fall within 2-5 nm. The figures so obtained are borne out by the measurements from small angle X-ray studies. Using similar free energy calculations, a hypothetical channel was allowed to form between two neighbouring inverted micelles and was found to have a diameter of 1.4±0.2 nm. This figure is consistent with data obtained from water transport experiments. The change in free energy that results in the formation of such a channel is only -11 J cm^{-3}; therefore, the theory suggests the channels are forming and closing continually at ambient temperatures.

Infrared studies of hydrated PFSA membranes have been carried out by Falk[3]. Hydrated polymer in the sodium form contains up to 21% of water by weight or 18 H_2O per $SO_3^-Na^+$ pair. Since it requires only six water molecules to complete the co-ordination sphere, the ion pairs can be expected to be fully surrounded by water with

the individual ions separated most of the time. This has been confirmed by infra-red and ^{23}Na NMR data.

Infra-red spectra show two different O-H stretches belonging to OH--O and OH--F_2C. These are in roughly 4:1 proportion, i.e. a quarter of the hydroxyl groups do not hydrogen bond. This coupled with the complete absence of water molecules in CF_2--HOH--F_2C environments leads either to the conclusion, based on considerations of surface area to volume ratios, that the cluster diameter is much smaller than that estimated by Gierke, or more likely that the clusters are highly non-spherical in shape with frequent local intrusions of the fluorocarbon phase. The strength of the hydrogen bonds in water absorbed in PFSA was estimated to be only 62% of that in bulk liquid water and so water in PFSA could be expected to behave significantly differently than bulk water.

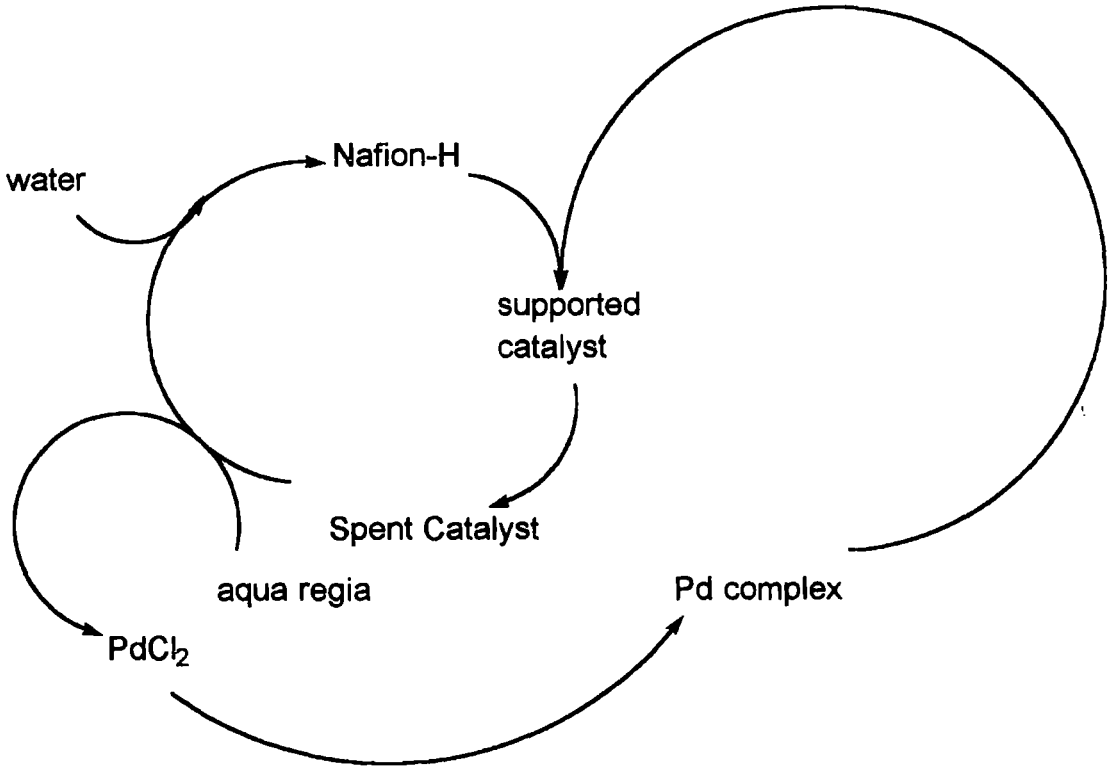
PFSA resins with an equivalent weight of 1200 Daltons contain tetrafluoroethene and the perfluorovinyl ether units in a ratio of 7:1. Similar fragments of the backbone tend to align with each other to increase order. These regions act as transient crosslinks in the polymer, thereby imparting to it some of the rigidity of conventional crosslinked polymers[4]. At higher temperatures, the clusters break up and the salt forms of PFSA behave as thermoplastic ionic polymers (ionomers). Even though PFSA is not cross-linked covalently, at room temperature it is effectively insoluble, but is swollen by immersion in hydrogen bonding solvents.

2.3 Conversion of acid form to alkali metal form

The 1250 equivalent weight form of Nafion-H^+ has 0.8meq/g of protons (i.e.0.8 mmol per gram). These are easily replaced by alkali metal cations if present in excess due to their greater binding affinity. Nafion-H^+ (1.0g) was stirred in 100 mls of 0.1M NaOH solution for 24 hrs, rinsed thoroughly with deionised water and dried *in vacuo* for an hour at 100°C. This procedure is generally applicable to alkali metal cations.

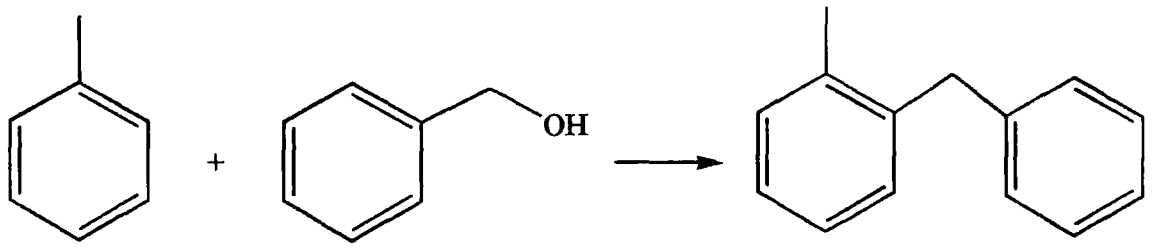
2.4 The regeneration of used Nafion

It is essential for the viability of using Nafion commercially as a catalyst support that it can be regenerated. Nafion was regenerated according to the following procedure. The spent beads were immersed for several days in aqua regia to convert all forms of metal complex, as well as any metal, into the chloride and to re-protonate the ion-exchange sites. The acid solution was drained off, the beads were rinsed in water and then placed in a Soxhlet extraction thimble and extracted for several days with refluxing deionised water. This is to remove all traces of soluble chloride ion and hydrolyse any esterified sulphonate groups. Finally much of the remaining colour can be removed by soaking the resultant beads in methanol.



Scheme 2.2 Regeneration cycle illustrated for palladium complexes

Nafion regenerated in this way may retain some discolouration. In order to demonstrate that regeneration had taken place, a sample of the regenerated Nafion was used as a Friedel-Crafts catalyst for the reaction between benzyl alcohol and toluene.



Scheme 2.3 Friedel-Crafts alkylation using Nafion as an acid catalyst

Benzyl alcohol (7.5mmol, 0.81g) and toluene (0.225 mol, 20.73 g) were mixed in a 100 ml round bottomed flask and degassed by three freeze-pump-thaw cycles. Regenerated Nafion (1.85g) dried *in vacuo* was added against flowing nitrogen and the mixture refluxed. Samples were taken at regular intervals for analysis using gas chromatography. The benzyl alcohol was 95% consumed within 30 minutes to give *meta, ortho* and *para* isomers in the ratio of 6.4: 41.7: 51.9 respectively. This is in line with the results obtained for Nafion beads used as received[5], namely, benzyl alcohol 100% consumed in 30 minutes using fresh Nafion (2.15g) to give *meta, ortho* and *para* isomers in the ratio of 6.3:43.3:50.4 respectively, indicating the suitability of the regeneration process.

In addition, recycled Nafion has been used to support $[Pd(OAc)_2(PPh_3)_2]$ for the hydroesterification of ethene (Chapter 3). Turnovers and yields were very similar to those obtained using pristine Nafion.

2.5 The swelling of Nafion

Ionomers consist of polymer chains containing ionic functional groups. When such a material comes into contact with water, the outermost functional groups are solvated and the randomly arranged polymer chains unfold to accommodate the larger solvated ions. A very concentrated internal solution of fixed ions and counter-ions therefore exists and the mobile counter-ions tend to diffuse out of the beads into the external solution. The fixed ions cannot diffuse and as a result external water molecules are forced into the resin to reduce the internal ionic concentration. The swelling is therefore the result of the equilibrium pressure due to the differences in concentration

between the internal and external ionic solutions. The swelling pressure may be as high as 300 atmospheres for resins of high exchange capacity.[6]

The degree and rate of swelling of Nafion were measured in three solvents, dichloromethane, methanol and water as follows. A single bead, previously dried by warming under vacuum, was placed under the probe of a DuPont Instruments 2940 Thermomechanical Analyser. The probe and base are made from quartz and are very smooth and mechanically highly stable. The probe is attached to a linear voltage differential transformer (LVDT) capable of measuring linear travel to fractions of a micron. The force on the probe is held constant. The bead was immersed in the solvent to be tested and the data collection by computer initiated. In the case of dichloromethane there was very slight shrinkage, less than 1%. In the case of water, swelling was observed to take place smoothly and exponentially, reaching a maximum of about 8% after 12 minutes. In the case of methanol, swelling took place smoothly and exponentially, reaching a maximum of 26% after 35 minutes (figure 2.1).
Visual observation of the behaviour of Nafion in most common laboratory solvents led to the view that it does not radically change in dimensions. Nafion is swollen by perfluorinated 2-propanol by about 30% estimated from crude measurements.
Nafion beads exposed to high temperatures in methanol can swell beyond these normal amounts and retain then their size unless exposed to a vacuum.

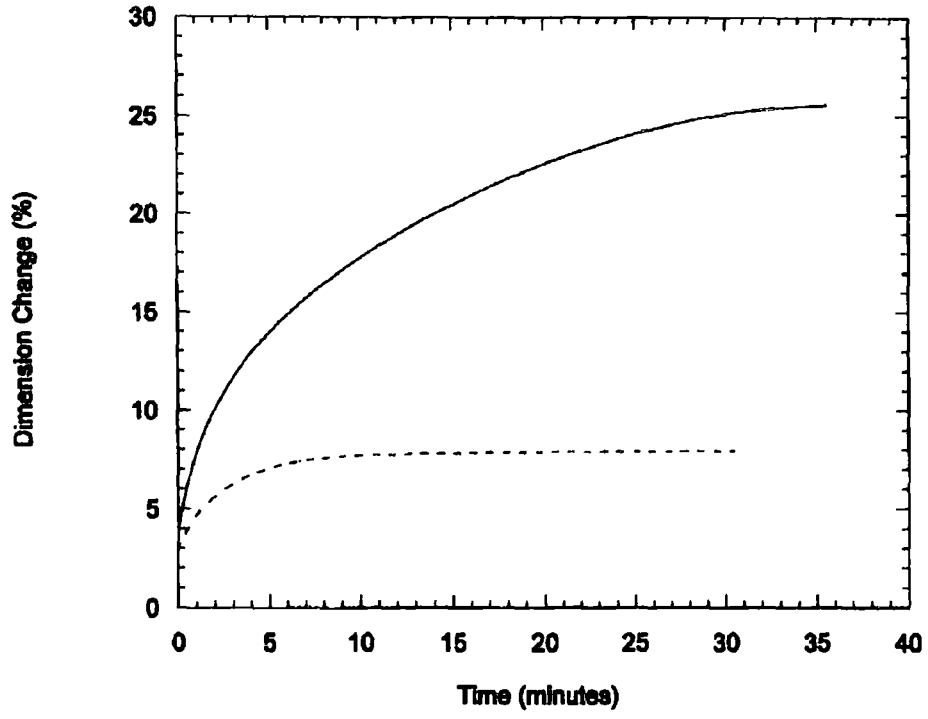


Figure 2.1: Absorption of water and methanol by Nafion-H

solid line: methanol

broken line: water

2.6 Catalyst absorption and leaching.

Catalyst complexes are absorbed into Nafion using three different methods;

i) ion exchange of ionic complexes;

ii) ligand exchange by the sulphonate groups;

iii) protonation of the complex by Nafion and its subsequent retention.

Each of these methods is dicussed below.

2.6.1 Ion exchange

Nafion-H behaves as a strong acid cation exchange resin such as those employed in ion-exchange chromatography.

Peters[7] *et al* rank the relative rates of absorption of cations as follows.

$Pu^{4+}>>$

$La^{3+}>Ce^{3+}>Pr^{3+}>Eu^{3+}>Y^{3+}>Sc^{3+}>Al^{3+}>>$

$Ba^{2+}>Pb^{2+}>Sr^{2+}>Ca^{2+}>Ni^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Zn^{2+}>Mg^{2+}>UO_2^{2+}>>$

$Tl^{+}>Ag^{+}>Cs^{+}>Rb^{+}>K^{+}>NH_4^{+}>Na^{+}>H^{+}>Li^{+}$

The following explanation for the selectivity of ion exchange materials is attributable to Haddad and Jackson[8].

From the ranking above it can be seen that an increase in charge increases the affinity of an ion for the resin through increased coulombic interactions. This trend is known as electroselectivity and is more pronounced for a more dilute solution in contact with the resin. Electroselectivity occurs due to the Donnan potential, which is the potential difference arising out of the imbalance in the ionic concentrations in the resin bead and the external solution. An exchange involving the replacement of two bound monovalent ions by one divalent ion causes this imbalance to be diminished and is thus a favourable process. The size of the solvated ion also exerts a significant effect, with ions of smaller solvated size showing greater binding affinity than larger ions. Thus the selectivity sequence $Cs^{+}>Rb^{+}>K^{+}>Na^{+}>H^{+}>Li^{+}$ is exactly the reverse of the sequence of ionic radii for the hydrated ions; the most strongly hydrated ion, Li^{+}, being held the most weakly. Polarisability also plays a role. Sulphonic acid anions show a greater affinity for the more polarisable Ag^{+} and Tl^{+} than for the alkali metal ions. Large, polarisable ions with a weak diffuse charge, do not easily form a well orientated layer of solvent molecules at their surface and so (in hydrogen-bonding solvents) tend to disrupt the surrounding solvent structure. This leads to an increase in free energy, which is the driving force for these ions to bind with the fixed ion thereby diminishing this free energy.

2.6.2 Ligand substitution

The sulphonate anion in Nafion is a very weakly coordinating ligand to metal ions, its coordinating ability being estimated as being between that of BF_4^- or PF_6^- and ClO_4^-. However some neutral complexes, notably acetates and acetylacetonates, are readily absorbed into Nafion by anionic ligand exchange. It is thought that the driving force for the coordination is provided by the production of acetic acid and acacH respectively and that these must be soluble in the solvent used and be free to diffuse out of the resin. The absorption of $[Pd(OAc)_2(PPh_3)_2]$ into Nafion in methanol resulted in the production of methyl acetate analysed by gas chromatography and identified by retention time. Similarly $[Fe(acac)_3]$ released acacH on absorption by Nafion-H^+. Further evidence to support this model comes from solid state NMR studies described in para.2.10. Soluble metal salts can be recovered from Nafion by its protonation with strong mineral acid.

2.6.3 Protonation

Absorption into Nafion by protonation depends on the equilibrium:

$$R_3N + \text{Nafion-}SO_3^-H^+ \rightleftharpoons \text{Nafion-}SO_3^-R_3NH^+$$

Scheme 2.4

Since Nafion is a very strong acid, this equilibrium usually lies comfortably to the right. However some nitrogen atoms are not readily protonated, such as those in aminophosphine ligands (Chapter 7) and consequently the absorption does not go to completion and takes considerably longer to reach equilibrium. Ferrocene is readily protonated and absorbed by Nafion to give blue beads containing the ferricinium ion.

2.7 The Measurement of Absorption and Leaching

The degree and rate of catalyst absorption in non-swelling solvents was measured as follows. A weighed amount of metal catalyst complex was transferred to a clean, dry, round-bottomed flask. Exactly 100mls of dry solvent were added under nitrogen and stirring commenced. When dissolution was complete, a 1 ml aliquot was removed to a glass vial as the initial sample. Nafion (3g), dried under vacuum, was added to the flask. Further samples of 1ml each were withdrawn by pipette after timed intervals to separate labelled vials. The solvent is allowed to evaporate to dryness in air in each vial. The contents were dissolved in the minimum quantity of aqua regia and allowed to dry once more. The residue in each vial was dissolved in 10 ml. of HCl taken from a stock solution of 50 ml. conc. HCl in 1L deionised water. The concentration of metal was measured against known standards using atomic absorption spectrophotometry.

This same measuring procedure was also applied to spent solutions from catalytic runs to determine the amount leached during the run.

Seen *et al* used UV-visible spectrophotometry[9] to show that leaching had not occurred. This method can only be semi-quantitative unless the complex of interest has an absorption maximum within the range where the solvent is reasonably transparent and Beer's law is obeyed.

2.7.1 The Absorption of $[Pd(OAc)_2(PPh_3)_2]$ by Nafion

A solution of $[Pd(OAc)_2(PPh_3)_2]$ (0.0556g) in 100mls degassed CH_2Cl_2 (79mg Pd l^{-1}) was added to 3g Nafion-H, previously dried by warming *in vacuo*. An initial 1ml sample was taken and stirring was commenced. Further 1ml samples were removed after the following time intervals: 30,60,120,240 minutes. The solution lost colour steadily and became colourless after 240 minutes. The concentration of each sample was determined by atomic absorption spectrophotometry and the data shown in Table 2.1.

Table 2.1

Absorption time (mins)	0	30	60	120	240
Solution Pd conc. (ppm)	9.4	8.5	7.2	4.9	4.8

These data were plotted, conforming well to the expected exponential behaviour. A best fit curve applied to the data resulted in a "time to half-concentration", t = 61.3 minutes. A Nafion bead, which was now very dark in appearance was sliced open to reveal that the compound had only partially penetrated the bead. On exposure to methanol the beads expanded and the compound migrated completely to the centre.

2.7.2 The Absorption of $[Pd(CH_3CN)_4][BF_4]_2$ in CH_3CN by Nafion

A solution of $[Pd(CH_3CN)_4][BF_4]_2$ (0.033g) in 100mls. degassed CH_3CN (79 mg Pd l^{-1}) was added to 3g Nafion-H, previously dried by warming *in vacuo*. An initial 1ml sample was taken and stirring was commenced. Further 1ml samples were removed after the following time intervals: 30,60,120,240 minutes. The concentration of each sample was determined by atomic absorption spectrophotometry and the data shown in Table 2.2.

Table 2.2

Absorption time (mins)	0	30	60	120	240
Solution Pd conc. (ppm)	6.16	2.07	0.75	0.28	0.1

These data were plotted and as before conformed well to exponential behaviour. A best fit curve applied to the data resulted in a "time to half-concentration," t = 18.2 minutes. A comparison of the two absorption experiments shows that absorption of an ionic complex proceeds faster than absorption by ligand exchange.

In methanol absorption is rapid and essentially complete within ten minutes, whether the complex is ionic or absorbed by ligand substitution. The rate of absorption of complexes by protonation depends on the basicity of the complex. Complexes containing pyridine such as $[RhCl(PPh_2py)_3]$ are also absorbed within ten minutes.

2.8 The dissolution of Nafion in alcohols

Nafion cannot be dissolved at room temperature in any single solvent or binary solvent system. This is due to the presence of regions of crystallinity in the polymer chains. Sufficiently high temperatures must be applied to melt these crystalline regions before dissolution can occur.

Commercially available Nafion films can be dissolved at 250°C, under pressure, in a 50:50 mixture of water and low boiling aliphatic alcohols, such as ethanol or propanol[10]. Solutions of up to 1% polymer obtained in this way are clear and homogeneous and are comparable to commercially available solutions. Discolourations in the commercially supplied films may be removed by suspending the film for 1hr in aqueous alcohol in an ultrasonic bath. Sonication of Nafion solutions leads to a lowering in their viscosity which is recovered on standing[11].

2.9 The casting of Nafion films

The solutions described in section 2.8 above, when allowed to evaporate in a flat bottomed container, produce a film which is very weak, brittle and likely to be discontinuous. Grot *et al.*[12] describe a procedure in which either DMSO, triethyl phosphate or 2-ethoxyethanol are added to the alcohol solution prior to the casting stage. Evaporation is allowed to take place at room temperature before the film is heated to 120°C to give a clear uncracked film. Moore *et al.*[13] used other high boiling polar solvents, such as DMF and ethylene glycol. They removed the water and alcohol at 80°C and then the high boiling solvent was removed by vacuum heating at around 20°C below its boiling point. A modification to this procedure is described by Thoen *et al.*[14] in which the initial membrane was first converted to the sodium form by soaking overnight in molar NaOH to assist high temperature treatment since the H^+ form can lead to darkening of the film. The solvent (DMSO) was removed from the casting dish in a vacuum oven at 170°C and 500 torr. The film was floated off the dish with water.

Following this procedure in the laboratory, 3mls. 5wt% solution (supplied by Aldrich) was allowed to evaporate to dryness in a casting dish. The weak film formed was soaked overnight in molar NaOH and rinsed with deionised water. The film was

redissolved in 15mls DMSO (1% solution) by refluxing for 4hrs. A small amount of film was obtained with sufficient mechanical strength to remove from the casting dish after removal of the DMSO at 170°C in a vacuum oven maintained at 700mbar. This film was soaked in a methanol solution of $[Pd(OAc)_2(PPh_3)_2]$, rinsed with methanol and dried. A transmission infra-red scan of the material showed the carboxylic stretch at $\nu = 1626\ cm^{-1}$ at a comparable value for the authentic compound in a KBr disc.

Combining the techniques described in this section and section 2.8, a 1.0g sample of 'as supplied' film, thickness 0.178mm., was heated with 25mls. deionised water/ 25 mls. ethyl alcohol at 250°C for 2 hrs under an atmosphere of nitrogen. Ninety-seven percent of the Nafion dissolved. A portion (15 mls) of the solution was poured into a 10 cm. dia. petri dish and heated in a drying oven open to the air. A satisfactory film was produced with a weight of 0.06g for 3.14 sq.cm. leading to an estimate of 0.09mm for the average thickness.

2.10 The attempted coating of inert supports with Nafion films

The ability to coat inert supports with Nafion would allow the same volume of Nafion to have a greatly increased surface area. This would increase the rate of diffusion of reactants and products in a catalytic reaction to and from the active sites and therefore improve the efficiency of the catalyst.

The same procedure described in section 2.8 was followed except ethylene glycol was substituted for DMSO. 1g of glass beads each nominally 1mm in diameter was added to a 250ml round bottomed flask containing the polymer solution. The solvent was removed at 150-160°C under a partial vacuum of approx. 0.5 bar.

The beads were not coated with the Nafion as was hoped. A similar experiment using alumina pellets failed in the same way. The Nafion preferentially coalesces into lumps rather than coating a surface. Glass and alumina surfaces are hydrophilic and the bulk of the polymer is hydrophobic so this failure is not unexpected.

2.11 Thermoanalytical studies of Nafion

A study of the dynamic mechanical properties of the Nafion precursor material

($R\text{-}SO_2F$) using a torsional pendulum reveals four transitions in the temperature region -195° to 125°C labelled α,β,γ and δ in order of decreasing temperature[15] . These transitions are identified with

(i) the glass transition of the fluorocarbon matrix

(ii) the relaxation of the ether side chains

(iii) local short range motions of the CF_2 backbone and

(iv) rotation of the $-SO_2F$ groups respectively.

The assignment of the transitions is based on the following evidence. The transition associated with the rotation of the $-SO_2F$ group is absent when samples of Nafion-Na or Nafion-H are studied. The transition temperatures of the α and β regions are shifted upwards by up to 100°C on neutralisation of the acid form by various alkalies. The γ transition is due to a relaxation which is also observed in the precursor material and in PTFE.

Studies by differential scanning calorimetry (DSC)[10] show two endotherms, at *ca.* 150° C and *ca.* 260° C. The former is assigned to the glass transition of the matrix and the latter to the glass transition of the ionic clusters. A change of counterion causes a dramatic shift in the position of the higher transition, increasing across the series; $Cs^+<Na^+<Zn^{2+}<Mn^{2+}<Mg^{2+}$. The ionic radius decreases in the order $Cs^+>Na^+>Mn^{2+}>Zn^{2+}>Mg^{2+}$. Recasting the film can also affect the ionic glass transition, lowering it by 30 degrees.

2.12 The preparation of Nafion for solid-state NMR studies

In order to study complexes supported in Nafion it was necessary to develop a procedure to make samples suitable for solid state NMR studies. Nafion film (2g) was dried *in vacuo*, and cut into small pieces. The pieces were cooled in liquid nitrogen to embrittle them and ground to a fine powder using a mortar and pestle whilst immersed in liquid nitrogen. The powder was subdivided into 6 portions (3 pairs of duplicates), each of which was added to a small Schlenk tube. To one pair of duplicates was added 0.02g $[Pd(OAc)_2(PPh_3)_2]$, to the second, 0.02g $[Pd(OAc)_2(PPh_2py)_2]$ and to the third, 0.016g $[Pd(OAc)_2dppe]$, corresponding to 0.027mmol in each case, this being the maximum theoretical loading. The complexes in each tube were dissolved in methanol

(10 mls) and stirred overnight. The methanol was decanted the following day, and each sample of Nafion was rinsed with fresh methanol and dried *in vacuo*. A similar procedure was followed for preparation of samples of Nafion which had been exposed to the phosphine ligands from each of the above complexes, i.e. PPh_3, PPh_2py and dppe.

2.13 Results of solid-state ^{31}P NMR studies of absorption

Metal complexes with acetate ligands exchange readily into Nafion apparently by direct exchange of anionic ligands. A series of solid state NMR experiments was performed to investigate this premise. Nafion was prepared as described above, stirring with methanol solutions of the compounds reported in Table 2.3. Of the three ligands, only the nitrogen containing PPh_2py is strongly absorbed into Nafion as would be expected (see Table 2.3). Oxidation of phosphorus takes place in many cases due to the preparation regime for spectroscopy.

Table 2.3 Solid state ^{31}P {^1H} NMR results

Compound in Nafion	Chemical Shifts (ppm) (signal strength)	Assignments
PPh_3	21 (weak)	$Ph_3P{=}O$
PPh_2py	-6 (strong)	PPh_2py or Ph_2PpyH^+
dppe	10, 23, 25, 44 (weak)	$\{dppeH\}^+$, protonated dppeO and $dppeO_2$
$Pd(OAc)_2(PPh_3)_2$ + Xs ligand	21 , 45 (strong)	compound and unknown
$Pd(OAc)_2(PPh_2py)_2$ + Xs ligand	-6, 13, 20, 25 (strong)	ligand, compound peaks
$Pd(OAc)_2$dppe + Xs ligand	10, 32, 56 (weak)	protonated ligand , ligand oxide, compound

In a related exercise the three palladium phosphine complexes reported in Table 2.3 were reacted with triflic acid in a series of solution NMR scale experiments. In each case the acetate anion is replaced by the more acidic triflic acid following the equation (see Scheme 2.5)
The triflate anion serves as a model for the Nafion sulphonate anion.

$$[Pd(OAc)_2P_2] + 2HOTf \Rightarrow [Pd(OTf)_2P_2] + 2HOAc$$

(where P_2 represents two monophosphines or a diphosphine ligand.)

Scheme 2.5

In the case of P = PPh_3 the resultant chemical shift of δ = 20.26 ppm is closer to the solid state figure of δ = 21.25 ppm than that of the corresponding acetate (δ = 15.99 ppm). Where P_2 = dppe the resultant chemical shift of δ = 55.73 ppm is also closer to the solid state figure than that of the corresponding acetate (δ = 59.36 ppm). For P = PPh_2py a complex spectrum results which bears no resemblance to the solid state spectrum. In fact the peak in the solid state spectrum at δ = 25.48 ppm is close in value to a peak seen in the solution spectrum of $[Pd(OAc)_2(PPh_2py)_2]$.
Whilst these results are far from conclusive they suggest that the acetate ligands are replaced by Nafion-SO_3^- anions. In the Nafion resin the $[Pd(OAc)_2(PPh_2py)_2]$ complex may be held by protonation of the pyridine groups. It is also absorbed by Nafion-Na^+, but only in methanol not in dichloromethane.This is thought to be due to the insolubility of sodium acetate in the latter solvent. If this is the case then $[Pd(OAc)_2(PPh_2py)_2]$ is absorbed by protonation in Nafion-H and by ligand replacement in Nafion-Na.

2.14 The modification of Nafion functionality

The sulphonic acid groups which form the ion-exchange sites in Nafion resin are also reactive centres which can be modified using suitable reagents in a manner analogous to solution chemistry. The inert nature of the fluorinated polymer chains in

Nafion allows the use of aggressive reagents without the complication of unwanted side reactions.

Nafion was converted into an anionic exchange resin following Scheme 2.6

1) **Polymer-SO_3H + $SOCl_2$ = Polymer-SO_2Cl + SO_2 + HCl**

2) **Polymer-SO_2Cl + $N(C_2H_4NH_2)_3$ = [Polymer-SO_2 $N(C_2H_4NH_2)_3$]$^+Cl^-$**

Scheme 2.6

The resin can now absorb species such as $R_4N^+[Rh(CO)_2I_2]^-$ for e.g. Monsanto-type carbonylation.
Nafion can also be converted to a phosphine functionality by following equation (1) with equation (3) of Scheme 2.7 or to a substituted cyclopentadiene by following equation (1) with (4) of Scheme 2.7.

3) **Polymer-SO_2Cl + PR_2Li = Polymer-SO_2-PR_2 + LiCl**

4) **Polymer-SO_2Cl + NaCp = Polymer-SO_2-C_5H_5 + NaCl**

Scheme 2.7

2.15 The synthesis of Nafion sulphonyl chloride

Nafion-H beads (5g) were refluxed overnight under nitrogen gas in 10 mls thionyl chloride. The beads, which had become opaque in appearance, were rinsed with 3 x 10 mls CH_2Cl_2 and pumped dry. Analysis for chlorine gave 0.46% This set of beads was identified as "batch 1". Given that Nafion-H corresponds to 0.8 meq/g, complete chlorination would be expected to produce a chlorine content of 2.8%. Obviously,

even under reflux conditions and in great excess, the reagent is not penetrating to the centre of the beads.

A second batch (batch 2) was prepared with a slight modification of procedure. The beads were allowed to swell in deionised water for 45 minutes. The surplus water was decanted off and the beads exposed to vacuum briefly until dry on the surface as indicated by their free movement in the flask. The remainder of the procedure was then identical to batch (1). Batch 2 contained 0.85% chlorine.

The Nafion sulphonyl chloride beads were made as a first step towards the synthesis of various forms of modified Nafion, details of which follow.

An overview of how the beads were used is provided as appendix (II).

2.16 The synthesis of Nafion amine salt

Beads of the Nafion sulphonyl chloride (2.26g) was covered with CH_2Cl_2 (25 mls), tris(ethylamino)amine (0.1 ml., 0.684 mmol) added and the mixture refluxed for 3 hrs. A sample of the solution was removed for IR analysis. The primary amine N-H stretch was absent (ν_{asym}= 3300 $cm.^{-1}$, ν_{sym}= 3379 cm^{-1}). A further 0.15ml (1.03 mmol) amine was added and refluxing continued for a further 3 hrs. Inspection by IR showed the amine to be present in solution and the reaction flask was allowed to cool. The solution was removed by cannula and the beads washed with 25 mls CH_2Cl_2 and 3 portions of MeOH (25 mls) to esterify any remaining chloride groups, allowing *ca.*60 minutes between each washing. It was observed that the beads failed to swell in methanol in the manner of Nafion-H. The beads were dried *in vacuo* and stored under N_2. For convenience the beads are henceforth referred to as Nafion-NR_3.

They were subsequently used for carbonylation (see Chapter 5).

2.17 The synthesis of Nafion diphenylphosphine

Nafion sulphonyl chloride (0.7g) (see section 2.15) was weighed into a two-necked round-bottomed flask. In another similar flask, triphenylphosphine (1.0g , 3.8 mmol) and lithium wire (0.14g , 20 mmol) were stirred rapidly under an argon

atmosphere. On addition of THF (10 mls, dry, distilled, degassed) and a little warming, reaction started to generate diphenylphosphinolithium. When conversion of PPh_3 was complete, confirmed by ^{31}P NMR, the THF solution of PPh_2Li was transferred by cannula filter to the flask containing the modified Nafion. The beads were stirred at room temperature for an hour before the THF solution was decanted and the beads rinsed thoroughly with fresh THF and methanol.

For comparison purposes, 0.25g of *p*-toluenesulphonic acid was taken through the same reaction sequence in parallel. The colour changes were similar to those observed for Nafion and the resultant solution was studied using ^{31}P NMR . The major peak was a singlet at $\delta = 43.09$ ppm with a minor peak at 72.26 ppm due to reaction between PPh_3 and $SOCl_2$. Consequently the phosphorus chemical shift of Nafion-SO_2PPh_2 would be expected to appear in the same region of the spectrum. A sample of similarly treated Nafion film was submitted for solid state NMR spectroscopy following the procedure described in section 2.12.

A good signal was obtained for ^{31}P NMR showing a singlet at $\delta = 34.5$ ppm. Proton NMR was also performed and this showed peaks in the aromatic region of the spectrum. There had been concern expressed that the PPh_2Li /THF reagent might attack the fluoropolymer backbone driven by the high energy of formation of LiF. There was, however, no evidence to show that this had occurred and the resultant polymer was clear and flexible. Modification of Nafion in this way has not been previously reported. However, a few examples exist involving the modification of polystyrene based polymers. For example Fenger and Le Drian[16] describe a similar procedure for the modification of Merrifield polymer to produce a polystyrene based phosphine. They report good results for its use with various palladium complexes employed for the Suzuki coupling reaction. The modified Nafion described in this section was subsequently used for hydroformylation studies described in Chapter 5.

2.18 The synthesis of Nafion di-*tert*-butyl phosphine

Chlorodi-*tert*-butyl phosphine (0.5 ml., 2.63 mmol) was dissolved in 25 ml THF and added by cannula to a Schlenk tube containing lithium wire (0.042g, 6 mmol) under argon. After 4 hrs stirring, a sample of the solution was taken for

^{31}P $\{^{1}H\}$NMR. This showed only lithiophosphorus species to be present. The solution was transferred by cannula filter to a second Schlenk tube containing 1.1g of previously prepared Nafion-SO_2Cl. The beads were allowed to remain immersed overnight. The solution was removed by cannula, and the beads washed with 3 portions of THF (10 mls) added by syringe, before being dried *in vacuo* and stored under nitrogen.

A reasonably good spectrum of the beads was obtained using conventional ^{31}P $\{^{1}H\}$NMR techniques showing a singlet (δ = 84.3 ppm) indicating that reaction had gone to completion. The modified Nafion described in this section was subsequently used for hydroformylation studies described in Chapter 5.

2.19 The synthesis of sodium cyclopentadienide

Sodium sand was produced as follows. Sodium metal (2.3g, 0.2 mol) was covered with 100 mls toluene in a 250 ml round bottomed flask and heated to reflux temperature. At this point, the metal melted and started to float. The heat source was removed and the flask shaken vigorously for about 10 seconds before being reclamped. After 30 minutes standing, the toluene was decanted and the metal "sand" washed with three portions of 50 mls dry 60-80° petroleum ether against a counter current of nitrogen. The sodium metal was then covered with 100 mls THF. Cyclopentadiene (7.5g, 0.114 mol) was added by cannula and stirring commenced. After approx. 2 hrs all the sodium had dissolved. Solutions of NaCp were colourless, faintly blue or pink.

2.20 The synthesis of Nafion cyclopentadiene

Nafion sulphonyl chloride (2.5g) was added to a Schlenk tube under nitrogen. Freshly prepared sodium cyclopentadienide in THF (20 mls, 1.0M) was added by syringe and the solution stirred overnight. The solution was then removed by cannula and the beads washed with 5 x 20 mls THF, each washing accompanied by long periods of stirring. The THF was removed and the beads pumped to dryness and stored in the glovebox. The modified Nafion described in this section was subsequently used for studies of cyclotrimerisation described in Chapter 6.

2.21 Discussion

Nafion shares with other hydrocarbon based ionomers the ability to exchange ions with those in solution. The differences Nafion has, compared to other ionomers, arise out of the fluorocarbon backbone which causes the structure of Nafion to organise itself into the two phases, hydrophobic and hydrophilic. The hydrophilic phase consists of a series of inverted micelle structures within the hydrophobic phase. The swelling experienced by Nafion in alcohols takes place within the micellar cavities and interconnecting channels. These are the sites where ion exchange occurs and where subsequent catalysis occurs involving supported catalysts. In contrast the swelling of a hydrocarbon based polymer is limited by cross links and occurs evenly throughout the polymer structure. Therefore, the degree of extra ionic mobility conferred by swelling is likely to be higher in Nafion than in a hydrocarbon based ionomer and the diffusion of neutral reactant and product molecules along the system of channels is likely to be faster than through a disordered structure. The fluorocarbon backbone also confers on Nafion a very high acidity and further reduces the coordinating ability of the polymeric anion over that for the hydrocarbon ionomers. The inert nature of the backbone allows the use of aggresive reagents and this facilitates the recycling process which was successfully demonstrated.

Modification of the Nafion functional group was carried out without difficulty and with success. It was hoped that some of the advantageous properties of Nafion would be retained after modification. The driving force for the swelling is the ionic nature of Nafion and modification of the functional groups destroys this particular property. The relatively unchanged overall bulk appearance of modified Nafion suggests that the internal structure remains organised into the micelle regions. Further work is required to investigate this premise using DSC or X-ray scattering techniques.

2.22 References

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Chapter 3

Hydroesterification

3.1 Hydroesterification of alkenes

Alcohols, carbon monoxide and alkenes react together in the presence of a suitable catalyst to form either esters or a polyketone polymer depending on the nature of the catalyst. The alcohol acts as both solvent and reactant.

1) $ROH + R'CH{=}CH_2 + CO = R'CH_2CH_2COOR$

2) $n\,R'CH{=}CH_2 + n\,CO = -(CH_2CHR'(CO))_n-$

In the simplest case, R and R' are H leading to propanoic acid from reaction (1) and no branching in the polymer formed in (2). Reppe[1] first observed the formation of polyketacids by the $K_2[Ni(CN)_4]$ catalysed co-oligomerisation of CO and C_2H_4 in water. Palladium is now the metal of choice for hydroesterification because of the relative stability of the zerovalent state. Several related reactions are also catalysed by palladium complexes.

In 1960 the Wacker process was introduced, in which acetaldehyde is produced from ethene[2] via an ethene-palladium chloride π-complex. Pd(II) is reduced to the zerovalent state easily, oxidising co-ordinated groups so that overall the process involves alkenes normally susceptible to electrophilic attack becoming activated towards nucleophiles. The reaction of the same ethene palladium chloride complex with carbon monoxide in benzene was shown to produce β-chloropropionyl chloride, the proposed mechanism involving insertion of the alkene into the Pd-Cl bond followed by insertion of CO into the Pd-C bond[3]. Tsuji studied the reaction of CO with ethene in

ethanol and found ethyl propanoate to be the main product[4]. Another reaction catalysed by palladium is carbon-carbon bond formation e.g. via intermolecular hydrogen shift involving alkenes which can be dimerised in the presence of a catalytic amount of $PdCl_2$ to give a mixture of butenes[5].

The synthesis of saturated carboxylic acids from α–alkenes, carbon monoxide and water can be achieved using catalytic amounts of a palladium phosphine complex $[PdCl_2(PPh_3)_2]$ under milder conditions than hitherto employed. The same complex produces esters if alcohols are used in place of water[6,7] at a temperature some 50° lower. The phosphine based complexes have advantages over the earlier $PdCl_2$ catalyst in terms of rate and selectivity, arising possibly from the phosphine ligands, which are π-acceptor ligands capable of stabilising low oxidation states in transition metals[8]. Bittler *et al*[7] recognised the role of phosphine stabilised palladium in activating the alkene but mistakenly postulated the next step to be nucleophilic attack by carbon monoxide "in a resonance form". The π–bonded Pd-alkene complex was not yet isolated at that stage though the existence of many similar compounds, notably Zeise's salt was already long established[9]. Fenton[10] systematically studied the production of saturated acids using catalysts of the generic form $[PdCl_2(PR_3)_2]$ applied to 1-octene. An increase in CO pressure led to a linear increase in yield. The maximum yield was obtained with a water concentration (in acetic acid solvent) of around 8% at a temperature of 150°C. The addition of hydrogen and to a lesser degree other reducing agents, improved both the rate and the ratio of straight chain acid to the α-methyl acid stereoisomer. It was proposed that reducing agents prevented unwanted oxidation of the catalyst to inactive forms. In general, electron donating substituents on the phosphines decreased the yield and selectivity.

The use of chelating phosphines in place of monophosphines was found by Sugi[11] to alter the ratio of steroisomers formed during the esterification of styrene. Using $[PdCl_2(PPh_3)_2]$, styrene was almost completely converted to ethyl 2-phenylpropanoate. When $[PdCl_2\{Ph_2P(CH_2)_4PPh_2\}]$ was used as the catalyst, the overall activity was reduced but the major product was 3- phenylpropanoate. The authors reported no activity with shorter chain chelating ligands. According to

Knifton[12], where the α-alkene contains three or more carbons, a mixture of normal and iso-acid esters results with the iso ester predominating. Greater selectivity towards linear products was achieved using a tenfold excess of tin(II) chloride as co-catalyst with $[PdCl_2(PPh_3)_2]$. Substituting arsenic for phosphorus in the catalyst reduced the activity to zero as did the substitution of iodide for chloride.

The use of non-coordinating solvents such as chloroform or dichloromethane led to co-polymerisation of CO with olefins. Lai and Sen[13] studied the copolymerisation of CO and C_2H_4 using catalysts of the general formula $[Pd(PPh_3)_x(CH_3CN)_{4-x}][BF_4]_2$ for x = 1-3. The product is a high melting, photodegradable white polymer of formula $-(CH_2CHR'(CO))_n-$ where $n > 2^7$ with a very high degree of regularity. The same polymer, when produced using free radical initiation or γ-ray induction, has a random structure. The same catalyst proved to be active for three different reactions. Applying broadly similar reaction conditions (T = 25-70°C, P = 900-1000 psi, t = 24 hrs.) to ethene in chloroform led to its dimerisation. Mixtures of ethene and carbon monoxide in chloroform resulted in the formation of the polymer described above and ethene and carbon monoxide in alcohol solution (ROH) led to the formation of a mixture of polyketo esters of general formula $RO(-COCH_2CH_2-)_nH$ where R = Me , Et.

The Pd(II) compound $[Pd(CH_3CN)_4][BF_4]_2$, corresponding to x = 0 from the series above, was rapidly reduced by CO to palladium metal. The intermediate compounds n = 1-3 were catalytically active but an excess of stabilising ligand, PPh_3, suppressed catalytic activity presumably due to the blockage of all available co-ordination sites.

These observations led Lai and Sen to formulate for the first time one of the now widely accepted mechanisms for the three related reactions. The mechanism involves the alternate insertions of CO and C_2H_4 into a preformed Pd-alkyl bond (Scheme 3.1). There appears to be a greater inherent tendency for CO to insert into transition metal-alkyl bonds when compared to the corresponding insertion of olefins[14]. In contrast, while the insertion of olefins into metal-acyl bonds is known, the corresponding insertion of CO has never been directly observed. Thus the proposed

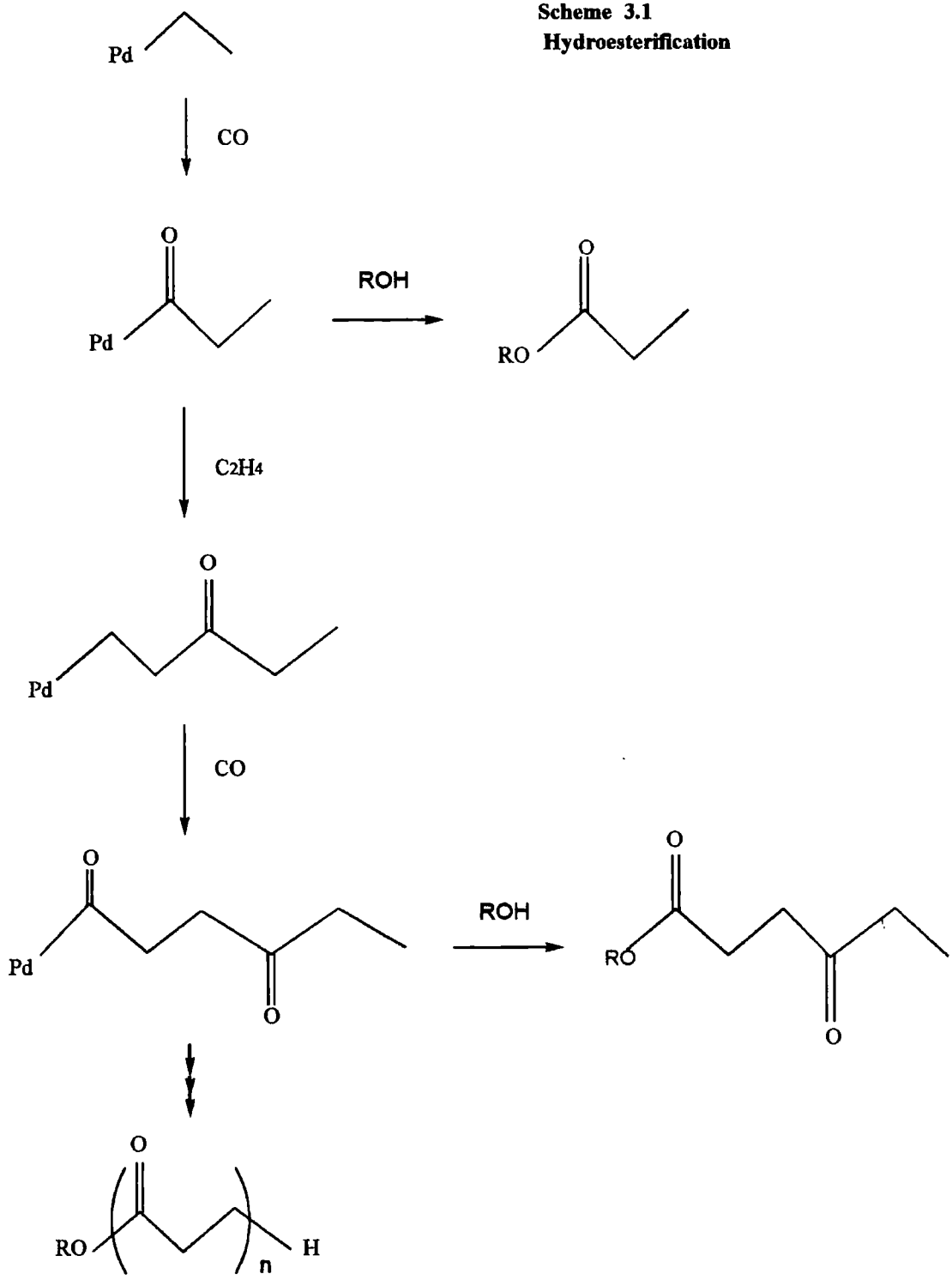
mechanism forces the alternate addition of carbon monoxide and ethene units to the growing polymer chain. The slow step in the chain propagation is almost certainly the insertion of ethene into the Pd-acyl bond. This is because, if the insertion of CO into the Pd-alkyl bond was slow, one should have observed products arising from a competing β-hydrogen abstraction step. In the absence of CO, C_2H_4 was rapidly dimerised indicating that β-hydrogen abstraction is fast compared to further insertion of C_2H_4.

In the absence of CO, the compounds $[Pd(PPh_3)_x(CH_3CN)_{4-x}][BF_4]_2$ (x = 1-3) were found to catalyse the rapid dimerisation of C_2H_4. The formation of C_4H_8 clearly indicated that β-hydrogen abstraction from Pd-alkyl species is fast compared to further insertions of C_2H_4. The intermediacy of cationic Pd(II)-alkyl and -acyl species in the copolymerisation reaction was supported by the observation that the species generated by the reaction of $AgBF_4$ with $[Pd(PPh_3)_2(Me)(I)]$ and $[Pd(PPh_3)_2(COMe)(Cl)]$, presumably $[Pd(PPh_3)_2(Me)(solv)]^+$ and $[Pd(PPh_3)_2(COMe)(solv)]^+$ respectively, were also active catalysts for the copolymerisation reaction under the same conditions. The corresponding neutral compounds, starting materials in the $AgBF_4$ reactions above, as well as $[Pd(PPh_3)_2Cl_2]$ and $[Pd(PPh_3)_4]$ were found by Lai and Sen to be completely inactive under the stated conditions. This contrasts with the work of Kutepow *et al.*, cited earlier, in which $[Pd(PPh_3)_2Cl_2]$ was their most active catalyst. The compounds corresponding to x = 0 and x = 4 in the above generic formula were also found to be inactive as catalysts.

Direct evidence for a mechanism involving a single mode of chain growth resulted from studies on the copolymerisation reaction in alcohols. The mechanism outlined in Scheme 1 involves the formation of Pd-acyl species as intermediates at every alternate step in the propagation sequence. Since the formation of esters through the reactions of transition metal acyls with alcohols is well precedented[8], it should be possible to intercept the propagation sequence if the copolymerisation was carried out in the presence of alcohols. The formation of esters of the type $RO(-COCH_2CH_2-)_nH$ was observed when the solvent for the copolymerisation reaction was ROH (R = Me, Et). The polyketo esters corresponding to n = 1-5 were separated and quantified and

the results analysed as Schultz-Flory plots in which W_p, the weight fraction of a given oligomer, is plotted against P the degree of polymerisation. The resulting straight line indicated a single mode of stepwise chain growth. Furthermore the difference in slope of the line in going from MeOH to EtOH indicated that the rate of termination was 1.74 times slower in EtOH than in MeOH. Only methyl esters were formed from a 1:1 mixture of MeOH and Bu^tOH indicating a substantially higher rate of termination with MeOH than Bu^tOH. Yields of polymer obtained using $[Pd(PPh_3)_2(CH_3CN)_2][BF_4]_2$ corresponding to x = 2 were the highest reported and represent approximately 75 grams per gram of palladium.

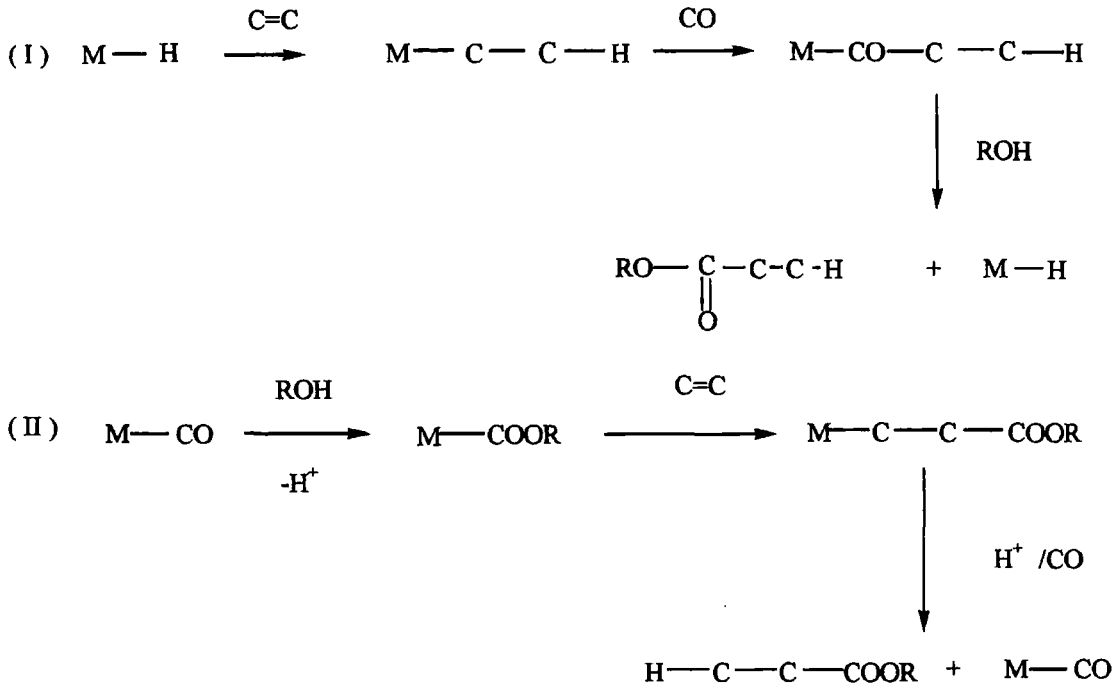
Scheme 3.1
Hydroesterification



The mechanism in Scheme 3.1 begins with a Pd-alkyl species; Cavinato and Toniolo[15] provide evidence to demonstrate that the Pd-alkyl species results from insertion of ethene into a Pd-H bond (Scheme 3.2 mechanism (I)) at the same time refuting the

possibility of the cycle starting with a Pd-COOR (Scheme 3.2 mechanism(II)). This assertion is based on the lack of reactivity of $PdCl(COOMe)(PPh_3)_2$ with 1-hexene.

Scheme 3.2 Two alternate mechanisms for hydroesterification



During the same period Drent[16] and co-workers studied cationic palladium complexes containing tertiary phosphine ligands and weakly co-ordinating anions as catalysts for the methoxycarbonylation of ethene to give methyl propanoate. In experiments using bidentate tertiary phosphine ligands of general formula $[Pd(OAc)_2Ph_2P(CH_2)_nPPh_2]$ it was observed that no methyl propanoate was formed. Instead high molecular weight polyketone was formed at very high rates (up to 6000 turnovers per hour) with yields above 10^6 grams of polymer per gram of palladium reported under mild conditions (90°C, 45 bar). The catalysts were formed *in situ* from $[Pd(OAc)_2]$ and $Ph_2P(CH_2)_nPPh_2$. Maximum turnover rate and maximum polymer molecular weights were obtained for n = 3, i.e. diphenylphosphinopropane, abbreviated to DPPP. The same catalyst systems would also catalyse the terpolymerisation of

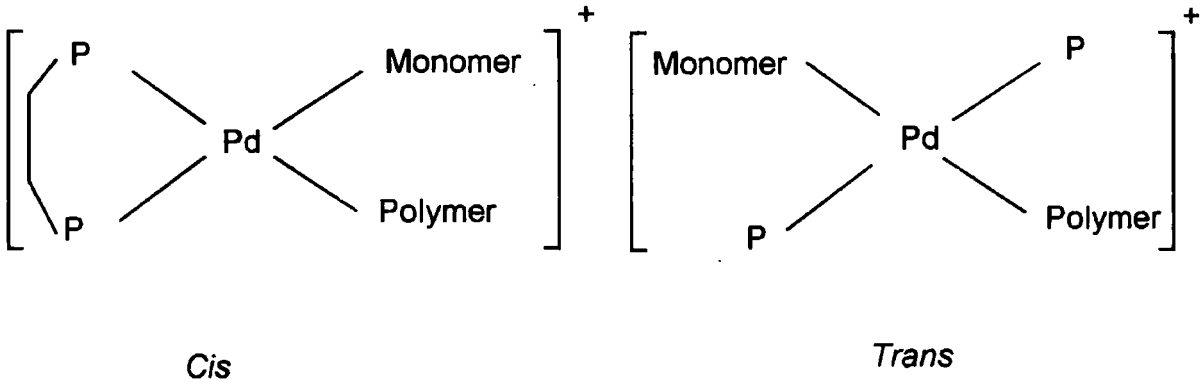
carbon monoxide with mixtures of ethene and propene to give a polymer of general formula $R[(CO)Z]_nCOOMe$ where Z represents the structures $\{-CH_2CH_2-\}$; $\{-CH_2CH(CH_3)-\}$; $\{-CH(CH_3)CH_2-\}$. The importance of bidentate ligands and weakly co-ordinating anions for high activity can be explained mechanistically. High activities were observed only when the added acid contained an anion which showed weak co-ordinating ability towards the palladium centre. It was suggested that the function of the acid was to replace the more strongly co-ordinated acetate groups on the palladium with weaker co-ordinating anions. This suggestion was supported by two observations: first, that treatment of diacetatopalladium(II) with, for example, *p*-toluenesulphonic acid or trifluoromethylsulphonic acid in acetonitrile resulted in quantitative replacement of the acetate groups to give respectively neutral or cationic complexes such as $[Pd(MeCN)_2(O_3Stol)_2]$ or $[Pd(MeCN)_4(O_3SCF_3)_2]$. Secondly, when these complexes were isolated and combined with DPPP, without further addition of acid, the products gave catalyst systems of similar activity for copolymer formation to those formed *in situ* by the combination of diacetatopalladium(II), DPPP and the appropriate acid.

The formation of a more positive palladium centre with the weakly co-ordinating anions was indicated by $^{31}P\{^1H\}$NMR spectroscopic monitoring of the stages in the preparation of the acid promoted catalyst systems. For example, addition of two mole equivalents of *p*-toluenesulphonic acid to an equimolar mixture of diacetatopalladium(II) and DPPP in acetone solution resulted in a shift to higher frequency of the phosphorus signal from 11.1 to 17.5 ppm. This deshielding of the phosphorus atoms can be attributed to the donation of electron density from the DPPP phosphorus atoms to a more positive palladium centre which is produced upon replacement of acetate ions by *p*-toluenesulphonic anions. Accessible co-ordination sites at which the catalytic transformations occur are then considered to be formed under the reaction conditions by nucleophilic substitution of the sulphonic acid anions by monomer or solvent molecules. The high reactivity is thought to stem from easy access of the substrate molecules, ROH, CO and olefin to co-ordination sites on the metal centre. Such biphosphine stabilised palladium complexes in which solvents form

weakly bonded ligands have been isolated and characterised[17] and the authors propose a ranking of the ability of weak solvent ligands to form cationic palladium(II) complexes of the type $[Pd(dppe)(solvent)_2]^{2+}$ as follows:

CH_2Cl_2~C_6H_6<<<EtOH<MeOH~thf<MeCN<Me_2CO<RCN<dmf<dmso<pyridine

The role of a bidentate phosphine was explained by Drent[21] as follows. Monodentate phosphine ligands can arrange themselves *trans* or *cis* to each other (Scheme 3.3). When these forms are in equilibrium with each other, isomerisation will lead to the interruption of the chain propagation and so will tend to decrease the ratio of the rate of propagation to the rate of termination.

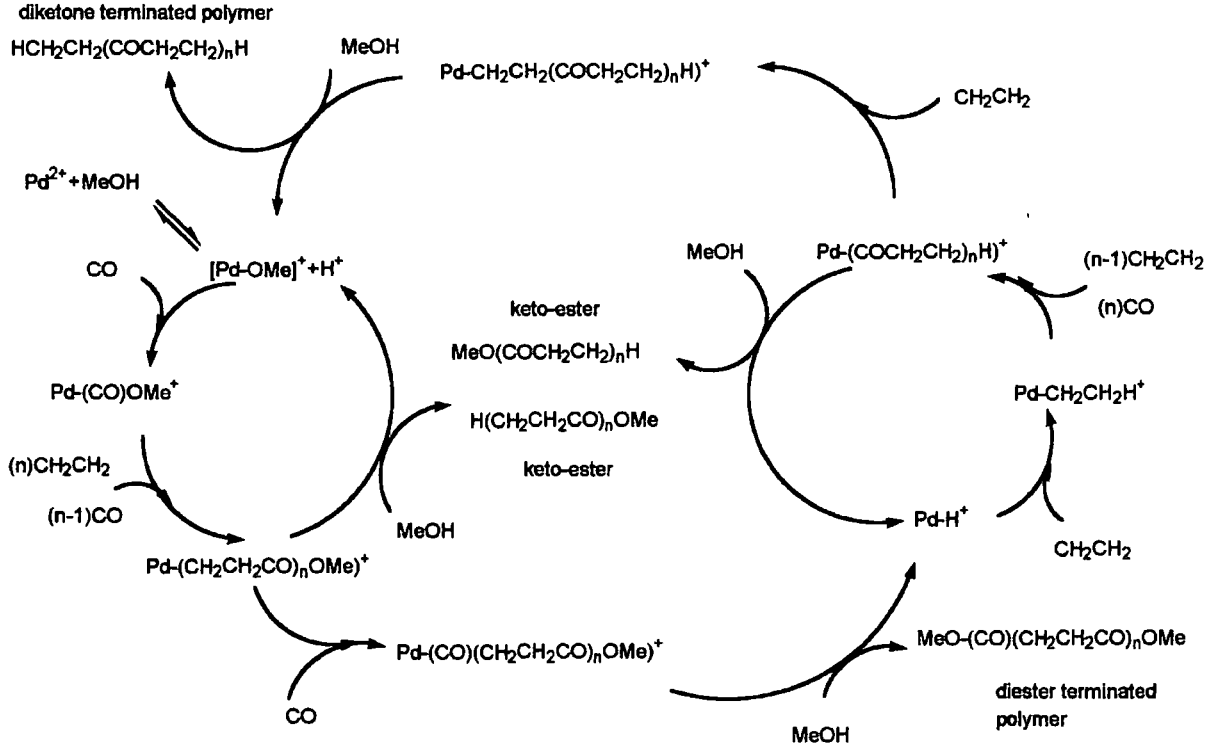


Scheme 3.3: comparison of monodentate with bidentate ligands

The bidentate ligand only allows formation of the *cis* form. However this is not the complete story since on this basis the *cis* form would also favour formation of methyl propanoate. A ligand backbone of three or four carbons is optimal in stabilising both the square planar ground state and the proposed trigonal bipyramidal transition state and these therefore result in maximum catalytic activity. Drent also postulates two alternate catalytic cycles, one starting with $[Pd\text{-}H]^+$ and the other with $[Pd\text{-}OMe]^+$ co-existing with each other (Scheme 3.4). This catalytic scheme also provides a route to diester and diketo compounds found as minor products during hydroesterification. Further insight into the mechanism of the copolymerisation and related reactions was

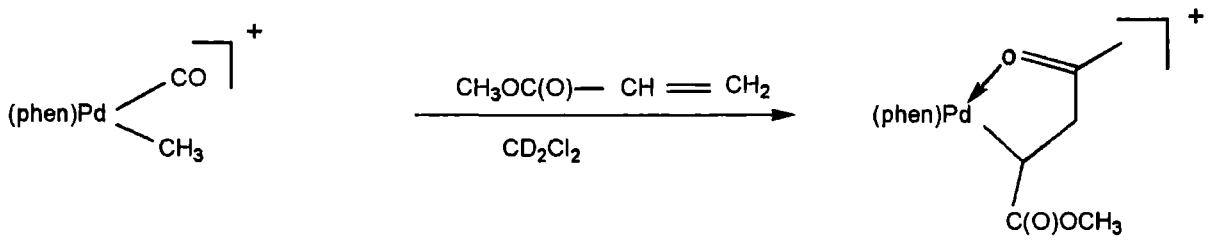
provided by Rix[18] *et al.* They studied the copolymerisation of ethene with CO initiated by the $[(phen)\text{-}Pd(CH_3)(NCCH_3)]^+$ precatalyst (where phen = 1,10-phenanthroline) and used a series of related compounds $[(phen)\text{-}Pd(CH_3)(L)]^+$ where L = CO, C_2H_4, $S(CH_3)(C_6H_5)$, CH_3CN and C_6H_5CN for mechanistic studies. They report a series of *in situ* low-temperature NMR studies of the kinetics of directly observed migratory insertion reactions of carbonyl alkyl, ethene acyl and ethene alkyl complexes and the relative binding affinities of ethene and carbon monoxide. They identify a stable 5-membered palladacycle intermediate in the migratory insertion of alkene and CO into the Pd alkyl bond (Scheme 3.5) and report the first direct observation of three related classes of migratory insertion reactions with the same metal centre. The $\Delta G^{\ddagger}$ for these reactions increase in the order:

$\Delta G^{\ddagger}(R \rightarrow CO) \approx 63$ kJ mol^{-1} (-66°C)$< \Delta G^{\ddagger}(Ac \rightarrow C_2H_4) \approx 71$ kJ mol$^{-1} < \Delta G^{\ddagger}(R \rightarrow C_2H_4) \approx 79$ kJ mol^{-1}.



Scheme 3.4 Competing catalytic cycles for polyketone formation

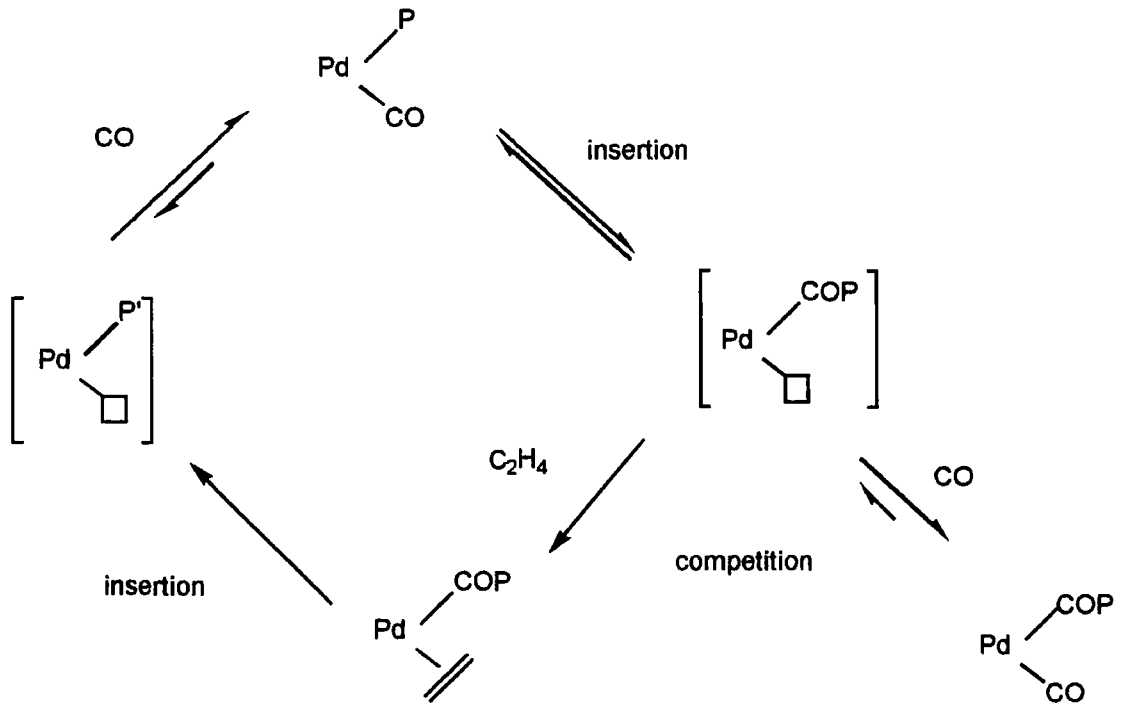
The five membered metallocycle ring identified by Rix using ^{13}CNMR bears a strong resemblance to the lactone rings produced by Alper and Leonard using a palladium catalyst for the carbonylation of allylic alcohols. The cyclisation was a general reaction but the authors offer no mechanism[19].



Scheme 3.5

5-membered palladacycle intermediate

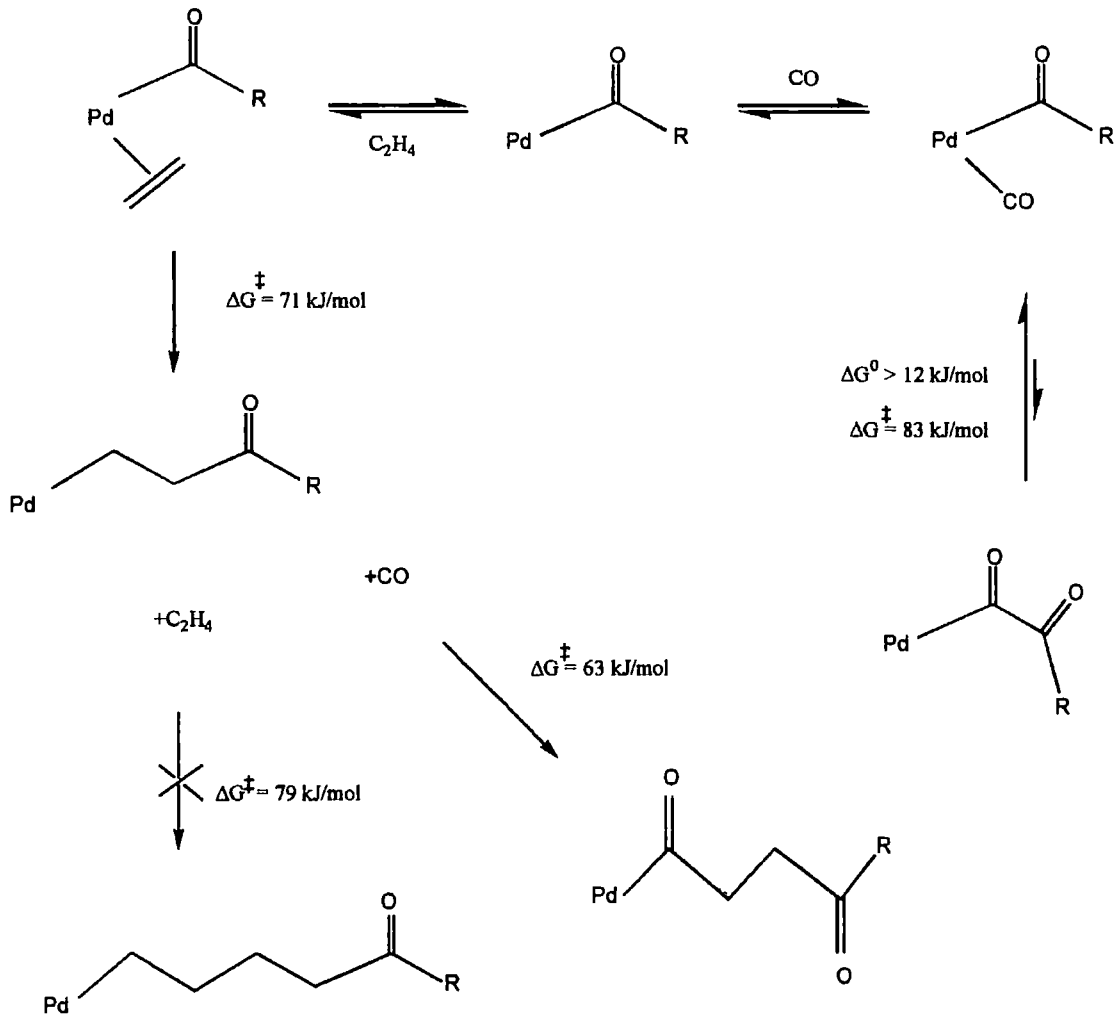
Studies by Sen et al.[20] of α-ketoacyl palladium complexes established the free energy profile for their decarbonylation. From this it can be stated that a double insertion of carbon monoxide would require > 106 kJ mol^{-1}. The error-free formation of polyketone which is encountered, requires that CO does not insert into a Pd-CO bond, ruled out by the high $\Delta G^{\ddagger}$ described above, and also requires that ethene does not insert into a Pd-alkyl bond. Drent and Budzelaar[21] in their review point out that although the latter is energetically favourable and in the absence of CO, ethene is dimerised or with an α-diimine catalyst even polymerised, nevertheless, ethene does not insert into a Pd-alkyl bond in the presence of CO. One reason is probably the stronger co-ordination of CO to palladium. Once a palladium alkyl bond is formed the stronger co-ordination of CO ensures that the next monomer to insert will be a CO molecule. Of course, CO also co-ordinates more strongly to a palladium-acyl but since the CO insertion is thermodynamically unfavourable, an equilibrium is established with the starting material which inserts ethene to continue the chain propagation (Scheme 3.6).



Scheme 3.6 Alternating insertion

P and P' represent the growing polymer chain.

To summarise, according to Drent and Budzelaar[21], a palladium metal centre with two monodentate phosphine ligands forms a hydride, either initially or from β-hydrogen abstraction from an alkyl group. From an equilibrium mixture of *cis* and *trans* forms, the former allows insertion of ethene and CO followed by termination through nucleophilic attack by a methoxy group to form methyl propanoate. When the phosphine ligands are bidentate the reactive sites are held *cis* to one another allowing multiple alternate insertions of CO and ethene to form a polyketone. The relative energies of activation ensure perfect alternation of the growing polymer chain.



Scheme 3.7 Energies of activation

This basic reaction has since found many variations. Use of propene instead of ethene will give a polyketone with pendant methyl groups, use of styrene will give pendant phenyl groups and so on. The use of chiral phosphine ligands will give asymmetric hydroesterification. Usually more forcing conditions are required than for methyl propanoate; however Hongying Zhou *et al.* [22] report a ligand system, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (DDPPI) which with palladium acetate and *p*-toluenesulphonic acid will catalyse the asymmetric hydroesterification of norbornene in good yield under comparatively mild conditions

and Oi *et al.* report the hydroesterification of styrene using a wide range of palladium based chiral phosphines[23].

The use of light energy in place of heat has also been reported. Tao *et al.* successfully methoxycarbonylated a range of olefins under ambient conditions using cobalt acetylacetanoate as the precatalyst[24]. The active catalyst was thought to be $HCo(CO)_3$(olefin) formed by photolysis under a CO atmosphere.

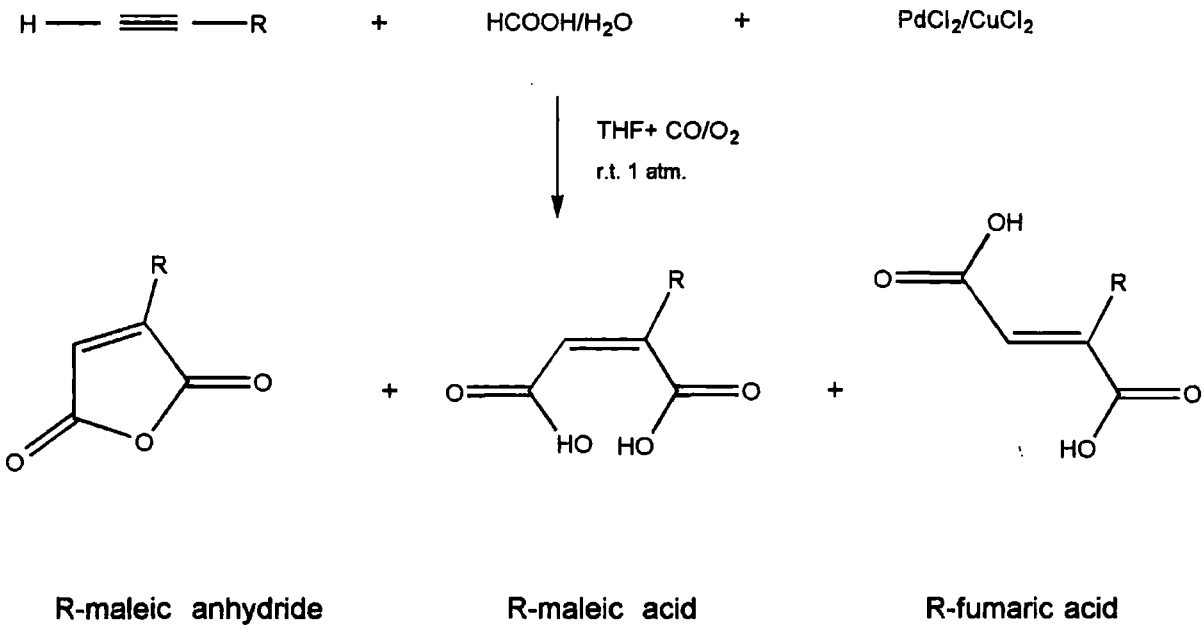
An alternative to using hazardous carbon monoxide gas is to use methyl formate. Grevin and Kalck[25] report the first use of methyl formate with no added carbon monoxide for the hydroesterification of ethene. The catalyst used was dichlorobis-(tri-t-butylphosphine)palladium.

The efficiency of catalytic activity can often be enhanced using a co-catalyst. It is recognised that non-coordinating acids are required in polyketone synthesis to provide non-coordinating anions (e.g. $[BF_4]^-$, $[O_3Stol]^-$ $[O_3SCF_3]^-$). This function can be filled by a group of compounds known as alumoxanes[26], three dimensional cage structures of general formula $[RAl(\mu_3\text{-}O)]_n$ where R is t-butyl in this study. When used in conjunction with $[(dppp)Pd(OAc)_2]$, two equivalents of alumoxane are required for each palladium. The first is thought to remove an acetate group from the palladium complex and replace it with a *tert*-butyl group followed by removal of the second acetate group by the second alumoxane to form a complex ion with a vacant coordination site on palladium. The authors also seek to rationalise the effect noted by themselves and previously by Drent that chain length in bidentate ligands is an important parameter. This they do in terms of bite angle. Chains longer than 3 carbons start to crowd the remaining space for co-ordination, therefore reducing the rate of turnover at the metal centre.

3.2 Hydroesterification of alkynes

In parallel to the development of alkene hydroesterification chemistry, similar additions of CO and alcohols have been studied across the alkyne triple bond. Bittler[7] compares the nickel halides efficacy for acrylic acid production from acetylene (30

atm. and 170°C) to propanoic acid production from ethene (200 atm. and 250-320°C). A specific feature of the palladium catalysed carbonylation of acetylenic bonds is the occurrence of extensive dicarbonylation rather than monocarbonylation[3]. Zargarian and Alper reacted formic acid and water with substituted terminal alkynes using mixtures of palladium chloride with copper(II)chloride [27]. They found three main products, the ratio of which depended on the bulk of the substituent (scheme 3.8) and was influenced heavily by the choice of solvent. With straight chain alkyl substituents, the Z:E ratio i.e. maleic to fumaric derivatives, is 2-3:1 whereas phenylacetylene gives exclusively the anhydride.



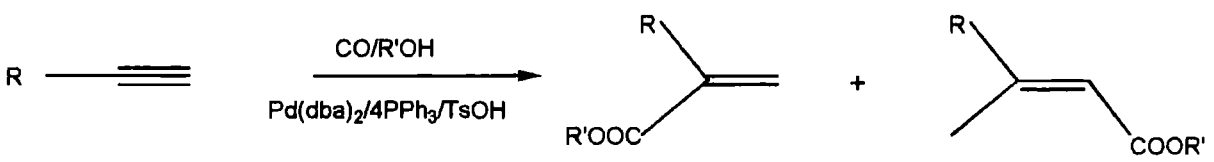
Scheme 3.8 Carbonylation of alkynes

In catalytic systems employing a combination of $PdCl_2$ and $CuCl_2/O_2$, the copper(II)/O_2 acts as a Wacker-type regenerator of the deactivated palladium catalyst. $CuCl_2$ is the oxidant for regenerating Pd^0 and HCl/oxygen are there to replenish $CuCl_2$.

$$Pd^0 + 2\,CuCl_2 \rightarrow Pd^{II} + Cu_2Cl_2$$

$$2Cu_2Cl_2 + O_2 + 4HCl \rightarrow 4CuCl_2 + 2H_2O$$

Normal hydroesterification of terminal alkynes with butanol (Scheme 3.9) proceeds smoothly and efficiently under 1 atmosphere of CO using a catalytic system of $Pd(dba)_2$ with triphenylphosphine and *p*-toluenesulphonic acid similar to the systems detailed above for the hydroesterification of olefins (dba = dibenzylideneacetone)[28].



Scheme 3.9 Hydroesterification of alkynes

(When R and R' are both methyl then the first product is methyl methacrylate (MMA)).

The authors[28] found that $Pd(dba)_2$-$4PPh_3$ gave a superior result to $Pd(PPh_3)_4$ alone for the reaction of phenylacetylene with n-butanol, giving butyl -2-phenyl-2-propenoate in 89% yield after 2hrs at 100°C and normal CO pressure. Reactions with symmetrical internal alkynes gave exclusively E isomers. The reaction of 1-phenyl-1-heptyne with n-butanol gave a mixture of butyl (E)-2-phenyl-2-octenoate and butyl (E)-3-phenyl-2-pentyl-2-propenoate.

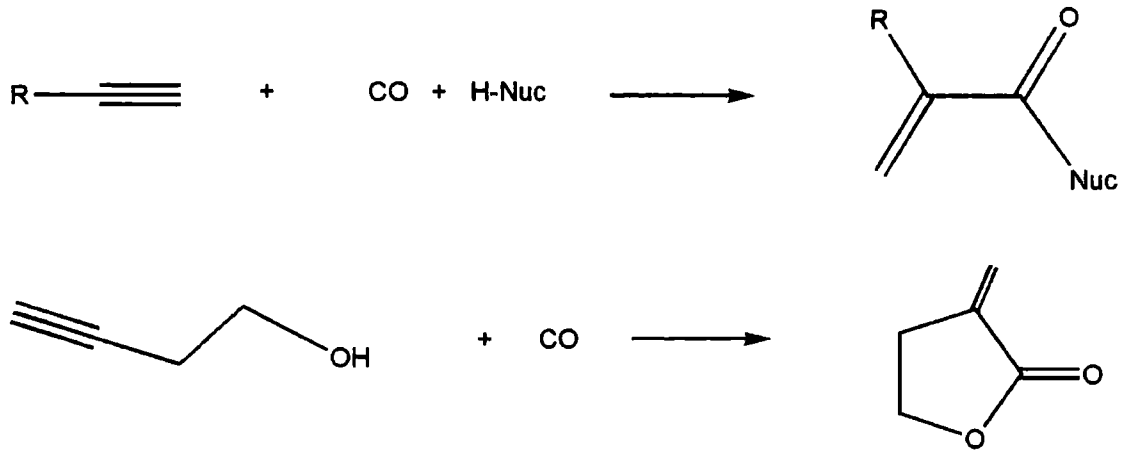
Tsuji *et al*[29] reported on the $PdCl_2/CuCl_2$ catalysed alkoxycarbonylation of acetylenes in NaOAc/alcohol at room temperature to give monocarbonylated products. An improvement on this technique was note by Vasilevsky[30] *et al.* by controlling the temperature exactly and adding the acetylene dropwise.

The product of industrial importance is MMA, which can in principle be manufactured by nickel or palladium catalysed carbonylation of propyne but until recently had not been attempted on a commercial scale because of the lack of a catalyst

with sufficient activity and selectivity. In 1993 Drent and co-workers[31,32] reported on the development of an effective new ligand system. Starting with palladium acetate plus excess triphenylphosphine and a Brønsted acid the reaction proceeded with a low rate but an acceptable selectivity (89%). A remarkable increase in activity and selectivity was observed upon replacement of PPh_3 with 2-pyridyl-diphenylphosphine. Even under considerably milder conditions (45°C instead of 115°C), the use of this promoter resulted in a rate increase by three orders of magnitude as well as an increase in selectivity to 98.9%.

A much lower rate enhancement was observed with 3-pyridyl-diphenylphosphine as the ligand whereas with 4-pyridyl-diphenylphosphine the results obtained were similar to those using PPh_3. It was observed that in order to obtain high activity, it is necessary to have an excess of acid over and above the 2 mol/(mol Pd) required for removal of acetate as acetic acid from the co-ordination sphere. Replacing further phenyl groups with pyridyl groups on the phosphine ligand had a deleterious effect. The only further (slight) improvement came with a *p*-methyl group in the pyridine ring.

Similar results were obtained with a variety of other alkynes, e.g. acetylene and phenylacetylene, as well as with nucleophilic reagents other than methanol, e.g. water, aliphatic alcohols (primary, secondary and tertiary), aromatic alcohols, thiols, carboxylic acids and amines, thus giving access to a variety of unsaturated carboxylic acids, thiol-esters and amides. The general reaction catalysed is depicted below in Scheme 3.10, together with the intramolecular version obtained when the nucleophilic reagent forms part of the alkyne substrate.



Scheme 3.10 Reactions of terminal alkynes

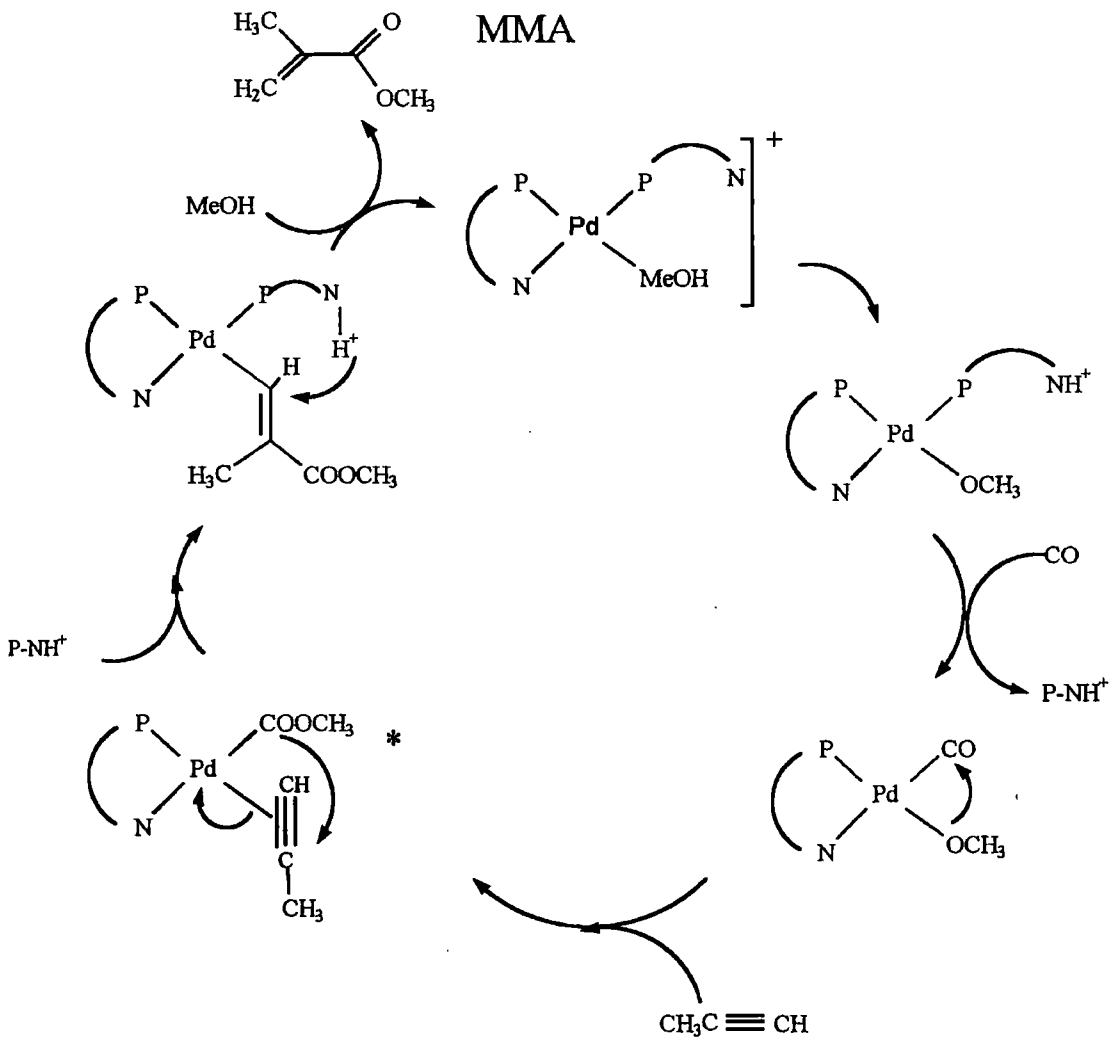
As with alkene hydroesterification, the acid plays an important role as a source of weakly co-ordinating anions.

Studies in the liquid state (NMR,IR) and in the solid state (X-ray) have shown that the co-ordination sphere around the metal can accommodate two PPh_2py ligands but that they are bonded differently. One is chelating the cation through phosphorus and nitrogen and the other is singly co-ordinated through the phosphorus only, i.e. $[(P\text{-}N)Pd(P\text{-}N)X]^+ X^-$ where P-N is shorthand for 2-pyridyldiphenylphosphine.

The initial step in the cycle probably involves the reaction of the above species with methanol to give the palladium-methoxy species. The next step involves attack by carbon monoxide and displacement of the monocoordinated ligand. It is likely that the nucleophilic displacement is an easy reaction since the monocoordinated ligand will spend most of the time protonated in the acid medium. Subsequently, migratory insertion of the carbon monoxide molecule into the palladium-methoxy bond will give a palladium-carbomethoxy species in which the resulting vacant co-ordination site can be occupied again by the (protonated) P-N ligand.

$$[(P\text{-}N)Pd(CO)OCH_3]X + P\text{-}NH^+X^- \rightarrow [(P\text{-}N)Pd(P\text{-}NH^+)(COOCH_3)]X_2$$

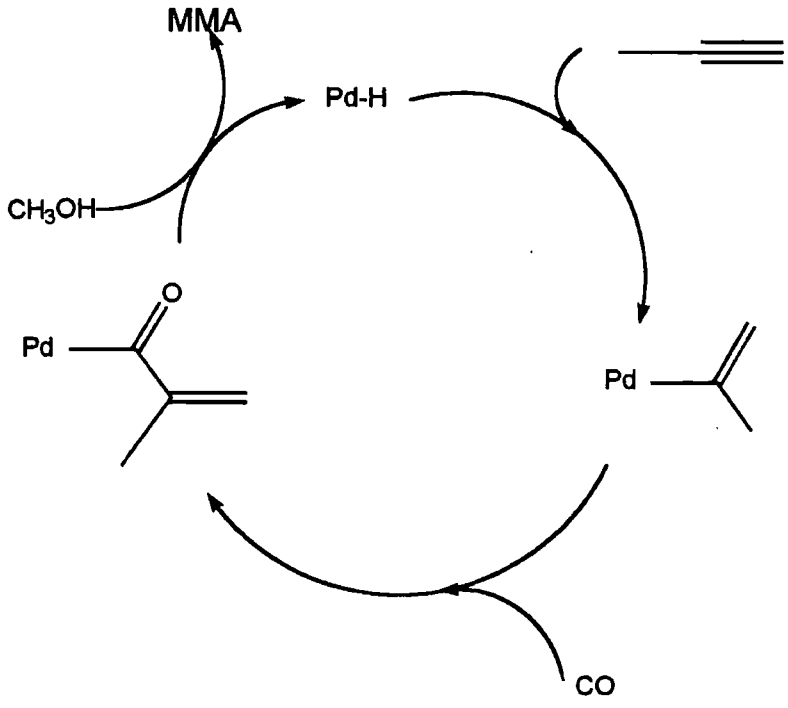
This in turn is displaced by propyne, which for steric reasons co-ordinates more or less perpendicular to the square ligand co-ordination plane. Migratory insertion follows again, this time of the carbomethoxy group to propyne (Scheme 3.11).



Scheme 3.11 Catalytic cycle for MMA production.

The observation that substituents on the 6-position on the 2-pyridyl group led to an increase in selectivity for MMA above methyl crotonate supports the catalytic cycle outlined in Scheme 3.11 as opposed to an alternate cycle via a palladium hydride species (Scheme 3.12) since at the stage when the propyne is co-ordinated to the palladium centre the 6-substituent hinders the rotation of the propyne and favours anti-

Markownikoff addition. Looking at the structure marked with an asterisk in Scheme 3.11, the propyne is sterically disfavoured from adopting the configuration in which the methyl group is alongside the 6-position of the P-N ligand. The palladium hydride cycle in scheme 3.12 is not influenced to the same extent by such steric factors.



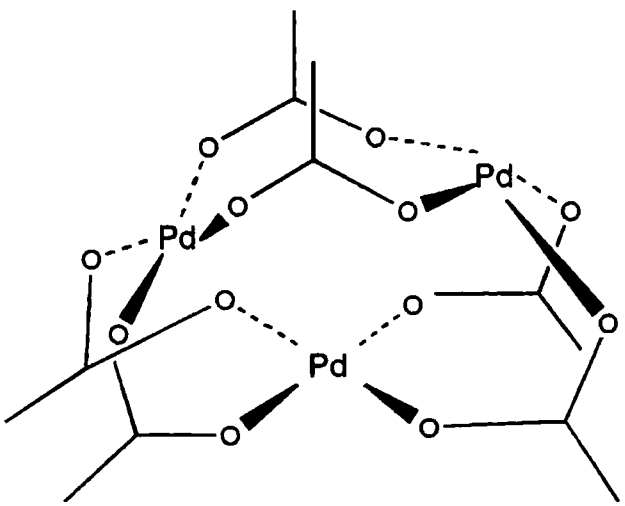
Scheme 3.12 Alternative catalytic cycle starting with hydride

3.3 Experimental: Syntheses

General experimental details are described in Appendix (I)

3.3.1 The Synthesis of Palladium Acetate

Palladium acetate exists in the solid form as a trimer.



$[Pd(C_4H_6O_4)]_3$

Scheme 3.13 Palladium acetate

Following a procedure by Stephenson and Wilkinson[33], Pd sponge (2.5g, 0.0235 mol.) was refluxed in 65 ml. glacial acetic acid with 2 ml. conc. HNO_3 for 2 hours. On allowing to cool the product appeared as a crystalline product washed with CH_2Cl_2 and dried *in vacuo*.

Yield 4.44g , 83.3%. IR: ν (O-C-O) 1595 cm^{-1} (lit.[33] 1600 cm^{-1})

3.3.2 The synthesis of bis(triphenylphosphine)bis(acetato)palladium(II)

In a clean, dry, 100 ml round-bottomed flask, palladium acetate (0.2g , 0.88 mmol) and triphenylphosphine (0.48g ,1.83 mmol) were dissolved in 50ml dry toluene at ambient temperature. An orange-yellow solution was formed which was reduced in volume. On the addition of (60-80) petroleum ether, a bright yellow crystalline solid

formed which was filtered under vacuum and washed with diethylether. Melting point obtained was 131°C, (lit.135°C). Yield 0.38g . 55.9% (Found : C, 63.35; H, 4.73; N, 0.0) $C_{40}H_{36}O_4P_2Pd$ requires C, 64.14; H, 4.84; N, 0.0%). IR: ν(O-C-O) 1636 cm^{-1}(lit[33] 1634 cm^{-1}) ; ν(P-Ph) 1436 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.78 ppm. ^1H NMR ($CDCl_3$): δ 7.67 ppm., (m, 15H, PC_6H_5); 0.77 ppm., (s, **3H,** $CH_3C{=}O$).

3.3.3 The synthesis of bis(triphenylphosphine)dichloropalladium(II)

In a clean, dry, 250 ml round-bottomed flask, palladium chloride (0.354g, 2mmol) was added to triphenylphosphine (1.049g, 4mmol) and dissolved in 50 ml. dry dimethylformamide. Bright yellow crystals formed immediately. These were removed by filtration under vacuum and weighed. MPt.(with decomposition ~ 260°C)(lit. 270°C). Yield 1.14g ,82% (Found : C, 61.31; H, 4.23; N, 0.0). $C_{36}H_{30}Cl_2P_2Pd$ requires C, 61.6; H, 4.31; N, 0.0%). IR: ν (*trans* Pd-Cl) 357 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 24.6 ppm.(s)

3.3.4 The synthesis of tetrakis(triphenylphosphine)palladium(0)

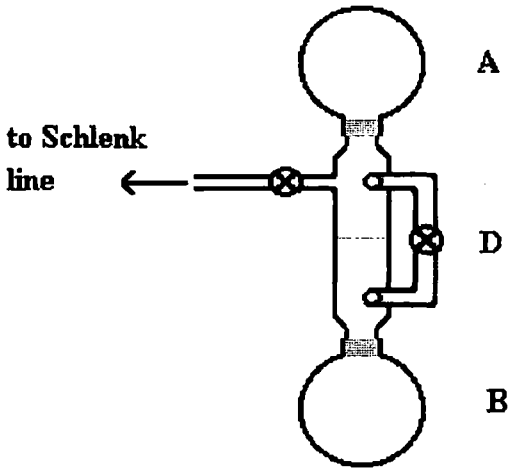
$$2PdCl_2 + 8P(C_6H_5)_3 + 5NH_2NH_2.H_2O \rightarrow 2[Pd\{P(C_6H_5)_3\}_4] + 4NH_2NH_2.HCl + N_2\uparrow + 5H_2O$$

Into a clean, dry, 2L, single-necked round-bottomed flask with a dual outlet adapter was weighed palladium(II)chloride (1.772g ,0.01 mol) and triphenylphosphine (13.1g, 0.05 mol). These were dissolved in 1200 mls of dried, degassed, dimethyl sulphoxide under an atmosphere of nitrogen. The contents were stirred and heated in an oil-bath to 140°C. On reaching this temperature, the oil-bath was removed and after a period of 15 minutes with rapid stirring, hydrazine hydrate (20g, 0.4 mol) was added within 1 minute by syringe. The evolution of nitrogen followed, and was allowed to escape via the Schlenk line. Slow cooling of the dark solution produced a precipitate which was separated by filtration, washed with ethanol then di-ethylether, and dried in a N_2 stream

overnight. The yellow crystals so obtained were shielded from the light and stored in a glovebox. Yield 9.75g, 85%.(Found : C, 73.33; H, 5.09; N, 0.0). $C_{72}H_{60}P_4Pd$ requires C, 74.84; H, 5.23; N, 0.0%).

3.3.5 The synthesis of tetrakis(acetonitrile)palladium(II)bis(tetrafluoroborate).

The synthesis follows the method given in Inorganic Synthesis v.28, p.62



Scheme 3.14 Apparatus for preparation of $[Pd(CH_3CN)_4][BF_4]_2$

In a N_2 glove-box a 100 ml. flask B was charged with 1g of palladium sponge and 2.2g of nitrosyl tetrafluoroborate (previously sublimed at 220°C under vacuum), and the apparatus depicted in scheme 3.15 asembled.It was then attached to a vacuum Schlenk line and evacuated to 10^{-3} torr, before acetonitrile (50 mls) was added by vacuum distillation from a CH_3CN/P_2O_5 slurry. Visible evolution of NO gas from the metal surface was noted and the solution was stirred until no metal remained. The solution was filtered by closing tap D, inverting the apparatus and cooling A to liquid nitrogen temperature. After filtration, D was opened to equalise the pressure. The solvent was

removed by vacuum to approximately 10 mls. A 40 ml. aliquot of diethyl ether was added by cannula to effect further precipitation. The suspension was filtered as before and the solid washed with 2 x 5 mls ether and dried overnight under vacuum. The bright yellow crystals (3.33g, 79.8%) were stored in the nitrogen glovebox. IR (KBr): ν (C≡N) 2353 cm^{-1} (lit.[13] 2335 cm^{-1}, Nujol) . (Found C, 19.43; H, 2.76; N, 11.53; $C_8H_{12}N_4B_2F_8Pd$ requires C, 21.63; H, 2.72; N, 12.61%).

3.3.6 The synthesis of bis(acetato)diphenylphosphinoethanepalladium(II)

Mirroring the procedure adopted for the preparation of bis(triphenylphosphine)bis(acetato)palladium(II), palladium acetate (0.25g, 1.106 mmol) in a clean, dry, 250ml , round-bottomed flask, was dissolved in 25 mls dry, degassed, toluene. In a dropping funnel, dppe (0.44g, 1.106 mmol) was also dissolved in 25 mls toluene. Under a nitrogen atmosphere the dppe solution was added dropwise with stirring to the palladium acetate solution. After reducing the volume to 20 mls by vacuum, petroleum ether (25 mls) was added to form crystals. Yield 0.48g , 69.6%.

IR: ν (O-C-O) 1568 cm^{-1} (s), 1610 cm^{-1} (sh) ν (P-Ph) 1433 cm^{-1} (s). (Found : C, 54.96; H, 4.84; N, 0.0) $C_{30}H_{30}O_4P_2Pd$ requires C, 57.84; H, 4.84; N, 0.0). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 58.8 ppm.(s);. An attempt was made to purify the sample by passage through a column of neutral alumina but was unsuccessful.

3.3.7 The synthesis of bis(acetonitrile)bis(triphenylphosphine)-palladium(II)bis(tetrafluoroborate) $[Pd(CH_3CN)_2(PPh_3)_2][BF_4]_2$

Following the procedure outlined by Sen[13], a clean, dry, 100 ml round-bottomed flask was taken into the glovebox and charged with $[Pd(CH_3CN)_4][BF_4]_2$ (0.26g, 0.586 mmol) and PPh_3 (0.31g, 1.18 mmol). The flask was attached to the Schlenk line and using standard Schlenk techniques CH_2Cl_2 (30 mls) was added by cannula. The solution produced was stirred for 1 hour before the solvent was removed

under vacuum and anhydrous ether added . However, an intractable red oil was produced. It was decided to redissolve this in CH_2Cl_2 and precipitate using hexane. A dark-yellow crystalline powder was formed. On recrystallising from hot dichloromethane some finely divided palladium metal was removed and bright yellow crystals formed. Analysis showed this not to be the intended product but a palladium chloride compound. The preparation was repeated substituting acetonitrile as solvent for dichloromethane and subtituting hexane as precipitating agent for ether. A different coloured yellow crystalline sample of the target complex was easily obtained with a yield of 0.43g (82.75%). IR: ν (C≡N) 2325 cm^{-1} (lit.[13] 2335 cm^{-1}, Nujol) ; ν (P-Ph) 1436 cm^{-1}; ν (BF_4^-) 1100-1000 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ = 34.3 ppm (s),(lit[13]. 32.1 ppm at -50°C).

3.3.8 The synthesis of $Pd(OAc)_2(PPh_2Py)_2$

Palladium acetate (0.1g, 0.44 mmol) and 2-pyridyldiphenylphosphine (0.24g, 0.9mmol) were dissolved together in toluene (50 mls), and the solution stirred for 60 minutes at ambient temperature under a nitrogen atmosphere. Approximately one half of the toluene was removed *in vacuo* and 25 mls of hexane added. The gelatinous orange precipitate formed was washed with more hexane and residual toluene removed by washing with diethyl ether. Yield 0.184g (49%) orange-brown powder. (Found C, 54.04; H, 4.15; N, 3.10; $C_{38}H_{34}N_2O_4P_2Pd$ requires C, 60.77; H, 4.56; N, 3.73%) and the Pd-Pd bonded dimer* $C_{38}H_{34}N_2O_4P_2Pd_2$ requires C, 53.23; H, 4.00; N 3.27%). IR: ν(O-C-O) 1718 cm^{-1}; ν(P-Ph) 1438 cm^{-1}. $^{31}P\{^1H\}$NMR (C_6D_6): δ 18.46. (* see chapter 7)

3.3.9 The synthesis of $Pd(OAc)_2(PPh_2Me)_2$

Palladium acetate (0.2g, 0.88 mmol) was dissolved in toluene (50 mls) in a Schlenk tube, and diphenylmethylphosphine (0.24g, 0.9mmol) was also dissolved in toluene (10 mls) in a second Schlenk tube. The phosphine was transferred to the palladium by cannula and the mixture stirred for 60 minutes at ambient temperature

under a nitrogen atmosphere. Approximately one half of the toluene was removed by pumping and hexane (25 mls) added. The colour changed from amber to salmon pink . A pale yellow precipitate formed, and after separation by filtration was washed with more hexane and residual toluene removed with diethyl ether. Yield 0.272 g , (50%) of pale yellow powder. (Found C, 57.30; H, 5.12; N, 0.0; $C_{30}H_{32}O_4P_2Pd$ requires C, 57.66; H, 5.16; N, 0.0%) $^{31}P\{^1H\}$ NMR: δ = 16.09 ppm (87P), 6.40 ppm(10P), 4.68 ppm(3P). ^1H NMR ($CDCl_3$): δ = 1.5-1.6 ppm (s,12 H), 7.2-7.7 ppm (m,20H).

3.3.10 The synthesis of diphenylphosphinoquinoline

An initial approach involved the synthesis and use of diphenylphosphine following a procedure described by Wittenberg and Gilman[36]. A mixture of triphenylphosphine (10g) was stirred with Li wire (1.4g) under an atmosphere of argon. THF (100mls) was added slowly with stirring over 60 minutes. The suspension was cooled to 0° C, excess lithium metal removed by filtration and diethyl ether (50 mls) added. This was shaken with acidified water (25 mls), then deionised water (2 X 25mls). The solvent was removed from the ether solution, and the residual liquid was distilled twice from $MgSO_4$ to yield 2.6g (36%) diphenylphosphine (b.p. 150-154° C, 11 mmHg).

A 250ml round-bottomed flask was charged with $Pd(PPh_3)_4$ (50mg) in the glovebox. Toluene (100ml), diphenylphosphine (2.6g) and triethylamine (10g) were added by cannula. 8-Chloroquinoline (1.7ml) was added by syringe with stirring and the solution refluxed under nitrogen for 3hrs.

However, monitoring of the reaction solution by ^{31}P NMR showed only a signal for starting material, and it was assumed that no reaction had taken place. This procedure is known to work using diphenylphosphine oxide and it was thought that the hydrogen on diphenylphosphine is insufficiently acidic to be removed by triethylamine.

Finally the following procedure was adopted. Triphenylphosphine (5g, 19.1 mmol) was stirred with Li wire (0.014g, 0.02 mol.) under argon. THF (50 ml) was added with stirring which was continued for 2 hours. The solution was filtered into a round-

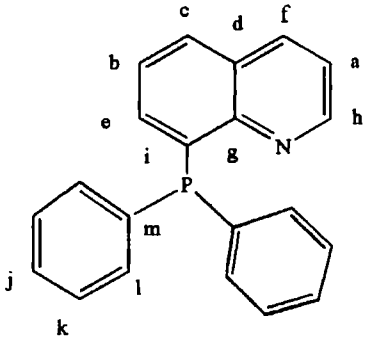
bottomed flask containing 8-chloroquinoline (2.5 mls, 0.02 mol.) in THF (25 mls) and stirred for 1 hour. The THF was then removed under vacuum and 40ml of degassed water added. The reaction mixture was agitated for 10 minutes then extracted with toluene (4 X 25 mls). The toluene extracts were passed through a column of silica before leaving in the freezer to crystallise. The white powder was further purified by dissolving in CH_2Cl_2 and passing through a plug of neutral alumina. The solvent was removed by evaporation and the residue dried at 100°C for 24 hours.

Yield of white product 1.3g (21%). Found (C, 77.12; H, 4.96; N, 4.26. $C_{21}H_{16}NP$ requires C, 80.50; H, 5.15; N, 4.47%)(Found $C_{21.02}H_{16.11}N$, residue incombustible).

$^{31}P\{^1H\}$NMR ($CDCl_3$): δ -13.8 ppm.

^1H NMR ($CDCl_3$): δ 7.04 (H_e dd, $^3J_{be}$ 7.2Hz, $^4J_{ce}$ 3.8 Hz 1H); 7.1-7.4 ($H_{c,b}$, C_6H_5, m, 13 H); 7.74 (H_a d,$^3J_{af}$ 8Hz., ^4J not resolved, 1H); 8.09 (H_f dd, $^3J_{af}$ 8.4Hz, $^4J_{hf}$ 1.6 Hz); 8.79 (H_h dd, $^3J_{ha}$ 4Hz, $^4J_{hf}$ 1.6 Hz) ppm.

^{13}C NMR: δ 150.029 (C_h d, $^1J_{CH}$ 2.15 Hz, 1C); δ 149.766 (C_g s,1C); δ 138.693(C_i d,$^1J_{CP}$ 12.07 Hz, 1C); δ 137.670 (C_m d, $^1J_{CP}$ 10.96 Hz, 1C); δ 134.370 (C_l dd, $^2J_{CCP}$ 19.03 Hz, $^1J_{CH}$ 2.16 Hz, 4C); δ 129.128 (C_e s, J_{CH} not resolved, 1C); δ 128.960 (C_d s, 1C); δ 128.713 (C_j s, J_{CH} not resolved, 2C); δ 128.563 (C_k d, $^3J_{CCCP}$ 6.9 Hz, 4C); δ 128.099(C_c d, $^1J_{CH}$ 2.21 Hz, 1C); δ 126.754 (C_b s, J_{CH} not resolved, 1C); δ 121.590 (C_a s, J_{CH} not resolved, 1C); ppm.



Scheme 3.15 assignments for diphenylphosphinoquinoline

3.3.11 The synthesis of bis(acetato)diphenylquinolylphosphinopalladium(II)

Palladium acetate (0.226g, 1.0 mmol) and diphenylphosphinoquinoline (0.313g, 1.0 mmol) were each dissolved in separate aliquots of toluene (20 mls). The phosphine solution was added slowly to the palladium solution forming an instant precipitate. The solution volume was reduced *in vacuo* to 20 mls and hexane (40 mls) added to complete precipitation. The suspension was filtered and the residue washed with 4 X 20 mls. diethyl ether. Yield 0.37g .

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 53.8 (s). IR (KBr): ν(O-C-O) 1584 cm^{-1}

3.3.12 The synthesis of dichlorodiphenylquinolylphosphinopalladium(II)

Diphenylphosphinoquinoline (0.1g , 0.32 mmol) and palladium dichlorobisbenzonitrile (0.15g, 0.32 mmol) were separately dissolved in CH_2Cl_2 (3 mls) in 10 ml. Schlenk tubes. On dropwise addition of the phosphine solution to the palladium solution a brick red precipitate formed. The precipitate was separated by filtration and washed with further dichloromethane and with petroleum ether (60-80°).

The product showed a new phosphorus NMR signal at δ 38.6 ppm. Crystals were submitted for analysis by x-ray diffraction which confirmed the structure of diphenylphosphinoquinoline. The structure of the palladium complex shows a five-membered chelate ring (appendix IV). (Found: C, 44.41; H, 2.65; N, 2.48; $C_{21}H_{16}NPCl_2Pd \cdot CH_2Cl_2$ requires C, 45.9; H, 3.15; N, 2.43%). IR: ν(*cis* Pd-Cl) 312 cm^{-1} (sh),286 cm^{-1} (s) (cf. lit. $PdCl_2$dppe ν = 310 cm^{-1} , 286 cm^{-1}).[34]

3.4 Procedure for the Catalytic Studies

The catalysed reaction is the hydroesterification of ethene.

$$CH_3OH + CH{=}CH_2 + CO = CH_3CH_2COOCH_3$$

Catalytic studies involved using the complexes prepared both as homogeneous catalysts and as supported catalysts in Nafion. The procedures for typical runs and the analysis of products are set out below using equipment described in Appendix (I).

3.4.1 Homogeneous Catalytic Run Procedure.

The glass liner and autoclave were washed and rinsed with acetone, then dried in the oven. The liner was charged with a pre-weighed quantity of metal complex (catalyst) and where appropriate a pre-weighed quantity of phosphine (usually an excess). A quantity of melted *p*-toluenesulphonic acid, representing an excess was transferred to the liner by syringe from a supply, previously dried following the procedure by Perrin and Armarego[36] and methanol (30 mls) was added by pipette. The glass liner was transferred to the autoclave and the assembly taken to the high pressure laboratory. The autoclave-lid was screwed in place with two O-rings forming the seal, one of Viton nearest the outside, the other of PTFE in contact with the reaction solution. The autoclave was flushed several times with N_2 gas and tested for pressure tightness with the same gas. The vessel was flushed twice, and then charged to a predetermined pressure with ethene. The pressure was then increased to a predetermined amount using CO (unless stated otherwise this was 20 bar for each gas). The valves were closed to isolate the autoclave with a minimum volume of pipework, the stirrer was started and the heating programme commenced. On reaching 30° the computer data collection system was started, monitoring and storing data from the in-line pressure transducer. When the autoclave reached the desired temperature, the timer was started to automatically cut the supply to the heater after a predetermined time.

After completion of the run, data storage was halted and the apparatus allowed to cool. When ambient temperature was attained, the valves connecting the autoclave to the manifold were opened and the excess pressure slowly vented to air. The autoclave was then flushed carefully, twice with N_2 gas and removed to the laboratory.

The contents were filtered, and a portion of the solution distilled under vacuum into a liquid nitrogen trap, then transferred to a storage bottle ready for subsequent analysis by gas chromatography.

3.4.2 Supported Catalytic Run Procedure

A 100 ml round-bottomed flask, the glass liner and autoclave were washed and rinsed with acetone, then dried in the oven. The flask was charged with a pre-weighed quantity of metal complex (catalyst) and where appropriate a pre-weighed quantity of phosphine, (usually an excess). Dichloromethane (30 mls), dried over molecular sieve, was added and the mixture stirred until complete dissolution was achieved. A pre-weighed quantity of dry Nafion beads was added to the solution and stirring continued overnight until the solution had lost all colour and the Nafion taken on that colour. The dichloromethane was removed by vacuum and the beads transferred to the glass liner. Methanol (30 mls), dried over molecular sieve, was added by pipette, plus another pre-weighed quantity of phosphine. The remainder of the procedure was identical with that for homogeneous runs.

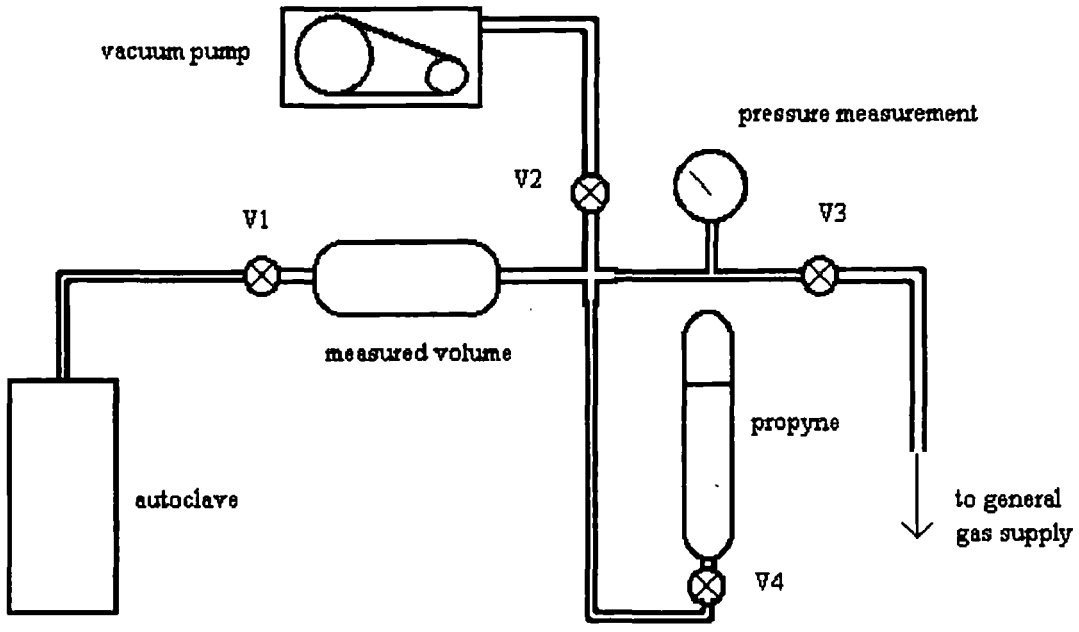
3.4.3 Modified Catalytic Run Procedures for Air/Moisture-sensitive components

For air-sensitive compounds, the glass liner was transferred to a glovebox and the weighed reactants and support added. The liner was then sealed with a bung, having a tap fitting, for connection to a Schlenk line. After removal from the glovebox, solvent was added to the sealed liner using standard Schlenk techniques. After fitting the liner into the autoclave, the seal was quickly removed against a flow of nitrogen.

3.4.4 Procedure for Propyne Hydroesterification

Propyne is a gas under normal laboratory conditions but liquifies under modest pressures. When contained in a cylinder it is present as both liquid and gas with a

pressure of 3-5 bar depending on ambient temperature. Pressure measurement, used for measuring the amounts of "permanent" gases added was not appropriate. Accordingly, to deliver a constant amount for a comparative series of catalytic runs, it was necessary to devise an experimental set-up in which the propyne was measured by filling a fixed volume. The gas system is depicted in Scheme 3.16 below. The propyne cylinder was inverted as shown.



Scheme 3.16 Pipework for Propyne Hydroesterification

Having charged the autoclave in the manner described in 3.4.1 , valves V2 and V4 were closed, V1 and V3 opened, allowing flushing of the autoclave with nitrogen. Valves V1 and V3 were then closed and V2 opened. The lines and measured volume were evacuated. V2 was then closed and V4 opened and the pressure noted. Valve V4 was closed again and V1 was opened and stirring commenced. The lines to V3 were flushed with CO and vented twice before pressurising with CO to approximately 10 bar. V3 was then opened allowing the CO pressure to drive the propyne into the autoclave. Finally V3 was closed again to reduce the volume heated during the experiment.

3.5 Procedure for The Determination of Products

3.5.1 Methyl Propanoate

Three standard solutions of methyl propanoate in methanol were prepared. 0.2g, 0.5g and 1.0g samples were weighed and dissolved separately in 10 mls methanol, equivalent to 0.6g, 1.5g and 3.0g in 30 mls. 1.0μl of each was injected into a HP 5890 Series II gas chromatograph with flame ionisation detector, containing a SE30 capillary column. The ratio of areas of the methyl propanoate peak to the methanol peak was determined in each case and found to fit a straight line plotted against concentration, thus establishing a linear response in this range. Each time the GC was used to measure the amount of propanoate produced, the most concentrated sample was also injected in order to determine the FID response. The methanol used in each run acts as an internal standard.

Any polymer produced was removed by filtration, washed and weighed. An infra-red spectrum was recorded to confirm the presence of the characteristic C=O stretch at 1690 cm^{-1} for polyketone.

3.5.2 Methyl Methacrylate

In a manner analogous to the procedure outlined in section 3.5.1 a series of 3 standards of methyl methacrylate was made by dissolving 2,5 and 10 g of MMA in methanol (100 mls) these being equivalent to 0.6g, 1.5g and 3.0 g respectively in 30 mls methanol. The three standards analysed by GC gave a linear response. Once again methanol acts as an internal standard in determining MMA concentration in reaction samples. A standard solution of methyl crotonate was also prepared to establish the retention time and response factor for this potential product.

3.6 Catalytic Studies

3.6.1 Ethene Hydroesterification

Amounts of methyl propanoate produced are reported as turnover frequency (TOF), quoted in mol (mol catalyst)$^{-1}$ hour^{-1}, and yield, quoted in grams (gram palladium)$^{-1}$. Polyketone, when produced, was removed by filtration and weighed, but yields and rates of its production are not quoted.

In total, seven catalyst systems were examined for their activity towards hydroesterification (reaction 1), or to the related polymerisation (reaction 2).

(1) $CH_2{=}CH_2 + CO + CH_3OH = CH_3CH_2COOCH_3$

(2) $n\ CH_2{=}CH_2 + n\ CO = -(CH_2CH_2CO)_n-$

Each of the seven in turn was immobilised in Nafion and its activity similarly measured. Reaction conditions were P_{CO} 20 bar, P_{ethene} 20 bar, T = 90°C . Reaction continued to the apparent completion stage as indicated by no further change in the pressure.

The results are shown below in Table 3.6.1.

Table 3.6.1 Comparison of Rates and Yields for Methyl Propanoate Formation using Homogeneous and Supported Homogeneous Catalysts.

	Run number	homogeneous		Run number	Nafion supported	
methyl propanoate rates and yields		TOF (mol/mol.hr)	Yield (g /g Pd)		TOF (mol/mol.hr)	Yield (g/g Pd)
$Pd(OAc)_2(PPh_3)_2$	#53	0	0	#47	258	1500
$PdCl_2(PPh_3)_2$	#54	258	432	#36-38	0	0
$Pd(PPh_3)_4$	#55	522	867	#35	0	0
$Pd(CH_3CN)_4[BF_4]_2$	#56	135	225	#34	0	0
$Pd(MeCN)_2(PPh_3)_2[BF_4]_2$	#66	0	0	#65	4.5	22.5
$Pd(OAc)_2$dppe	#57	0	0	#49	0	0
$Pd(OAc)_2(PPh_2Me)_2$	#88	0	0	#87	0	0
$Pd(OAc)_2 + PPh_3$	various	240-648	201-540	#63	27	114

homogeneous catalysis with 20 molar excess ligand and 10 molar excess *p*-toluenesulphonic acid, supported catalysis with 20 molar excess ligand

From Table 3.6.1 it can be seen that the most active catalyst for methyl propanoate production in the supported state was $Pd(OAc)_2(PPh_3)_2$.

Using this catalyst system, variations in experimental parameters were explored. Firstly the effect of temperature on rates and yields of products was determined. $Pd(OAc)_2(PPh_3)_2$ (0.01g) together with triphenylphosphine (0.3g) was dissolved in CH_2Cl_2 (30 mls) and stirred overnight under nitrogen with 3g of Nafion beads. The solution was removed by cannula and the beads dried *in vacuo*. The beads were divided into three portions of 1g, for each of the runs 40,41 and 42. Each run was of 7 hours duration.

The results are shown in Table 3.6.2 below.

Table 3.6.2 The effect of temperature on rates and yields.

Run number	#41	#40	#42
Temperature (P_{total} = 40 bar)	80°C	90°C	105°C
grams ester	0.819	0.744	0.828
Turnover mol/mol.hr	282	258	285
Yield g/g Pd	1653	1500	1671

Secondly the effect of varying the total pressure was observed. Triplicate samples of Nafion (1g) were produced as described above for the temperature study, two of which were used with existing data. Again each run was of seven hours duration. The results are shown in Table 3.6.3 below.

Table 3.6.3 The effect of pressure on rates and yields

Run number	#41	#43	#45
Pressure (bar) (T = 80°C)	40	60	80
grams ester	0.819	1.77	1.26
Turnover mol/mol.hr	282	612	435
Yield g/g Pd	1653	3573	2544

Thirdly, the effect of increasing the amount of excess phosphine ligand was determined. Again triplicate samples of Nafion (1g) were produced as above and the excess triphenylphosphine was added to the methanol reaction solution.
The results are tabulated below in Table 3.6.4.

Table 3.6.4 The effect of excess added phosphine

Run number	#46	#47	#48
Excess phosphine (T = 80°C,P = 40)	2-fold	20-fold	200-fold
grams ester	0.552	0.744	1.23*
Turnover mol/mol.hr	267	258	270
Yield g/g Pd	1113[1]	1500	2481*

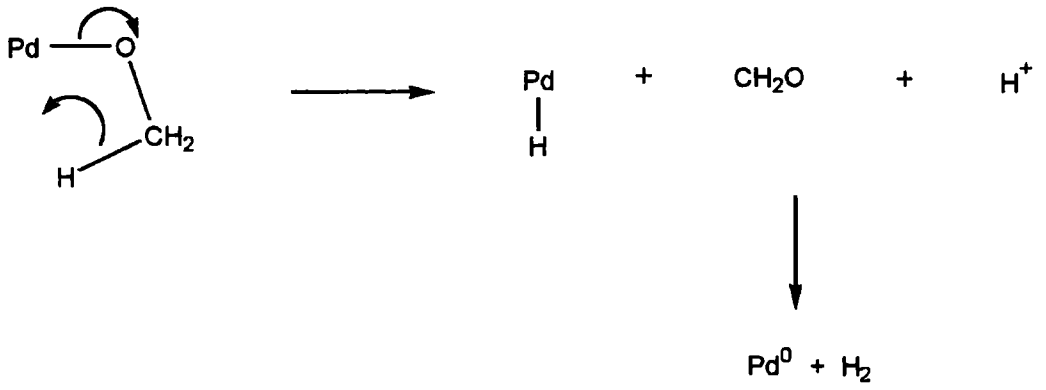
[1]stopped after 5 hrs *reaction continuing after 10 hrs

Finally, the effect of the loading of palladium complex in the Nafion was studied, with the results presented in Table 3.7.5 below.

Table 3.6.5: the effect of catalyst loading

Run number	#60	#61	#62
Catalyst loading in g.complex/g Nafion	0.01 (3X std.)	0.02 (6X Std.)	0.04 (12X Std.)
grams ester	1.086	1.713	0.87
Turnover mol/mol.hr	231	168	60
Yield g/g Pd	765	603	153

The reason for adding excess phosphine in methanol solutions is to protect the palladium against reduction to the metal by the solvent. Methanol slowly causes reduction of the palladium to the metal by β-elimination. Solutions recovered after catalysis using the Nafion supported complexes in some cases were coloured by the complex due to leaching and sometimes darkened by colloidal palladium metal.



Scheme 3.17: β-elimination of methanol

An important aspect of the study is to determine the ability to regenerate the Nafion for re-use. Run #64 used 1g of regenerated Nafion (see Chapter 2 for procedure) with $[Pd(OAc)_2(PPh_3)_2]$, this being the most effective supported catalyst. The turnover and yield were unaffected by the reclamation process (300 mol/mol Pd.hr and 1740 g/g Pd respectively, cf # 47, 258 mol/mol Pd.hr and 1500 g/g Pd).

Other forms of Nafion were investigated as a support for $Pd(OAc)_2(PPh_3)_2$, in which the acid sites are fully or partially replaced by alkali metal ions (Chapter 2, para. 2.3). Lithium carbonate was used as the source of lithium ions. The results are tabulated below in Table 3.6.6.

Table 3.6.6 : Forms of Nafion*

	Run Number	TON (mol/mol.hr)	Yield (g/g Pd)
Nafion-H^+	#40	258	1500
Nafion-Na^+	#26	276	2301
Nafion-Li^+	#68	0	0

*The results here are based on single runs, polymer formation (~80mg) was noted with the alkali metal forms of Nafion.

Concluding the section on catalytic runs, run #70 explored the ratio of Nafion to methanol solvent, while keeping the catalyst to Nafion loading standard. The catalyst used was $Pd(OAc)_2(PPh_3)_2$, 5 grams of Nafion were taken in place of 1g. There was some leaching and darkening of the beads and the turnover and yields were unremarkable at 293 mol/mol Pd.hr and 729 g/g Pd respectively.

3.6.2 Propyne Hydroesterification

A few initial runs were performed using $[Pd(OAc)_2(PPh_3)_2]$ as catalyst without detectable product formation.

The compound $[Pd_2(OAc)_2(PPh_2py)_2]$ (0.0035g, 0.008mmol) together with 0.1g excess ligand was dissolved in CH_2Cl_2 to give a yellow solution and stirred overnight with 1g vacuum dried Nafion beads. Interestingly the beads took on a red colouration (Chapter 7). The beads were used in a catalytic run following the procedure outlined in para.3.5.4 using the following reaction conditions: temperature 100°C , P_{CO} 20 bar, duration 5 hours. Analysis by GC showed production of 0.91g MMA corresponding to a TOF of 390 mol/mol.hr and yield of 1842 g/g Pd. Methyl crotonate was not detected. A similar experiment was performed using 1g of Nafion-Na^+ . It was necessary to introduce this in methanol as no absorption took place in CH_2Cl_2 (sodium acetate is insoluble in this solvent). There were no products detected by GC and the reaction solution contained colloidal palladium metal.

A direct comparison between a homogeneous run and a supported run was then performed using reaction conditions that resembled those used by Drent[32] as closely as possible.[†]

$[Pd_2(OAc)_2(PPh_2py)_2]$ (0.007g, 0.016mmol), PPh_2py (0.13g, 0.5 mmol) and *p*-toluene-sulphonic acid (0.344g, 2 mmol) were dissolved in degassed methanol (19g) to give a bright red solution and introduced to the autoclave following the procedure described in section 3.4.3. Reaction conditions of 40 bar CO, 80°C for 2 hours gave 0.539g of product equivalent to a yield of 337 mol/mol catalyst. Propyne was still present in the solution as detected by IR, and catalyst precursor was still detectable by phosphorus NMR, but pressure data indicated the reaction to be virtually complete.

$Pd_2(OAc)_2(PPh_2py)_2$ (0.0042g, 9.8μmol), PPh_2py (0.13g, 0.5 mmol) were dissolved in 28.2g degassed methanol and this introduced to 1g vacuum dried Nafion-H under nitrogen in the autoclave glass sleeve. The beads took on a red colour and the solution became colourless. The sleeve was introduced to the autoclave and using the same reaction conditions as before 0.94g of MMA was produced equivalent to a yield of 962 mol/mol catalyst. There was no visible catalyst leaching.

Two further catalytic runs were made, one using $Pd(OAc)_2PPh_2Q$ (0.009g, 0.016 mmol) with excess ligand (0.03g, 0.1 mmol) and *p*-toluene-sulphonic acid (0.344g, 2 mmol) and one using $Pd(OAc)_2PPh_2Q$ (0.0042g) with excess ligand (0.04g, 0.13 mmol) introduced into 1.0 g Nafion-H. Neither experiment produced any catalysis.

3.7 Discussion

It is common practice in research into homogeneous catalysis, particularly in industry, to allow the catalyst system to form in the reaction vessel by the addition of a ligand to a metal complex precursor. However catalysts formed *in situ* may fail to work in Nafion for the simple reason that in most cases one of the components fails to

[†] Drent conditions: 30mls propyne, 30 mls MeOH, 30 mls *N*-methylpyrrolidone, 60 bar CO, 0.025 mmol palladium acetate, 1 mmol ligand, 2 mmol p-CH_3PhSO_3H. Turnover frequency 40,000 mol(mol Pd^{-1} hr^{-1})

be absorbed. For example, palladium acetate and triphenylphosphine mixed *in situ* gave significantly higher rates and yields homogeneously than in the presence of Nafion for the simple reason that triphenylphosphine was not well absorbed by Nafion. Consequently the palladium acetate was preferentially absorbed and much of it was reduced to palladium metal.

Comparing the most active supported catalyst for methyl propanoate production, $[Pd(OAc)_2(PPh_3)_2]$, with the homogeneous analogue formed *in situ*, it can be seen that the rate of reaction was faster in the homogeneous case but that final yields obtained were higher in the supported case. Evidence from pressure measurements indicate that the homogeneous reaction was terminated well within 60 minutes (the figure the rate calculations are based upon) due to catalyst deactivation. In the supported case, reaction continues for the full seven hours of the run and has not gone to completion.

$[PdCl_2(PPh_3)_2]$ showed activity towards the production of methyl propanoate in the homogeneous case. In addition about 70 mg of polyketone was produced. Introduction into Nafion was hindered by the poor solubility of the complex in methanol and the poor absorption from CH_2Cl_2 solutions. The resultant Nafion supported complex produced only polyketone in similar amounts to the homogeneous case. The homogeneous results compare favourably with literature results.Bittler[7] *et al* reported the production of ethyl propanoate with 90% conversion of the ethene from a 0.35% catalyst solution under 300 atmospheres of CO. They rank this catalyst above the corresponding acetate under their conditions. Knifton[12] reported a yield of 42 mol/mol Pd for the production of methyl octanoate from 1-heptene at 80°C after 6 hours under 240 atmospheres CO.

Hydroesterification was achieved using $[Pd(PPh_3)_4]$ under homogeneous conditions. The mechanisms outlined in Scheme 3.4 start with Pd(II) species so to comply with these mechanisms palladium must be undergoing oxidation. Kushino[28] *et al* reported the successful hydroesterification of phenylacetylene using this catalyst. $[Pd(PPh_3)_4]$ was only slightly absorbed into Nafion. No methyl propanoate was produced, though a trace of polyketone was detected.

$[Pd(CH_3CN)_4][BF_4]_2$ is known to be inactive as a catalyst[13] without excess phosphine. The result quoted in Table 3.7.1 follows the standard practice for that series of experiments in that excess phosphine was added, leading to *in situ* generation of $[Pd(CH_3CN)_2(PPh_3)_2][BF_4]_2$ which is known to be an active catalyst. In contrast, the addition of excess phosphine to $[Pd(CH_3CN)_2(PPh_3)_2][BF_4]_2$ led to the *in situ* generation of $[Pd(PPh_3)_4][BF_4]_2$ which is known not to be an active catalyst. The complex $[Pd(CH_3CN)_2(PPh_3)_2][BF_4]_2$ remained intact during absorption into Nafion in the presence of excess ligand, however, and catalysis using the beads was successful. The literature study by Lai and Sen[13] of this class of compounds is directed towards the production of polyketone and therefore figures for the production of methyl propanoate are not quoted. Nafion supported run number 34 produced 0.3g polyketone equivalent to 280g/(g Pd) compared to the 75 g/(g Pd) quoted by Lai and Sen[13] for a similar system.

The catalyst system $[Pd(OAc)_2dppe]$ is known to be highly active for polyketone production[16] but inactive towards production of methyl propanoate. The lack of catalytic activity under the conditions of this study was most probably due to the large excess of ligand used, in contrast to the equimolar quantities used in the literature experiments.

The studies of the effect of reaction parameters showed that temperature had very little effect on the rate or yield of ester production. It was noted that decomposition to metal could occur at 90°C and above. Given this and the likelihood of increased side reactions at higher temperatures, as well as thermodynamic considerations (appendix III), all subsequent runs were performed at 80°C. An increase in pressure led initially to an increase in rate and yield but a further increase brought no extra improvement. One possible explanation for this is that the initial rate increase demonstrates that the addition of CO is the rate determining step in the catalytic cycle but that above a certain concentration of either CO or ethene the metal is fully coordinated and the cycle terminates. An increase in the amount of excess triphenylphosphine led to an increase in yield without a rate increase. The reaction continued for longer. The effect of catalyst loading is in agreement with the findings of

Seen *et al.*[35] in their study of ethene dimerisation. Improvements in rate and yield are obtained at lower catalyst loadings. This would appear to be a general effect and in all subsequent catalytic studies using Nafion, low loadings have been used as a matter of routine.

Production of methyl methacrylate from propyne is also improved by supporting the catalyst in Nafion under the conditions employed for the comparison. The results obtained for rates of MMA production, described in section 3.6.2., are considerably lower than those obtained by Drent[32] who used far higher concentrations of propyne and higher ligand to metal ratios than those used here. Optimised homogeneous conditions do not always relate to optimised supported conditions and so a compromise is sought to enable fair comparison.

3.8 References

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Chapter 4

Hydrogenation

4.1 Introduction

The use of Nafion as a support for hydrogenation catalysts is addressed in this chapter. The chapter starts with an historical overview of the development of hydrogenation using homogeneous catalysts, followed by examples of work reported in the literature of the use of polymers to support homogeneous hydrogenation catalysts. After the literature review, an experimental section follows in which the synthesis of established hydrogenation catalysts is described. Catalytic studies of these catalysts are performed in which their activity supported in Nafion is compared with their homogeneous activity. Finally the results obtained are tabulated and discussed.

4.1.1 Wilkinson's catalyst

The hydrogenation of unsaturated compounds using homogeneous catalysts was made a practical possibility in the 1960's, when the team led by Geoffrey Wilkinson[1] discovered the catalyst now named after him. The use of strong π-acceptor (π-acid) ligands such as phosphines was known to stabilise rhodium complexes against reduction to the metal and it was found that with an excess of triphenyl-phosphine, rhodium(III) chloride could be reduced to tris(triphenylphosphine)-chlororhodium(I).

The compound exists in two crystalline forms, red and orange, and is known to readily dimerise in concentrated solutions, forming the chlorine bridged dimer which has low solubility. The dimer can be reverted to the monomer by heating in ethanol with a 10 molar excess of ligand. In more dilute solutions the complex is in equilibrium with the bistriphenylphosphinechlororhodium(I) complex.

$$2RhCl(PPh_3)_3 = 2RhCl(PPh_3)_2 + 2PPh_3 = [RhCl(PPh_3)_2]_2 + 2PPh_3$$

Scheme 4.1

It is the vacant coordination sites generated by the loss of ligand in Scheme 4.1 that are the basis for the catalytic activity seen for this complex. The loss of ligand is thought to be driven by a combination of electronic effects (the *trans* effect[2]) and relief of steric crowding of the bulky phosphine groups.

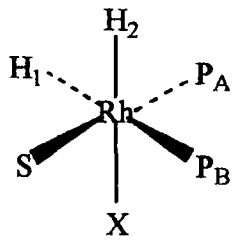
$RhCl(PPh_3)_3$ undergoes apparently irreversible reaction with CO to form the compound *trans*-$Rh(CO)Cl(PPh_3)_2$ and the affinity of $RhCl(PPh_3)_3$ for CO is sufficient for abstraction of CO from aldehydes to occur at room temperature leading to the same product complex[3]. The reaction of $RhCl(PPh_3)_2$, arising from the equilibrium in Scheme 4.1, with ethene leads to the ethene complex, which is readily isolated as yellow crystals from benzene or chloroform solutions, but in solution the complex is labile (Scheme 4.2), even at -50°C, and broad peaks are observed in the ^1H NMR spectrum.

$$RhCl(PPh_3)_2 + C_2H_4 = RhCl(PPh_3)_2(C_2H_4)$$

Scheme 4.2

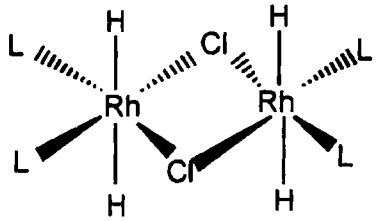
Solutions of $RhCl(PPh_3)_3$ react with 1 mole equivalent of molecular hydrogen, changing colour from red to yellow in the process. Purging with nitrogen gas restores the colour and the cycle can be repeated apparently indefinitely. In chloroform the solubility of the hydrido complex is low and white crystals are formed which analyse for $RhCl(PPh_3)_2H_2$. From dichloromethane yellow crystals of $[RhCl(PPh_3)_2H_2]_2.CH_2Cl_2$ can be obtained. The dihydro compounds are further characterised by infra-red data showing the metal-hydrogen stretches and bends (Nujol mull of solid 2078 cm^{-1} (m), 2013 cm^{-1} (m) and 785 cm^{-1} (m) respectively) and by proton NMR spectra showing low frequency hydrides ($CDCl_3$: δ -18.2 ppm (s, H(2), 1H) ; δ -10.15 (d, H(1), J_{PH} = 152 Hz, 1H). The coupling with phosphorus is consistent with an octahedral structure in which the phosphorus atoms are *cis* to each other and the hydrides are *cis* to each other, as depicted in Scheme 4.3. This was the first report of a rhodium hydride

species detected; however hydrides of ruthenium and osmium had been previously reported[4].

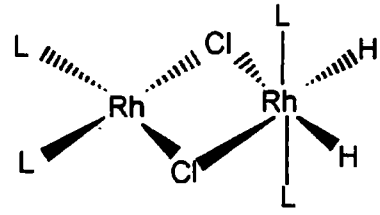


Scheme 4.3

$[RhP_2Cl]_2$ is dimeric and absorbs hydrogen to form a complex having the structure (A) shown in Scheme 4.4 . However, this structure was disputed by Tolman *et al.*[5] who suggested structure (B) in Scheme 4.4 following studies of $RhClL_3$ where L = *p*-tolyl.



A



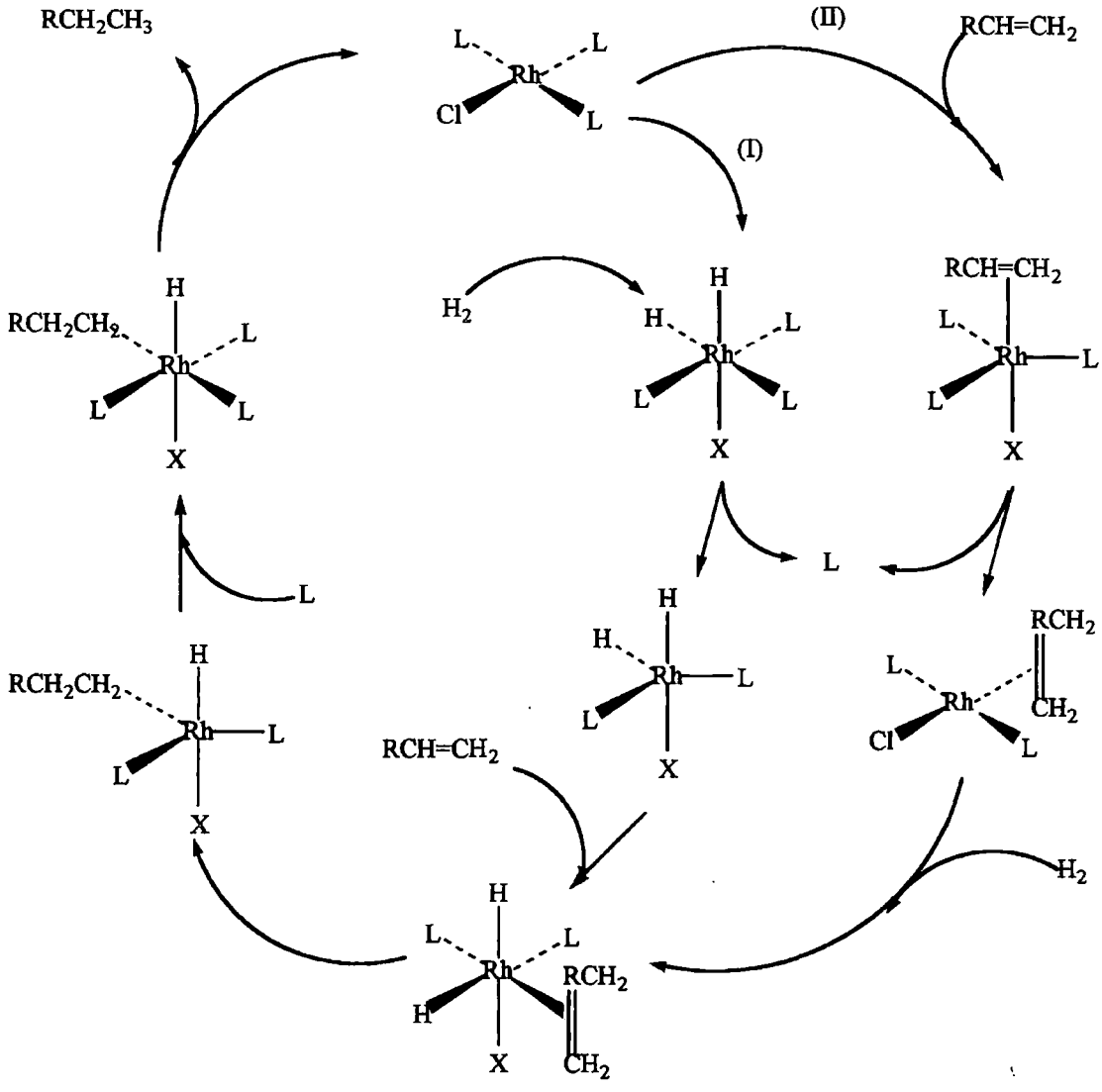
B

Scheme 4.4 Hydrogenated form of the dimer

In benzene or similar solvents, the tris(triphenylphosphine)halogenorhodium(I) complexes are efficient catalysts for the hydrogenation of non-conjugated alkenes and alkynes at ambient temperatures and pressures. Other functional groups are not readily reduced under these conditions. Terminal alkenes are hydrogenated more rapidly than internal alkenes. The iodo and bromo forms of the catalyst are more active than the chloro form. A related complex, $HRuCl(PPh_3)_3$, shows similar attributes but is more active than its rhodium counterpart.[6]

The initial step in the hydrogenation of an alkene is activation of molecular hydrogen by rhodium. The ability of rhodium to activate hydrogen is strongly

influenced by the nature of the phosphines coordinated to it. Montelatici *et al.*[7] continued the work described above by exploring the effect of modifying the electronic properties of the phosphine. Replacing the hydrogen in the *para*-position of the phenyl groups with fluorine results in a 10 fold decrease in the rate of hydrogen uptake during the hydrogenation of cyclohexene. Conversely, replacement of the *para*-hydrogen with a methoxy group increases the rate by 50%. Since neither structural change would be expected to alter the steric bulk of the ligands, the observed changes in rates can be unambiguously assigned to electronic effects. The CO stretching frequencies for *trans*-$RhCl(CO)(PR_3)_2$ are: R= *p*-$MeOC_6H_4$, ν(C=O)1950; R= C_6H_5, ν(C=O)1970 ; R= *p*-FC_6H_4, ν(C=O)1990 cm^{-1}. An electron releasing group lowers the effective oxidation state of the metal, increasing the metal-carbon bond order, which in turn lowers the carbon-oxygen bond order and hence its stretching frequency. However, an even more striking change occurs when mixed alkyl/aryl phosphines are used in comparison with triphenyl phosphine. Replacing one phenyl group with ethyl leads to a large drop in reaction rate. Replacing more than one phenyl group effectively leads to no reaction. For triphenylphosphine complexes the authors[7] considered the rate determining step to be displacement of coordinated solvent by incoming alkene. They attribute the lower reactivity of trialkylphosphine complexes to the rate determining step becoming transfer of the hydrogen atoms to the alkene. The full catalytic cycle is depicted below in Scheme 4.5.



Scheme 4.5 Catalytic cycle for hydrogenation of alkenes using 'Wilkinson type' catalysts.

The proton decoupled ^{31}P spectra of $RhClL_3$ solutions performed under 6.89 bar H_2 pressure at -25°C allow unambiguous assignment[5] of the species present in solution as *cis*-$[H_2RhClL_3]$. It can be seen from Scheme 4.5 that there are two routes before the hydrogen transfer step. Tolman[5] considered hydrogen addition, route (I), to occur considerably faster than ethene addition, (route II), and therefore most of the alkane is produced via route (I). Halpern and Chun[8] studied the kinetics for the reaction in the context of the various species depicted in Scheme 4.1 and established that the 3 coordinate rhodium complex is present only in very low concentration. Secondly, they

showed that this species reacts sufficiently fast with hydrogen to stop significant dimer formation and, at ligand concentrations below 0.15M, it provides the major pathway for hydrogen absorption. The 5-coordinate intermediates formed in both route (I) and route (II) were always assumed to contain phosphines in equatorial positions. However, a series of NMR experiments[9] suggested the presence of *cis*-phosphine intermediates. This is further supported by considerations of orbital overlap in the 4-centre transition state immediately prior to the intramolecular migratory insertion and loss of alkane. The migratory insertion step has been established as the rate determining step from kinetic studies[10] and an *ab initio* MO study of the cycle[11]

A closely related catalyst precursor is $HRh(CO)(PPh_3)_3$ which loses a phosphine in solution[12] to become the active catalytic species. This compound is highly selective for terminal alkenes[13] and is also very active towards isomerisation and hydroformylation (see Chapter 5).

4.1.2 Cationic rhodium catalysts

Rhodium hydrogenation catalysts made a further development in 1971 when Schrock and Osborn[14] synthesised a group of cationic complexes of the general formula $[Rh(diene)L_2]^+A^-$, where the diene could be cyclooctadiene or norbornadiene and the anion was usually non-coordinating such as ClO_4^-, BF_4^-, or PF_6^-. Treatment of solutions of these cationic species with hydrogen leads to addition and subsequent loss of the diene as alkane to leave species of the form $[RhL_2H_2S_2]^+$ where S represents a solvent molecule. Isolated $[RhL_2H_2S_2]^+$ species exhibit solid state infra-red spectra characteristic of *cis* bound hydride ligands and *cis* bound solvents. Synthesis of complexes of the form $[Rh(diene)L_2]^+A^-$ was usually achieved by the removal of chloride ions from the bridged dimer $[Rh(diene)_2Cl]_2$ in the presence of a phosphine.

In a suitable solvent, e.g. acetone or THF, $[RhL_2S_2]^+$ complexes are very active for the hydrogenation of alkenes[15]. The step involving loss of diene as alkane, has a notable influence on the rate of reaction, since complexes with norbornadiene (NBD) as diene react 100 times faster than complexes with cyclooctadiene (COD) as diene,

yet after loss of alkane the same species is formed. The complexes are also effective isomerisation catalysts for terminal alkenes such as hex-1-ene. The *cis* and *trans* hex-2-enes formed by isomerisation are hydrogenated more slowly than hex-1-ene and are not reduced or isomerised until the concentration of terminal alkene is low. Rates of isomerisation in the absence of hydrogen, increase when L varies, in the order $PPh_2Me < PPhMe_2 < PMe_3$, i.e. with increasing basicity.

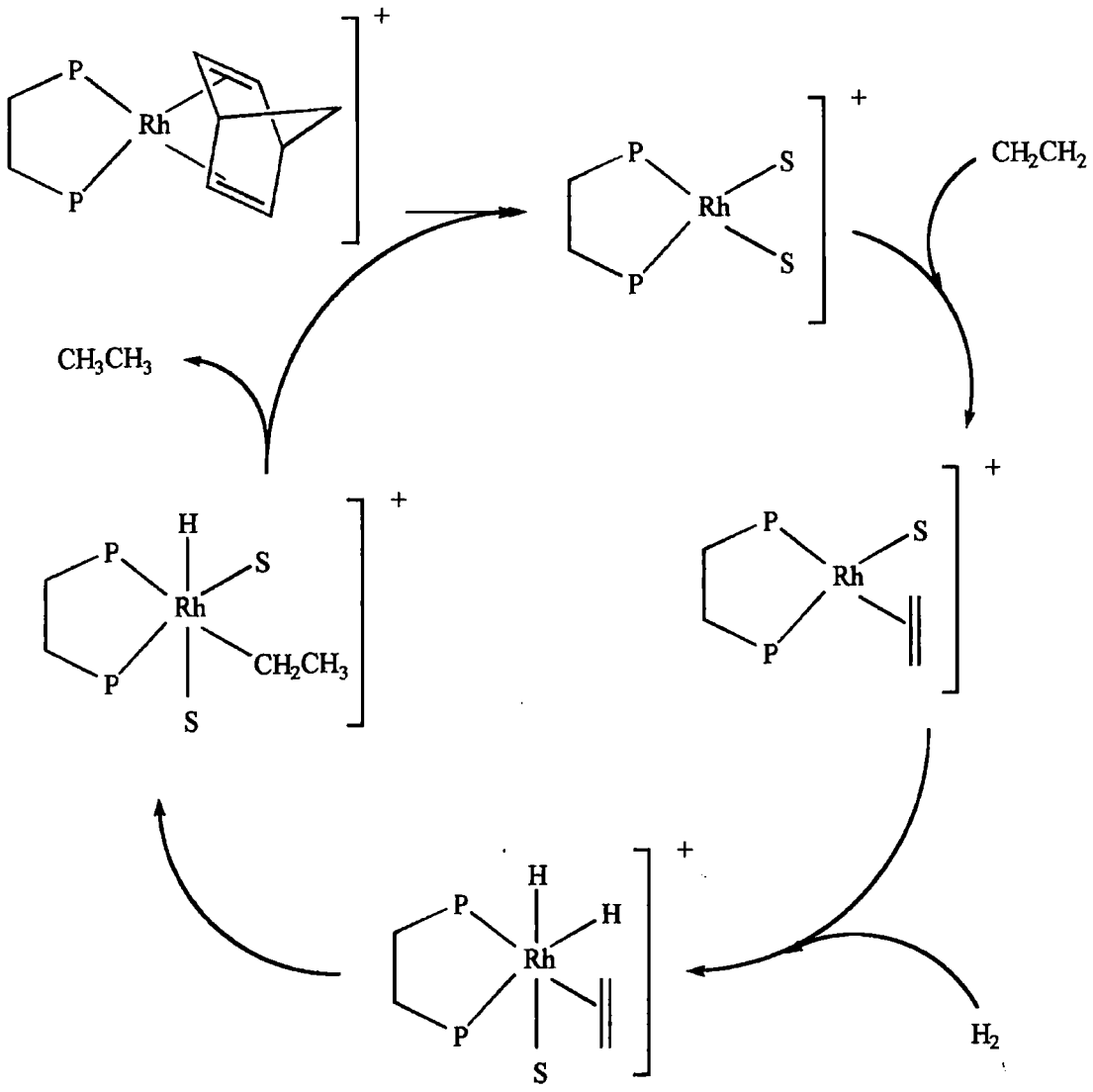
The replacement of the two monodentate phosphine ligands with a chelating phosphine leads to a change in the initial step of uptake of hydrogen[16] .In the case of monodentate phosphines, 3 moles of hydrogen are absorbed to form a rhodium(III) intermediate (Scheme 4.6). In the case of bidentate phosphines, only 2 moles are absorbed.

1) $[Rh(NBD)(diphos)]^+ + 2\ solvent + 2H_2 = [Rh(diphos)(solvent)_2]^+ +$ norbornane

2) $[Rh(NBD)(PPh_3)_2]^+ + 2\ solvent + 3H_2 = [RhH_2(PPh_3)_2(solvent)_2]^+ +$ norbornane

Scheme 4.6

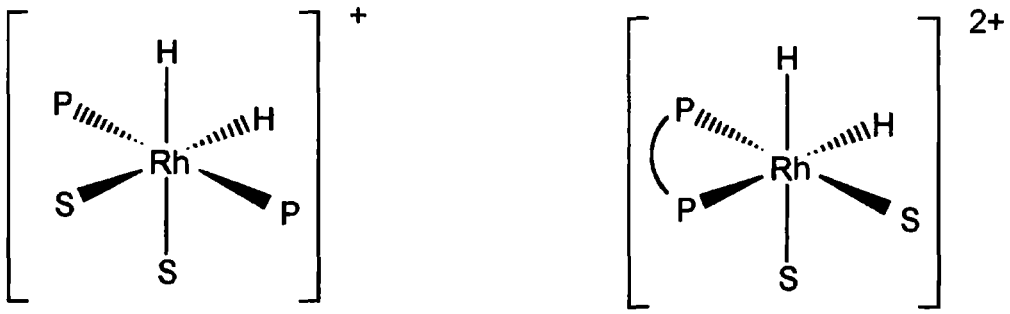
$[Rh(diphos)(solvent)_2]^+$ has been isolated as a BF_4^- salt and the crystal structure determined.The presence of weakly coordinated solvent molecules leads to it rapidly accepting incoming ligands such as alkene. The catalytic cycle is depicted in scheme 4.7



Scheme 4.7 Catalytic cycle for hydrogenation using a cationic rhodium complex having a chelating phosphine

The different reactivities of $[Rh(NBD)(diphos)]^+$ and $[Rh(NBD)(PPh_3)_2]^+$ towards H_2, shown in equations (1) and (2), highlight differences in the mechanisms of hydrogenation for each species. Whereas $[Rh(PPh_3)_2(solvent)_2]^+$ can form a H_2 adduct of structure 4.8.1 in which neither H is *trans* to a phosphine ligand, this is not possible (assuming *cis* disposition of the two H atoms) in the case of a chelating diphosphine ligand. This is expected to contribute to the instability of the H_2 adduct of $[Rh(diphos)(solvent)_2]^+$ and to result in a reduced equilibrium constant for the oxidative addition of H_2. The addition of a noncoordinating acid to a methanol or acetonitrile solution of

$[Rh(diphos)(solvent)_2]^+ BF_4^-$ led to facile oxidative addition of one hydrogen ligand. The structure 4.8.2 accounts for the ^1H NMR spectrum which revealed the *cis* hydride ligand coupled to rhodium and two equivalent P atoms.



1 2

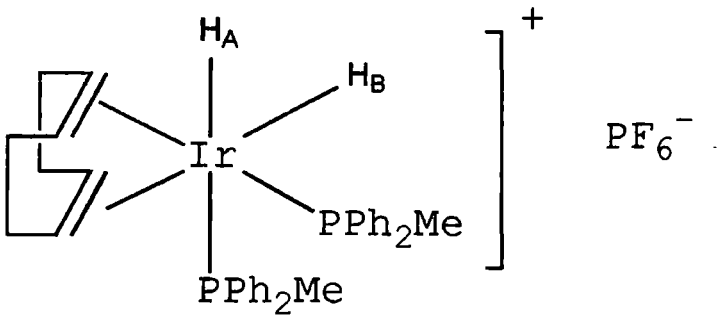
Scheme 4.8 Hydrogen complexes of rhodium having monodentate and bidentate phosphine ligands

4.1.3 Iridium catalysts

The properties of rhodium as a hydrogenation catalyst might be expected to be mirrored within the same group. The cobalt and iridium analogues of Wilkinson's catalyst, however, are entirely inactive, though for different reasons. The cobalt complex fails to react with hydrogen while the iridium analogue binds irreversibly with hydrogen to give the stable adduct $[IrClH_2(PPh_3)_3]$. Unlike the rhodium analogue, this adduct fails to dissociate PPh_3 to provide a vacant coordination site for subsequent alkene addition. Likewise ionic complexes of iridium of the form $[Ir(diene)L_2]^+A^-$ were considered virtually inactive as catalysts. Crabtree[17] set out to generate a catalytically active iridium species by attempting to dissolve these ionic complexes in non-coordinating solvents. Initial experiments in benzene, toluene and hexane yielded only precipitation. However the precipitates could be taken up in chlorinated solvents and it was discovered that the resultant solutions were highly active hydrogenation catalysts. The mixed ligand complex $[Ir(COD)PCy_3(py)]PF_6$ was found to be the most active

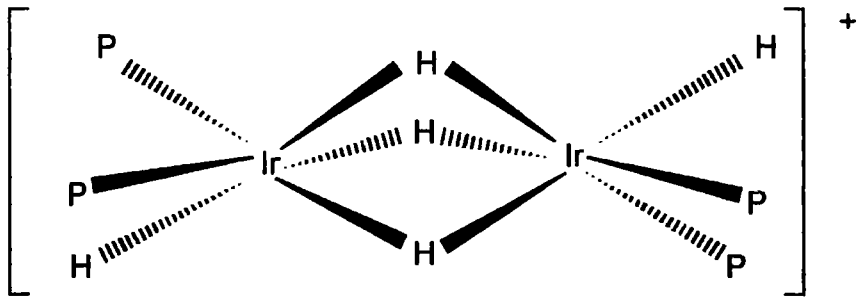
catalyst for a range of alkene substrates and could rapidly reduce hindered alkenes, such as tetramethyl ethene or 1-methylcyclohexene, in contrast to Wilkinson's catalyst, which failed completely with these alkenes. Reduction of unhindered alkenes proceeded 2 orders of magnitude faster than the case using Wilkinson's catalyst.

Solutions of $[Ir(COD)(PPh_2Me)_2]PF_6$ in CH_2Cl_2 (also a very active system) are red in colour. On addition of hydrogen they become colourless. Flushing with nitrogen restores the red colour and this process can be repeatedly cycled. A proton NMR spectrum[18] at -80°C of $[Ir(COD)(PPh_2Me)_2]PF_6$ in CD_2Cl_2 under hydrogen allowed the structure to be determined (Scheme 4.9). Two hydride resonances were observed, a triplet, due to H_B coupling to two *cis* phosphorus nuclei, and a doublet of doublets, due to H_A, coupling to one *trans* and one *cis* phosphorus nucleus. Other spectral features were also consistent with the structure shown.



Scheme 4.9 Iridium complex hydrogen adduct

Catalytic hydrogenation of alkene proceeds until the alkene is consumed, and then the solution takes on a yellow colouration due to the formation of the hydride-bridged dimer shown in Scheme 4.10, the structure of which was elucidated by X-ray crystallography and low temperature ^1H NMR.



Scheme 4.10 Dimers formed on depletion of alkene substrate

Similarly, addition of hydrogen before addition of alkene leads to immediate deactivation. The catalyst $[Ir(COD)PCy_3(py)]PF_6$, forms a deactivated trimeric species when all the substrate has been consumed.

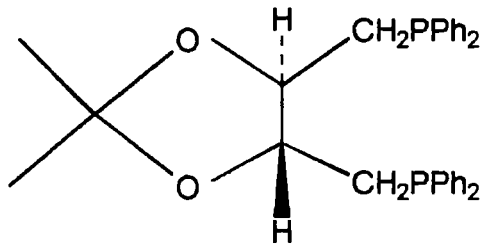
Once the species in Scheme 4.9 has been formed, hydrogen is transferred to the coordinated COD which is lost as cyclooctene. In the presence of excess COD a new complex ion is formed which differs from that depicted in Scheme 4.9 in that the hydrogens are now *trans* to the COD and further hydrogenation cannot take place. The *cis* complex in Scheme 4.9 benefits from coplanarity of the M-H and C=C bonds.

4.1.4 Asymmetric hydrogenation catalysts

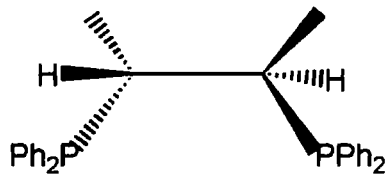
Homogeneous, catalytic hydrogenation generates the most commercial interest when applied to asymmetric systems. The ability to generate one enantiomer, in high excess, is exclusive to homogeneous systems and of great importance to the manufacture of biologically active molecules. Selectivity can be conferred on the catalyst by suitable design of the ligand system. The cationic rhodium diphosphine complexes described in para.4.1.2 function with a wide variety of chelating phosphines and it is the design of chiral chelating phosphines that has been the centre of research efforts. Replacement of two of the PPh_3 ligands in Wilkinson's catalyst by an optically active, chelating diphosphine was an early approach.

An example of a chiral phosphine, now serving as a benchmark for future developments was reported by Kagan[19] in 1972. Starting with (-)-tartaric ester the phosphine known as DIOP was synthesised (Scheme 4.11). This was allowed to react with $[RhCl(cyclooctene)_2]_2$ *in situ* to form the active catalyst.

N-acetyl-(R)-phenylalanine was produced in high yield and 70% optical purity from a range of precursors. Fryzuk and Bosnich[20] prepared CHIRAPHOS from a (-)(2R,3R)-butanediol (Scheme 4.11). This they allowed to react with $[Rh(NBD)_2]ClO_4$ to form a cationic rhodium catalyst. A range of amino acids was produced from unsaturated substrates with optical yields ranging from 70-100%. The list of chiral phosphines now available is extensive.



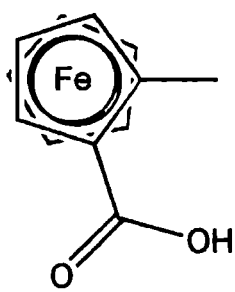
DIOP



S,S-CHIRAPHOS

Scheme 4.12

More recently, considerable interest has been shown in the use of modified ferrocene based diphosphines as chiral ligands. Two different substituents on the same ferrocene ring confer chirality to the molecule (Scheme 4.12).



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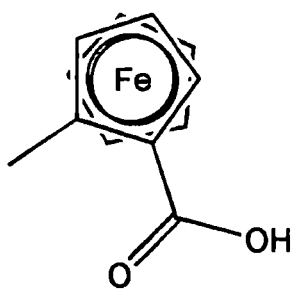
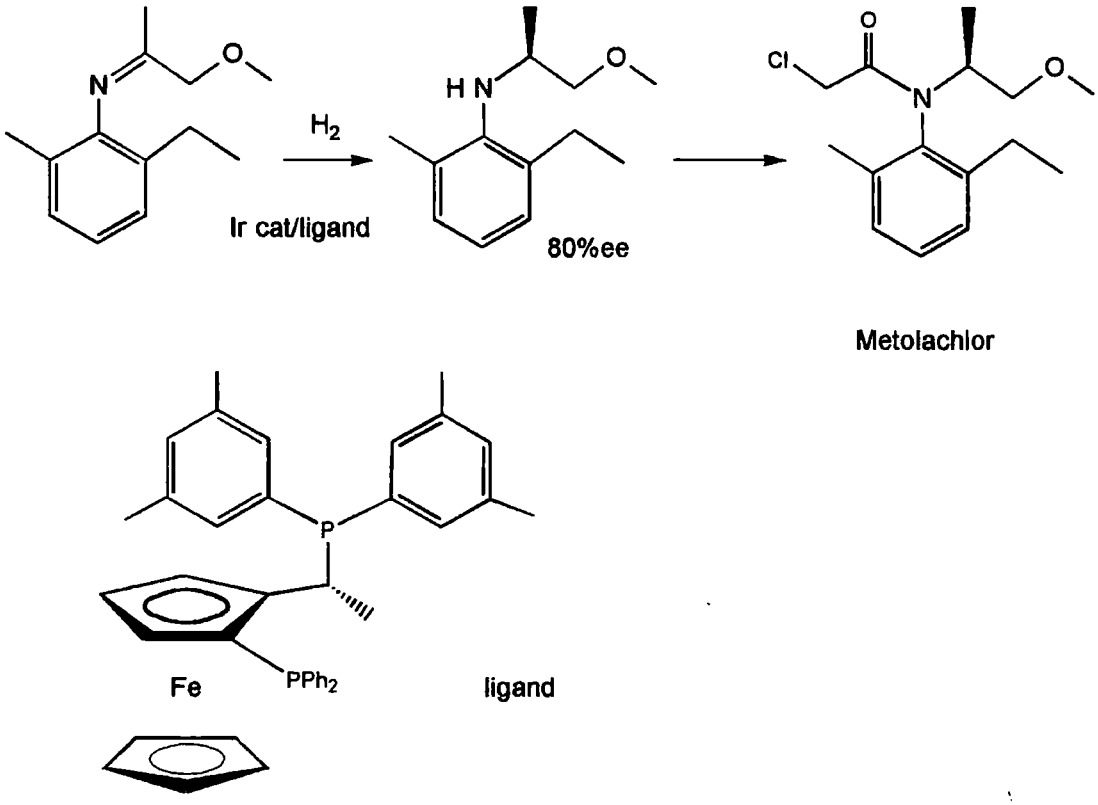


R

Scheme 4.12 Chirality in disubstituted ferrocenes

A comprehensive review of the synthetic methods involved in the production of chiral ferrocenyl phosphines has been written by Togni[21]. Among the examples quoted is one of the first industrial applications of this class of ligand, for the production of the herbicide Metolachlor (Scheme 4.13)



Scheme 4.13 Industrial production of Metolachlor

A related ligand, known as Josiphos, differs from the ligand depicted in Scheme 4.13 in that the xylene groups are replaced by cyclohexyl groups. Conveniently, it can be synthesised in two steps in high yield from commercially available starting materials[22]. Solutions of 1 mol % $[Rh(NBD)_2]BF_4$ + Josiphos catalysed the hydrogen reduction of dimethyl itaconate to dimethyl (S)-2 methylsuccinate in 100% chemical yield and 98% optical purity after 30 minutes. These figures had hitherto only been matched by a ruthenium-BINAP system. Chirality can also be introduced at the phosphorus atom[23],

whilst maintaining the C_2 symmetry of the ferrocene centre. No further improvement of performance results from this approach however.

4.1.5 Supported catalysis

The analogue of Wilkinson's catalyst bound to polystyrene was found to show reduced activity for the hydrogenation of alkenes, particularly those with greater bulk[24]. It is not inevitable, however, that catalysts polymerised through their ligands will work more slowly than their homogeneous analogues. Grubbs[25] *et al.* report a sixfold rate increase in the rate of hydrogenation of hexene and cyclohexene using a polymer attached titanocene catalyst. It is important to note here that the usual catalyst deactivation route is via chlorine bridged dimerisation. The deliberate use of a highly cross-linked polymer limits this deactivation route. Even when polymerised Wilkinson type catalysts are used, the rate decrease can be ameliorated by using low degrees of cross linking and finely divided beads.[26]

The use of resin bound catalysts also opens up the possibility of sequential reactions in the same reactor, either by two catalysts bound to the same resin, or by two separate resin bound catalysts contained within the same reactor. Pittman and Smith[27] employed this methodology to sequentially cyclooligomerise butadiene to 4-vinylcyclohexene and subsequently hydrogenate this to ethylcyclohexane. Nafion has been used as a support for hydrogenation catalysts[28], as described more fully in Chapter 1. The authors reported lower rates of hydrogenation compared to unsupported catalysis but were operating at high catalyst loadings, now known to be detrimental to high rates[29].

4.2 Experimental

General experimental details are described in Appendix (I)

4.2.1 The synthesis of phenyldipiperidylphosphine

Triethylamine (0.1 mol, 13.94mls) and piperidine (0.1 mol, 9.88mls) each vacuum distilled from P_2O_5, were dissolved in toluene (50 mls). Dichlorophenylphosphine (8.98

mls, 50 mmol) was freeze-thaw pump degassed in toluene (25 mls) and added dropwise to the solution of amines at -50°C. The solution was allowed to warm to room temperature and stirred for a further hour. A white precipitate of triethylamine hydrochloride formed. This was removed from the solution by filtration and the solution was reduced in volume. Hexane (25 mls) was added, and the flask allowed to stand overnight in a freezer. The white product separated and was removed by filtration, washed with diethyl ether, and dried *in vacuo*. Yield 5.8g (42%) of a hygroscopic, white solid. (Found: C 65.79; H 8.76; N 9.50; $C_{16}H_{25}N_2P$ requires C 69.54; H 9.12; N 10.14)

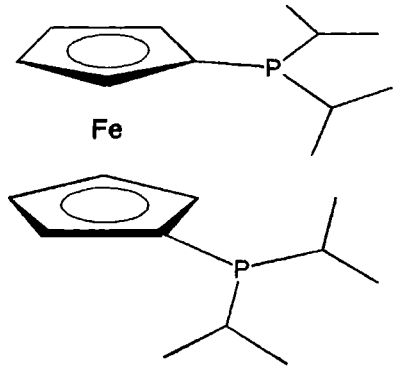
$^{31}P\{^1H\}$NMR ($CDCl_3$) δ = 97.28 ppm; ^1H NMR ($CDCl_3$) δ = 7.1-7.5 (m, 5H, C_6H_5); δ = 2.989 (t, $^2J_{HH}$ = 5.2 Hz, 8H, NCH_2); δ = 1.476 (dt, $^2J_{HH}$ = 6.0 Hz., 12H, CH_2CH_2) ppm; ^{13}C NMR ($CDCl_3$) C_{ipso} δ = 141.2 (d, $^1J_{PC}$ 4.7 Hz,1C); C_{meta} δ = 131.2 (d, $^3J_{PC}$ = 15 Hz, 2C); C_{ortho} δ = 128.3 (d, $^2J_{PC}$ = 3.32 Hz, 2C); C_{para} δ = 127.4 (d, $^4J_{PC}$ = 1.81 Hz, 1C); δ = 51.3 (d, ^2J = 14.28 Hz, 4C, NCH_2); δ = 28.2 (d, ^3J = 6.2 Hz., 4C, NCH_2CH_2); δ = 25.5 (s, 2C)ppm; IR $\nu_{P\text{-}Ph}$ (sh)1440 cm^{-1}.

4.2.2 The synthesis of diphenylpiperidylphosphine

Triethylamine (50 mmol, 6.97mls) and piperidine (50 mmol, 4.94mls) each vacuum distilled from P_2O_5, were dissolved in 30 mls toluene. Chlorodiphenylphosphine was freeze-thaw pump degassed and 8.98 mls (50 mmol) was added dropwise to the solution of amines at -50°C. The solution was allowed to warm to room temperature and stirred for a further hour. A white precipitate of triethylamine hydrochloride formed. This was removed from the solution by filtration and the solution was reduced in volume, an equal volume of hexane was added, and the mixture allowed to stand overnight in a freezer. The solution was filtered a second time and the filtrate washed with diethyl ether and dried *in vacuo* to give a hygroscopic, white solid. (Found: C 73.43; H 7.41; N 4.99; $C_{17}H_{20}NP$ requires C 75.81; H 7.48; N 5.20). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ = 63.60 ppm; ^1H NMR ($CDCl_3$): δ = 7.1-7.4 (m, 10H, C_6H_5); δ = 2.799 (t, $^2J_{HH}$ = 4.0 Hz, 4H, NCH_2); 1.398 (m, 6H, CH_2CH_2) ppm; ^{13}C NMR ($CDCl_3$); C_{meta} δ =

131.12 (d, $^3J_{PC}$ = 19 Hz, 4C); C_{ortho} δ = 128.3 (s, 4C); $C_{para.}$ δ = 128.19 (s, 2C); δ = 51.26 (d, ^2J = 13.5 Hz, 2C, NCH_2); δ = 27.50 (d, ^3J = 6.6 Hz., 2C, NCH_2CH_2); δ = 24.6 (s, 1C) ppm.

4.2.3 The synthesis of 1,1'bis(diisopropylphosphino)ferrocene



The procedure reported by Butler *et al.*[30] was followed.

2-Chloropropane (19ml., 208 mmol) was degassed by three freeze-thaw pump cycles and transferred slowly by cannula to a 250 ml. round bottomed flask fitted with a reflux condenser and containing previously dried magnesium turnings (5.8g, 240 mmol.) in 100 ml diethyl ether with continuous, rapid stirring. At the start of the reaction evidenced by evolution of hydrogen and heat, the apparatus was lowered into an ice bath. When virtually all the magnesium was consumed the ice-bath was removed. A second 250 ml. round bottomed flask was prepared containing previously distilled PCl_3 (14.3g, 104 mmol.) in 150ml diethyl-ether. The mixture was degassed by three freeze-thaw pump cycles and cooled to -70°C in an acetone, dry-ice slush bath. The isopropylmagnesium chloride was transferred slowly from the first flask by cannula filter with nitrogen pressure. Reaction takes place quite rapidly. The mixture was stirred for 15 minutes after addition was complete and allowed to warm to ambient temperature. Under inert atmosphere, the magnesium chloride was removed by filtration and washed once with diethyl ether and twice with CH_2Cl_2. The solvents were removed by vacuum to leave a clear liquid which was distilled under nitrogen. Yield 6.85 g , 8%, which is low partly due to the very large bulk of magnesium

chloride produced. NMR $^{31}P\{^1H\}$ of the reaction solution δ = 134 ppm. ^1H NMR ($CDCl_3$) δ = 1.87(septet, ^1J = 7.2 Hz, 2H, $ClP(CH_3CHCH_3)_2$); δ = 1.09 (m, 12H, $ClP(CH_3CHCH_3)_2$) ppm.

In a 200 ml Schlenk tube, ferrocene was purified by sublimation onto a water-cooled cold finger. Following a procedure developed by Rausch[31], the sublimed material (4.6g, 24 mmol) was dissolved in 150 mls hexane in a 250 ml Schlenk tube. In a similar flask, nBuLi (37.5 ml, 1.6M in toluene solution ; 60 mmol) and TMEDA (9 ml, 60 mmol) were dissolved in hexane (50 mls) and stirred for 10 minutes. The nBuLi-TMEDA adduct solution was added by cannula to the ferrocene solution at room temperature. Stirring was continued for a further 6 hours, during which time a precipitate of lithiated ferrocene appeared, before the hexane was removed by cannula and replaced with diethyl ether. The lithiated ferrocene was then cooled to -78°C in an acetone/dry ice bath and then the chlorodiisopropylphosphine added dropwise by cannula. The solution was allowed to warm to room temperature and stirring continued overnight. The resulting solution was filtered twice by cannula filter to remove LiCl. The solvent was removed to reveal a crystalline solid with some oil retaining the characteristic ferrocene colour. To remove excess chlorophosphines, the solution was hydrolysed with 50 mls degassed water containing Na_2CO_3. The organic layer was extracted with diethyl ether which in turn was dried with $CaCl_2$. The material was adsorbed onto activated alumina and eluted twice through a column of activated neutral alumina using a 50:50 diethyl ether:hexane mixture under nitrogen. Remaining ferrocene starting material was removed by gentle vacuum sublimation and the residual material was allowed slowly to crystallise from hexane solution in a freezer.

$^{31}P\{^1H\}$NMR ($CDCl_3$): δ = 40.67 (s) ppm. ^1H NMR ($CDCl_3$): δ = 4.26-4.42 (m, 8H); δ = 1.98 (septet, $PCH(CH_3)_2$,4H); δ = 0.99-1.28 (4d, $PCH(CH_3)_2$, 24H) ppm; ^{13}C NMR ($CDCl_3$): δ = 70.66 (d, J_{PC} 9.5 Hz, 4C); δ = 70.33 (d, J_{PC} 10.66 Hz, 4C); δ = 70.33 (d, J_{PC} 10.66 Hz, 4C); δ = 68.95 (d, J_{PC} 15.74 Hz, 2C); δ = 28.43 (d, J_{PC} 71.8 Hz, 4C); δ = 14.04 (s, 8C) ppm.

4.2.4 The synthesis of $[Ir(COD)Cl]_2$

The procedure was adapted from that described by Lin *et al.*[32]

$$2\ Na_2IrCl_6.6H_2O + 2\ COD + 3\ CH_3CH(OH)CH_3 =$$

$$[Ir(COD)Cl]_2 + 4\ NaCl + 3\ (CH_3)_2CO + 6\ HCl + 12\ H_2O$$

A clean, dry, 100 ml. round-bottomed flask containing 2.00g (3.58mmol) $Na_2IrCl_6.6H_2O$ was evacuated and refilled with N_2. In a separate, similar flask, 20 mls. de-ionised water mixed with 2-propanol (10 mls,135.6 mmol) and distilled COD (3 mls, 24.4 mmol) were degassed by bubbling N_2 through for 60 minutes. This mixture was then transferred by cannula to the iridium salt and the suspension heated to reflux temperature for 16 hours under N_2.

The bright red, microcrystalline product was allowed to cool to room temperature, then cooled in ice before filtering through a no.4 frit. The crystals were washed with 30 mls. de-ionised water, then 3 x 20 mls. ice-cold ethanol and dried *in vacuo.*

Yield 0.951g (79%). (Found C, 28.67; H, 3.59; $C_{16}H_{24}Cl_2Ir$ requires C, 28.61; H, 3.60%).

^1H NMR δ 1.52 (s), 1.55 (q) (resolved only as doublet with shoulders), 2.25 (m, broad), 4.25 (d) (vinyl protons) ppm.

4.2.5 The synthesis of $[Ir(COD)(PPh_2Me)_2][PF_6]$

Following a procedure reported by Haines and Singleton[33], $[Ir(COD)Cl]_2$ (0.3g, 0.45mmol) was weighed into a 100 ml. round-bottomed flask and suspended in degassed ethanol (10 mls). PPh_2Me (0.3g, 1.5 mmol) was added by syringe and stirred for 30 minutes. During this time the whole solution takes on a bright red colour. A saturated solution of NH_4PF_6 (0.2g) was prepared in degassed ethanol. Both solutions

were transferred by cannula filter to a third flask. On cooling to 0° C, a precipitate formed which was removed by filtration under nitrogen, washed with cold ethanol, then ether, to give a pink-red powder. Yield 0.563g, 74%. (Found C, 48.41; H 4.51. $C_{34}H_{38}F_6P_2Ir$ requires C, 48.28; H 4.53%). Spectroscopy: $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 2.826 (q),

δ -143.073 (five peaks visible from septet J_{PF} = 713 Hz) ppm. ^1H NMR δ 7.2 (m), δ = 4.011 (s)(vinyl protons), δ 1.024 (s) P*CH*$_3$ ppm.

^{13}C NMR δ =129-133 (m, 24C), δ = 87.166 (s, 4C, vinyl carbons), δ = 31.073 (s, 4C, *C*H_2 (COD)) ppm.

4.2.6 The attempted synthesis of chlorotris(diphenylpiperidylphosphino)-rhodium (I)

In a 100 mls. round-bottomed flask, $[Rh(C_2H_4)_2Cl]_2$ (0.08g , 0.2 mmol.) and diphenylpiperidylphosphine (0.336g , 1.25 mmol.) were dissolved in 30 mls. dried, distilled, degassed THF and stirred overnight. The solution was reduced to dryness and redissolved in a minimum of diethyl ether. Hexane was added and the tube stored in the freezer to effect precipitation. The precipitate was removed by filtration under nitrogen.

$[Rh(C_2H_4)_2Cl]_2 + 6PPh_2(C_5H_{10}N) = 2\ RhCl(PPh_2\{C_5H_{10}N\})_3 + 4\ C_2H_4$

Yield; 0.24g, 63.4%. NMR $^{31}P\{^1H\}$: δ 26.5 ppm (*cis*), δ 46.26 ppm (*trans*)

4.2.7 The attempted synthesis of chlorotris(phenyldipiperidylphosphino)-rhodium (I)

In a 50 mls Schlenk tube, $[Rh(C_2H_4)_2Cl]_2$ (0.174g , 0.45 mmol.) was dissolved in THF (10 mls) under nitrogen and in a second similar tube

phenyldipiperidylphosphine (1.35g , 4.89 mmol.) was dissolved in THF (30 mls). The rhodium complex solution was added slowly by cannula to the phosphine solution and the mixture stirred for 5 hrs.

$$[Rh(C_2H_4)_2Cl]_2 + 6PPh(C_5H_{10}N)_2 = 2\ RhCl(PPh\{C_5H_{10}N\}_2)_3 + 4\ C_2H_4$$

The solution was reduced to dryness and redissolved in a minimum of diethyl ether. Hexane was added to effect precipitation. The precipitate was removed by filtration under nitrogen. The precipitate was eluted through a column of neutral alumina with 100% diethyl ether to separate from excess ligand which was discarded. The remainder was eluted with 100% methanol which was removed to produce a red oil. This is the dimeric species. NMR $^{31}P\{^1H\}$ ($CDCl_3$): δ = 27.12 (s) ppm. ^1H NMR (CDCl3): δ = 7.2-7.7 (m, 5H, C_6H_5); δ = 2.959 (s, 8H, NCH_2); δ = 1.453 (s, 12H, CH_2CH_2) ppm. IR: ν (Rh-Cl-Rh) 273 cm^{-1}, 261 cm^{-1}; ν (Rh-P) 364 cm^{-1}.

4.2.8 The synthesis of chlorotris(diphenyl-2-pyridinophosphine)rhodium (I)

$$[Rh(C_2H_4)_2Cl]_2 + 6PPh_2(C_5H_5N) = 2\ RhCl(PPh_2\{C_5H_5N\})_3 + 4\ C_2H_4$$

In a 100 mls. round-bottomed flask, $[Rh(C_2H_4)_2Cl]_2$ (0.08g , 0.2 mmol.) and diphenyl-2-pyridinophosphine (0.33g , 1.25 mmol.) were dissolved in THF (30 mls) and stirred overnight with the light excluded from flask. The solvent was removed *in vacuo* and the residues redissolved in toluene. An equal amount of hexane was added and the flask stored in the freezer. The solid produced was filtered from the solution and washed with 3 x 25 mls diethyl ether.

NMR $^{31}P\{^1H\}$ (THF) δ 15.6 ppm (cis) δ 21.3 ppm (trans) δ -1.0 ppm (free ligand) (see chapter 7 on P-N ligands)

4.3 Catalytic studies

4.3.1 High pressure reactions

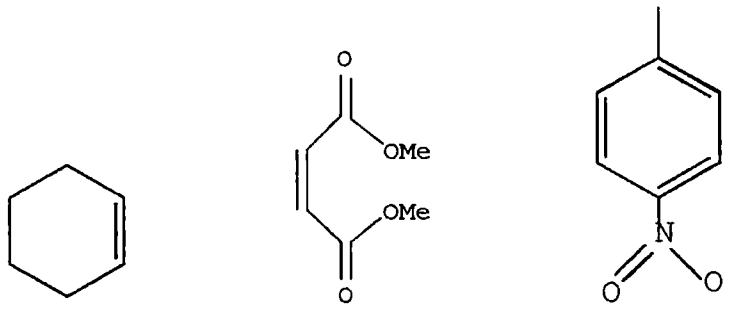
The procedures adopted for catalytic hydrogenation experiments follow the procedures outlined in sections 3.4.1-3.

A few initial experiments were performed using the preformed rhodium complex, $[Rh(PCy_2Me)_2(NBD)][BF_4]$, available in the laboratory, as catalyst. The complex (0.01g) was absorbed into1g Nafion-H in methanol and the hydrogenation of hex-1-ene attempted. At a temperature of 80°C and a pressure of 50 bar H_2, after 8 hours only a modest yield of 13 mol product/mol catalyst was achieved. A similar attempt at hydrogenating acetonitrile under the same conditions gave no measureable products. The combined hydrogenation and esterification of oleic acid using the same catalyst and conditions was more successful. Three peaks were seen in the GC trace with retention times of 22.2, 22.3 and 22.5 minutes respectively (oleic acid gives a broad peak at 22.8 minutes). Examination of the reaction solution by infra-red showed a displacement in the carboxyl stretching absorption, from 1710 cm^{-1} to 1743 cm^{-1} and a disappearance of the broad OH absorption around 2500-3500 cm^{-1}. Integration of the peaks in the ^1H NMR spectrum inferred approximately 10% hydrogenation giving a yield of about 44 mol product per mol catalyst.

$[RhCl(PPh_2py)_3]$ (0.01g) was allowed to absorb into Nafion (1.0g) in methanol in the presence of a 5 molar excess of ligand. The Nafion was added to hex-1-ene (2 mls) in cyclohexane (30 mls) and heated in the autoclave to 80°C and pressurised to 50 bar H_2, but after 8 hours only a trace of hexane was detected.

Tolman and Faller[34] demonstrate that rates of hydrogenation of hex-1-ene for 'Wilkinson' type catalysts, i.e. $RhClL_3$, vary by up to a factor of 5000. The most active catalyst identified from their review corresponded to L = Ph_2P-(NC_5H_{10}). However this was a misquotation from the original paper by L.Sajus[35] who reported results for the ligand L = PhP-$(NC_5H_{10})_2$.

The catalyst [RhCl{ PhP-$(NC_5H_{10})_2$}$_3$], together with two other catalysts of reported high activity[17,35], were synthesised (*vide supra*). A series of three substrates, chosen for a comparative study of hydrogenation is shown in Scheme 4.14

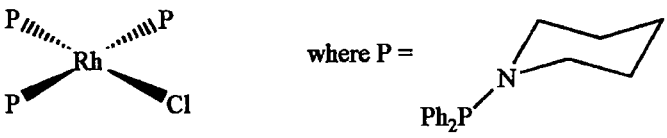


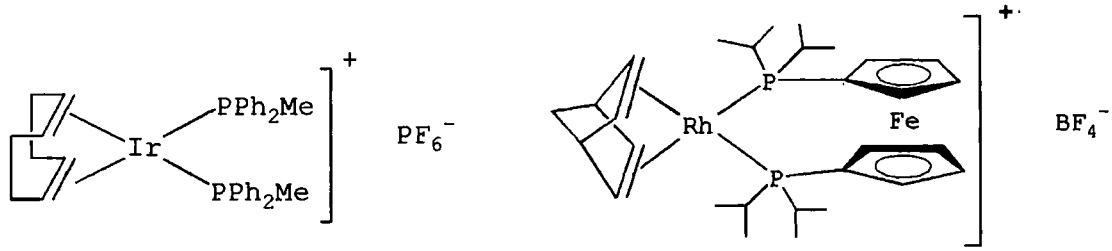
a) cyclohexene b) dimethyl maleate c) nitrotoluene

Scheme 4.14 The three substrates used for the study

Cyclohexene was purified of peroxides following a procedure described by Perrin and Armarego[37], distilled, dried and degassed. Dimethyl maleate was degassed using 3 freeze-thaw pump cycles, prior to use, nitrotoluene was used as received.

1) $[RhCl\{ Ph_2P\text{-}NC_5H_{10}\}_3]$





2) $Ir(C_8H_{12})(PPh_2Me)_2PF_6$ **3) $Rh(C_7H_8)(dPr^iPFc)BF_4$**

Scheme 4.15: The three catalysts used for the study

Catalyst (1) was expected to protonate and be absorbed by Nafion, whereas catalysts (2) and (3) were expected to be absorbed by ion exchange. In each case an accurately weighed amount of catalyst, approximately 10^{-5} mol, was introduced into

Nafion-H in 10 mls degassed methanol. Stirring was continued until the solution colour faded completely and the beads assumed the colour. In the case of catalyst (1) this process did not go to completion. Therefore yields quoted for reactions involving this catalyst represent minimum values and are based on the assumption that all the metal complex was absorbed by the Nafion. A discussion of aminophosphine ligands and an explanation of this behaviour is included in Chapter 7. Leaching is a problem with catalyst (1) for the same reasons that absorption is incomplete. Measurements of leaching led to an estimate of 10% loss of catalyst during the reaction.

4.3.2 Results obtained from hydrogenation reactions

A general overview of the results obtained is presented below in Table 4.1 Yields are in moles of substrate hydrogenated per mole of catalyst used. Rates are in moles of substrate hydrogenated per mole of catalyst used per hour for the duration of the reaction (consumption of hydrogen had reached a minimum).

	cyclohexene	dmm	nitrotoluene†
Catalyst	**yield mol.mol^{-1}**	**yield mol.mol^{-1}**	**rate mol/(mol.hr)$^{-1}$ (% converted)**
1	**100**	**790**	**3900 (89%)**
1 + Nafion	**260**	**520**	**3700 (100%)**
2	**270**	**670**	**60 (7%)**
2 + Nafion	**800**	**4400**	**1600 (98%)**
3	**43**	**530**	**5800 (99%)**
3 + Nafion	**68**	**220**	**4500 (100%)**

Conditions: Stirred in degassed methanol for 5 hrs. at 80°C and 40 bar H_2: Wilkinson's catalyst gave a yield of 1400 mol substrate reduced/mol catalyst for the reduction of cyclohexene. † Nitrotoluene was hydrogenated completely and with great facility in most cases hence rates are compared.

Table 4.1: Results of high pressure hydrogenation

Percentage substrate conversion is calculated from GC peak integrals as follows:

$$\% \text{ conversion} = \frac{\text{area of product peak x FID factor}}{(\text{area of product peak x FID factor}) + \text{area of starting material}} \times 100\%$$

where 'FID factor' is the ratio of responses of the flame ionisation detector to starting material and product, based on weighed standards.

The yields do not necessarily represent the optimum conditions for each system but for the conditions chosen for comparative purposes. For example it is known that for the iridium catalyst, the use of non-coordinating solvents, especially CH_2Cl_2, will improve yields. A repeat of (2 + Nafion) with dimethyl maleate in CH_2Cl_2 gave a yield of 18,000 mol/mol catalyst. A yield of 8200 mol/mol catalyst was also obtained for a single run of (2 + Nafion) with 3g maleic acid, which was completely converted to the ester dimethyl- butanedioate in methanol. Nafion was converted to the sodium form (para. 2.2), and used to absorb catalyst (2). These beads were used in a run with nitrotoluene to give 17.8% product with a maximum rate of 180 mol/mol/hr.

A sample of Wilkinson's catalyst run under the same, standardised conditions gave a yield of 1400 mol substrate reduced/mol catalyst for the reduction of cyclohexene.[38]

In addition to the high pressure reactions tabulated above, the catalyst $[RhCl\{ PhP\text{-}(NC_5H_{10})_2\}_3]$, an analogue of (1) above, was used for the hydrogenation of cyclohexene under the same conditions used to generate table 1. For both the homogeneous and supported cases a yield of only 16 mol substrate/mol catalyst was obtained. Furthermore nearly 90% of the catalyst leached from the Nafion. For the hydrogenation of nitrotoluene only a single homogeneous run was attempted. Nitrotoluene was 9% converted into *p*-toluidine in 3 hours correponding to a rate of 67 mol/mol.hr.

4.3.3 Products obtained

Under these conditions cyclohexene was hydrogenated to cyclohexane as expected and dimethyl maleate was hydrogenated to butanedioic acid dimethyl ester. Further reduction to the alcohol was not seen. Nitrotoluene was hydrogenated completely in methanol to *p*-toluidine with great facility in most cases and hence rates are compared.

A blank run using Nafion-H and nitrotoluene dissolved in methanol remained unchanged after 2hrs under standard reaction conditions.

4.3.4 Low temperature hydrogenation

An attempt was made to study Nafion as a support for catalyst (2) under the conditions described by Morris[39]. Cyclohexene (0.82g) was dissolved in 20 mls. CH_2Cl_2 (0.5M) in a 100 ml Schlenk tube under nitrogen, connected to a double Schlenk line. The flask was cooled in an ice-bath to 0°C. A 250 ml round bottomed flask was charged with the iridium complex (0.017g, 0.02mmol), filled with nitrogen and cooled in the same ice-bath. The cyclohexene solution was cannula transferred by nitrogen pressure to the flask containing the catalyst forming a red solution. The nitrogen supply to the line was disconnected and a H_2 supply connected in its place. The lines were flushed with hydrogen. A 2 litre round bottomed flask was evacuated and filled with hydrogen and connected to the reaction flask to act as a reservoir. The reaction flask was carefully evacuated and refilled with hydrogen 3 times leading to a complete loss of colour of the solution. The stirrer was started and the time noted as time t = 0. Samples (0.1ml) were removed at 10 minute intervals for analysis by gas chromatography. Several attempts were necessary in order to (nearly) recreate the rates observed by Morris, during which the importance of the apparatus design and strict adherence to the procedure became apparent. The maximum rate observed was 1134 (Table 4.2) compared to 3800 reported by Morris. However, close inspection of the graphs produced by Morris shows that he achieved 100% conversion after 30 minutes, only marginally faster than the rates reported here. The remaining differences between the figures reported here and those reported by Morris can be attributed to differences in apparatus and to the comparison of measurements of instantaneous rates obtained from H_2 uptake with rates over 10 minute periods measured by GC.

Time (mins)	% conversion	TOF per period mol/mol/hour
10	29	865
20	67	1134
33	94	620

Table 4.2 Low temperature hydrogenation results

The procedure described above was then repeated with Nafion beads (1g) containing 0.0113 g catalyst (2), introduced in methanol which was then removed under vacuum. The beads initially have a bright red colour in common with the homogeneous solution. On addition of hydrogen the beads lose this colour after only about 5 seconds. On using these beads in an identical reaction to that described above only a trace of hydrogenation product was formed and the beads became faint yellow, the colour associated with deactivated catalyst. Several more unsuccesful attempts were made with slight variations in conditions, e.g. a longer induction period before addition of hydrogen or mixtures of methanol and CH_2Cl_2, etc., but in each case the catalyst was quickly deactivated.

4.4 Discussion

Introduction of the complexes into Nafion was achieved following the procedures described in Chapter 2. The two ionic complexes were readily absorbed from solutions of methanol as expected. Trials were always conducted using freshly prepared samples since overnight storage of beads containing $[Ir(COD)(PPh_2Me)_2]PF_6$ (catalyst 2) led to a loss of the initial bright red colour which could be indicative of loss of activity. The complexes with aminophosphine ligands, $[RhCl\{ Ph_2P\text{-}NC_5H_{10}\}_3]$ (catalyst 1), and its analogue $[RhCl\{ PhP\text{-}(NC_5H_{10})_2\}_3]$, were only slowly absorbed. The P-N bond gives the nitrogen some sp^2 character and as a result it is not strongly protonated. A fuller discussion of this is included in Chapter 7.

The failure of Nafion supported $[Ir(COD)(PPh_2Me)_2]PF_6$ (catalyst 2) to work in the experiments conducted at low temperature and pressure is readily explained. In homogeneous catalysis, when the alkene substrate drops to a low concentration, the catalyst is deactivated due to the formation of the catalytically inactive hydride dimer (Scheme 4.10). The rapid decolouration of the beads on exposure to hydrogen gas proves that hydrogen is capable of rapidly dissolving into solution and diffusing into the Nafion. The cyclohexene substrate in the beads will become rapidly depleted by hydrogenation and the rate of its diffusion into the beads is far slower than that of hydrogen gas, therefore it will be unable to maintain a full coordination sphere around the catalyst, which forms the hydride instead and deactivates. It is intriguing that this process does not occur during high pressure reactions. It is possible that the higher temperatures involved disfavour the formation of the hydride bridged dimer. In fact, it can be seen from Table 4.1 that with all three substrates, supporting catalyst (2) in Nafion has a very beneficial influence. Given the fact that catalyst (2) achieves the highest rates in non-coordinating solvents such as CH_2Cl_2 , the beneficial influence could be due to the fact that the methanol present in the Nafion cavities is likely to be protonated and therefore also non-coordinating. To test this hypothesis, a single run was performed in which sodium Nafion was used. The maximum rate achieved was 180 mol/mol/hr, better than the homogeneous figures but still far short of the value obtained for Nafion-H. The performance of catalyst (1) shows mixed results depending on the substrate. Supporting in Nafion has only a small influence on the yields and rates, one way or the other. The poor performance of catalyst (3) with cyclohexene is not readily explained. The figures were replicated using three batches of catalyst.

It is generally assumed that supporting a catalyst in a polymer may or may not improve the final yields obtained from a reaction, but that it will certainly have a detrimental effect on rates due to diffusion limitations. It can be seen from the results obtained for nitrotoluene that rates are only slightly reduced by supporting catalysts in Nafion.

The catalyst reported by Sajus[35], $[RhCl(PhP\text{-}\{NC_5H_{10}\}_2)_3]$, was synthesised three times. The first synthesis used $[Rh(COD)Cl]_2$ as starting material. The second

and third syntheses used $[Rh(C_2H_4)_2Cl]_2$ with equimolar, and ten molar excess of ligand, respectively. In all cases the same product was formed which displayed only a single phosphorus NMR environment and metal-chlorine stretching frequencies in the infra-red spectrum characteristic of a bridged dimer. Catalytic reactions were performed with and without 5 molar ligand excesses but low yields of hydrogenation products were always the result. The nitrogen atoms attached to the phosphorus in the ligands reduce the electron density on the phosphorus atom making it a poorer nucleophile less likely to break the chlorine bridge present in $[Rh(C_2H_4)_2Cl]_2$. It is also likely that the very bulky nature of the ligands makes nucleophilic attack more difficult. The similar complex, formed from PCy_3 ligands, is in equilibrium with its dimer in the manner of scheme 4.1, but the equilibrium lies further towards the monomer, $[RhCl(PPCy_3)_2]$, which can be isolated and forms stable adducts with atmospheric gases. Notwithstanding the increased monomer concentration, the complex is a poor hydrogenation catalyst[40,41].

4.5 References

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Chapter 5

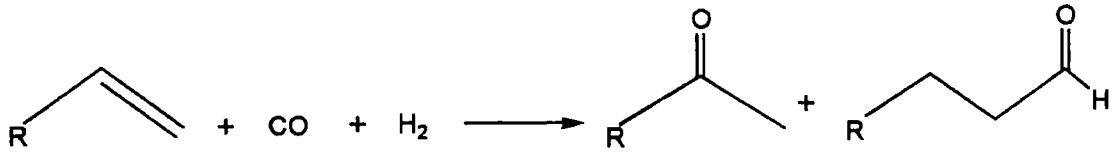
Hydroformylation

5.1 Introduction

This chapter is concerned with the use of Nafion as a support for hydroformylation catalysts. The chapter starts with a brief overview of the literature concerning homogeneous hydroformylation catalysts. An experimental section follows in which the synthesis of a number of complexes is described as well as the use of modified forms of Nafion as supports. The synthesis of a number of ligands was described in Chapter 4. These ligands are used again in Chapter 5 to form complexes by displacement of NBD from $[Rh(NBD)_2]BF_4$. The resulting complexes are used for a comparative study of the hydroformylation of hexene. An attempt is made to place the ligands in order of phosphine π-acceptor strength based on spectroscopic data.

5.1.1 Cobalt catalysed hydroformylation

Hydroformylation, also known as the "Oxo" process, is the addition of -CHO and hydrogen across an olefinic double bond.

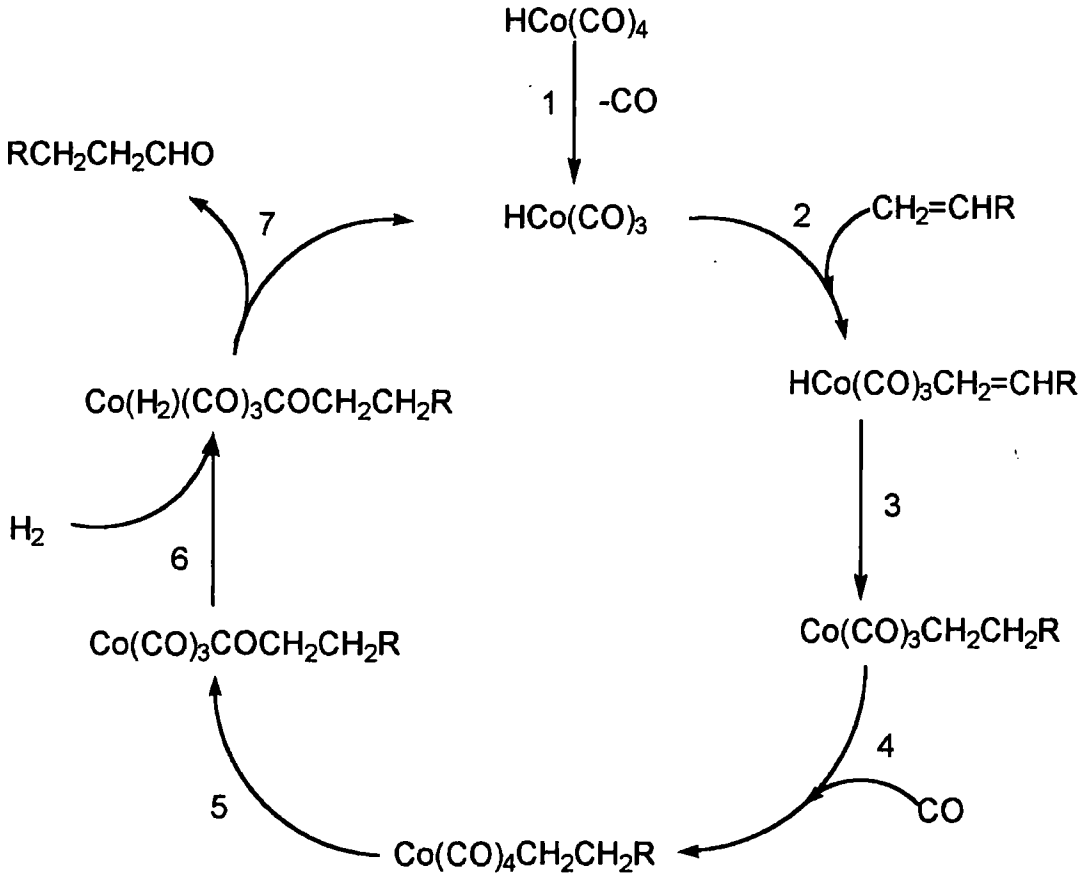


The first catalysts were Fischer-Tropsch catalysts of cobalt on a mixed oxide support, the active species formed under the reaction conditions being correctly identified as $HCo(CO)_4$ by Otto Rölen who discovered the reaction[1]. The usual catalyst precursor is $Co_2(CO)_8$, or analogues of this in which carbonyl groups have been replaced with tertiary phosphines to aid subsequent hydrogenation to alcohols. Spectroscopic studies under reaction conditions[2] show that the equilibrium in Scheme 5.1 lies comfortably to the right.

$$Co_2(CO)_8 + H_2 = 2HCo(CO)_4$$

Scheme 5.1 Generation of active species.

The rate determining step depends, to a degree, on the nature of the substrate. In reactions involving internal alkenes or where phosphine replaces CO as ligand, the rate determining step is the interaction of alkene with the metal-hydride species (step 2 in Scheme 5.2). Hydroformylation of simple terminal alkenes is rate limited by hydrogenolysis of the acyl species (step 6).

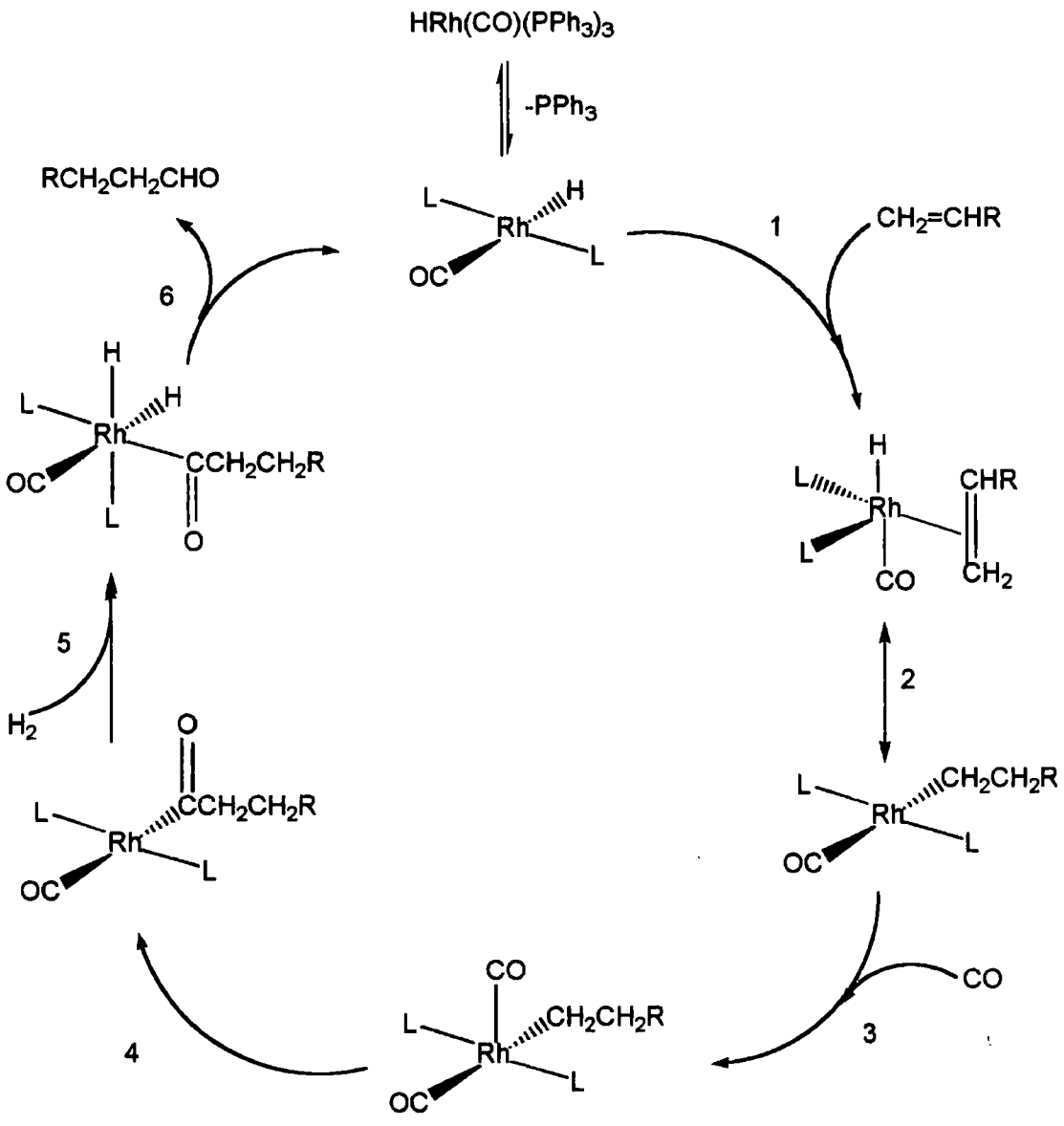


Scheme 5.2 Catalytic Cycle for Cobalt Mediated Hydroformylation

Mixed alkene isomers are usually used in the process, and undergo double bond shift isomerisation in the presence of a catalyst. Isomerisation of the alkene takes place at a much faster rate than hydroformylation, but because terminal alkenes react much faster to give hydroformylation products, the products derived from the other isomers are not generated in significant quantities. The greatest drawback of cobalt as a hydroformylation catalyst is the need for comparatively high temperatures and pressures (90-150 °C, 100-400 bar).

5.1.2 Rhodium catalysed hydroformylation

In the knowledge that rhodium salts added to the cobalt catalyst systems allowed less forcing conditions, Wilkinson's group explored the use of his hydrogenation catalyst[3], which immediately proved to be effective under milder conditions (70°C, 100 bar). It became quickly apparent that the active catalyst precursor formed under reaction conditions was *trans*-$RhCl(CO)(PPh_3)_2$ which could be recovered quantitatively from reaction mixtures. Use of the halide species involved an induction period before reaction commenced, corresponding to the replacement of chlorine by hydrogen. A more effective precursor is the stable $HRh(CO)(PPh_3)_3$ which undergoes loss of phosphine in solution to give a catalyst, highly active for hydroformylation even at 25°C and ambient pressure. This catalyst is now the basis for the Union Carbide/JME/KPT industrial hydroformylation process. Industrially, rhodium catalysed hydroformylation is normally conducted at 100°C, at pressures up to 50 bar and in the presence of a large excess of phosphine ligand, and can even be carried out in molten PPh_3. In addition to the complexes described above, catalyst precursors include $RhCl_3.3H_2O$, $(acac)Rh(CO)_2$ and Rh_2O_3.



Scheme 5.3 Rhodium catalysed hydroformylation of a terminal alkene illustrated for the formation of the linear product.

Where rhodium starts in a higher oxidation state, reduction *in situ* by H_2 and CO takes place.

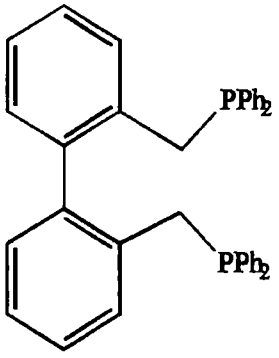
Many factors influence the final product distribution between linear and branched aldehydes. Pruett and Smith[4] showed there to be several species in solution in equilibrium (Scheme 5.4).

$$HRh(CO)_4 \underset{-L + CO}{\overset{+L - CO}{\rightleftharpoons}} HRh(CO)_3L \underset{-L + CO}{\overset{+L - CO}{\rightleftharpoons}} HRh(CO)_2L_2 \underset{-L + CO}{\overset{+L - CO}{\rightleftharpoons}} HRh(CO)L_3 \underset{-L + CO}{\overset{+L - CO}{\rightleftharpoons}} HRhL_4$$

Scheme 5.4 Phosphine and carbon monoxide as competing ligands

Each rhodium phosphine carbonyl has its own catalytic cycle for hydroformylation with a different linear to branched aldehyde product ratio. As L is replaced by CO the steric crowding in the transition state is relieved, increasing the overall reaction rate but reducing the percentage linear product. Increasing the size of the phosphine (L), represented by its cone-angle (θ), decreases the amount of linear product obtained[5] despite the increase in steric crowding. This is thought to be as a result of altering the position of equilibria in Scheme 5.4. Reaction conditions can also have a considerable influence on the normal to branched ratio. The original work by Wilkinson[3] showed that at the low temperatures made possible by the use of $[HRh(CO)(PPh_3)_3]$, a ratio of 20:1, linear:branched products could be obtained, compared to only 2:1 at temperatures >70°C, required by the chloro complex. Addition of a small amount of diphosphine, such as dppe, to a solution containing $[HRh(CO)_2(PPh_3)_2]$, the predominant complex under CO/H_2 atmospheres, leads to loss of monophosphine and binuclear bridging[6]. The dimer, $[HRh(CO)_2(PPh_3)_2]_2$dppe, has an increased activity over the starting material. However, further additions of dppe lead to a fall off in activity due to oligomerisation. Other structures have been proposed when bulky diphophines are employed[7], such as DIOP or diaryl substituted ferrocenes, in which three ligands are shared between two metals, one bridging and two chelating. Where diphosphines are employed then Tolman's cone angle is no longer the main consideration. Dierkes and van Leeuwen[8] compiled data from the Cambridge Crystallographic data base to show that, irrespective of metal or oxidation state, any given diphosphine has a preferred "bite-angle". The bite-angle is the angle between the two M-P bonds. Even where the diphosphine has a relatively flexible backbone, such as dppb, the standard deviation around the mean value does not exceed

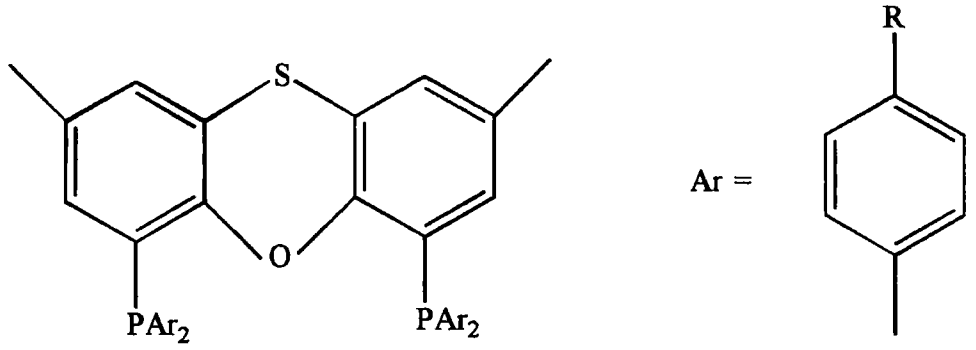
3° of arc and therefore relatively few examples exist where the ligand has been forced to adopt a bite angle outside this range. During hydroformylation, rhodium adopts 4,5 and 6 coordinate structures. For ligands arranged mutually *cis* to each other, that corresponds to angles of 90° for square-planar, octahedral and apical-equatorial in the trigonal bipyramid case while bis-equatorial bonding demands 120°. For ligands arranged mutually *trans*, whether a bite-angle has any meaning relies on the ligand backbone being sufficiently long to bridge the positions. The five coordinate intermediate formed after step 3 in Scheme 5.3 exists in solution in two forms,[9] with PPh_3, bis-equatorial and equatorial-apical present in a ratio of 85:15. A chelating diphosphine is likely to alter this ratio. The importance of bite angle to hydroformylation was demonstrated by Casey[10] *et al.* They describe a series of experiments on complexes in which two PPh_3 groups from the Wilkinson catalyst are replaced by the chelating phosphine 2,2'-bis[(diphenylphosphino)methyl]-1,1'-biphenyl (BISBI, Scheme 5.5). Variable temperature ^{31}PNMR experiments show that BISBI remains coordinated to rhodium under hydroformylation temperatures while



Scheme 5.5 BISBI diphosphine ligand

the remaining PPh_3 is readily dissociated. The complex [HRh(CO)(PPh_3)BISBI] was isolated and the crystal structure determined. The BISBI ligand spans two equatorial sites with a bite angle of 125°, somewhat larger than the calculated free bite angle of 112.6°. The complex shows very high selectivity for linear aldehydes with a normal:branched ratio of 66:1. The authors found a correlation between the free bite angle of a ligand and the proportion of linear aldehyde produced. The most linear

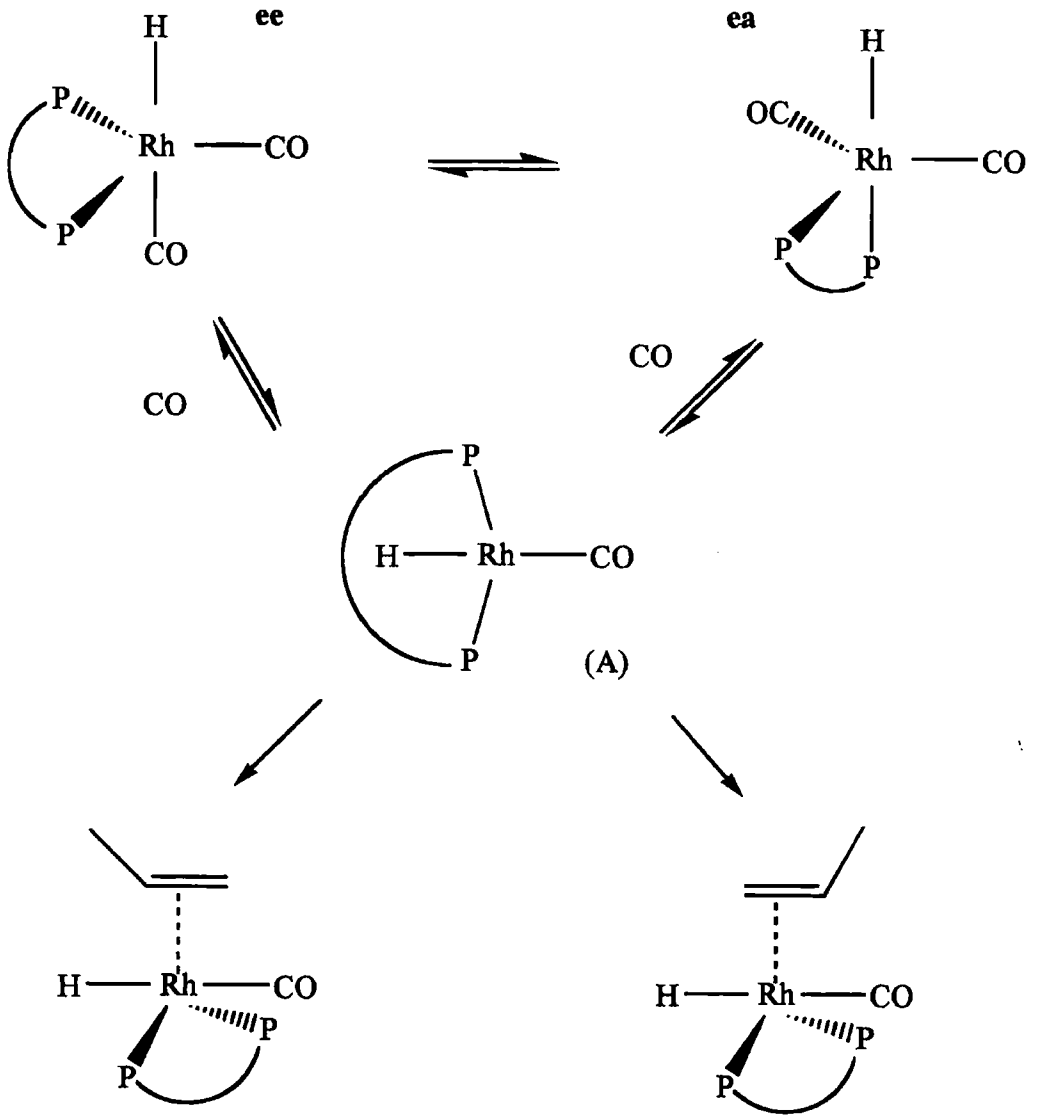
aldehyde was produced when ligands had a free bite angle close to 120°, the angle between equatorial positions. The importance of this may well be overemphasised however. Subsequent studies[11] employed a family of "thixantphos" ligands (Scheme 5.6) with the same basic structure but different electronic properties depending on the nature of R



Scheme 5.6 The Thixantphos ligand family.

The ligands were allowed to complex with rhodium to form a family of $[HRh(CO)(PPh_3)(thixantphos)]$ compounds. The carbonyl stretching frequency of each was measured using infra-red spectroscopy. The compounds were then studied during hydroformylation of 1-octene using high pressure infra-red techniques and the 4 bands (a combination of ν(M-H) and ν(CO) for each of two species) assigned with the aid of deuterated analogues, allowing the ratio of bisequatorial (**ee**) to equatorial-apical (**ea**) isomers in solution to be determined. As Ar is changed from electron donating substituents to electron withdrawing ones, the intensities of the bands of the **ea** isomer are diminished in favour of those of the **ee** isomer. The $[(diphosphine)HRh(CO)_2]$ complexes were the only carbonyl species present during hydroformylation, implying that the rate determining step occurs before their formation. However, no electronic effect of the ligands on the selectivity for linear aldehydes was observed. The selectivities for linear aldehyde across the range of R ligands were all between 92 and 93 %. In contrast the ratios of **ee** to **ea** isomers ranged from 1 for $R= N(CH_3)_2$ to 9 for $R = CF_3$. The barrier between conversion from **ee** to **ea** isomers has been estimated at less than 40 kJ mol^{-1}, hence interconversion is rapid. The authors propose that the

square planar complex formed by loss of ligand at the start of Scheme 5.3 is in equilibrium with the two (**ee** and **ea**) dicarbonyl isomers (Scheme 5.7). Addition of alkene to the square planar complex goes via a short lived transition state to form a "pro-linear" or "pro-branched" 5-coordinate state which then proceeds to form linear or branched aldehyde respectively.



Scheme 5.7 Transition states which determine whether normal or branched products are formed

Industrially produced aldehydes from hydroformylation processes are often taken through an extra hydrogenation step in order to produce alcohols. The complex $[\eta^5\text{-}(C_5H_5)Rh(CO)(PBu_3)]$ has been reported[12] as being capable of direct production of alcohols from alkenes in a ratio of 1:1 linear to branched. This has also been achieved under mild conditions using the catalyst precursor $[HRh(PEt_3)_3]$ in ethanolic solution[13]. More recently, it has been discovered, following experiments with deuterated starting materials, that alcohol production using this catalyst proceeds directly and not via aldehyde intermediates[14].

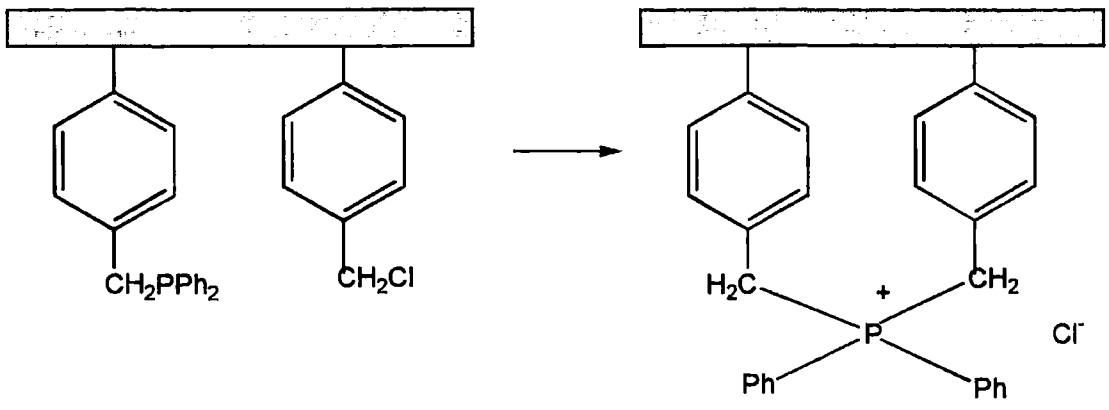
Ligands which bear structural similarities to the family shown in Scheme 5.6, described earlier, can be tailored to favour the hydroformylation of internal alkenes[15]. The authors report good yields of linear nonanal from 2-octene and 4-octene. Rhodium cationic species can also catalyse hydroformylation. Kostas and Screttas[16] report the hydroformylation of styrene using a P,N-bidentate ligand *o*-Diphenylphosphino-[N-(2-methoxyethyl)-N-methyl]aniline to replace one COD from $[Rh(COD)_2]BF_4$. Aldehydes were produced quantitatively after 22 hours with a TON of 1484. Interestingly the products were 95% branched aldehydes.

A high regioselectivity for branched aryl aldehydes was also reported for a cationic rhodium complex ligated with bis(dioxaphospholane). Branched alkyl products were also favoured to a lesser degree[17].

5.1.3 Hydroformylation using supported catalysts

The high cost of rhodium and increasingly large investment in time to prepare complex ligand structures encourages research into supported catalysis for all reaction types and hydroformylation is no exception. In general the catalysts are grafted onto polymeric supports by ligand exchange. A polymer with pendant benzyl chloride groups can be phosphonylated by reaction with bisarylphosphinolithium and the

resultant polymeric diphosphine used to replace PPh_3 groups from the homogeneous catalyst precursor. One danger with this strategy comes when neighbouring pendant groups are in close proximity. Partial phosphonylation can lead to quaternisation which in turn gives a very poor hydroformylation catalyst[18] (Scheme 5.8).

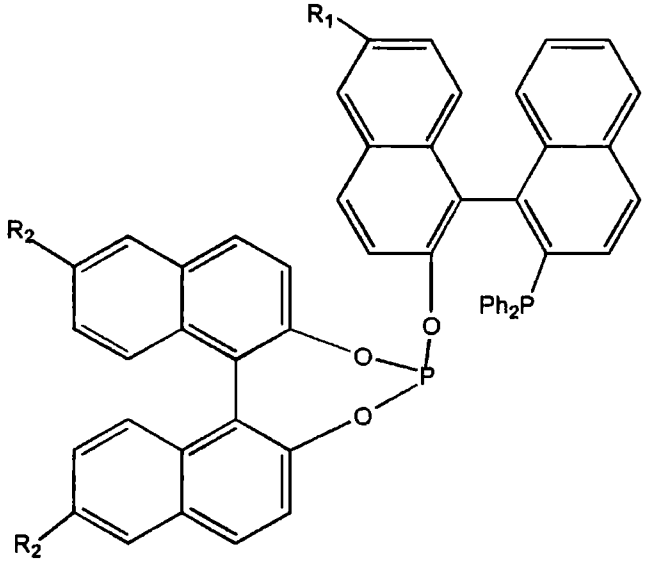


Scheme 5.8 Phosphorus quaternisation

Despite this potential drawback, Evans *et al.* reported[19] the exchange of *trans*-$[RhCl(CO)(PPh_3)_2]$ with a diphenylphosphine based polymer derived from chloromethylated polystyrene. The resultant polymer was active for the hydroformylation of 1-pentene. The linear to branched ratio was 3:1 and no alcohols were produced. A variation on this theme was provided by Allum[20] *et al.* who incorporated $[Rh(acac)(CO)_2]$ into diphosphine derivatised cross-linked polystyrene beads. They achieved a 41% yield of aldehyde after 4 hrs at 80°C under an atmosphere of 43 bar 1:1 H_2:CO. The molar ratio of alkene to rhodium was 10^4:1. Given that the normal to branched ratio using the supported catalyst was 2.5:1, much higher than that expected from $[Rh(acac)(CO)_2]$ in solution, the authors concluded that the polymeric phosphine had played a role in the reaction. Pittman and Smith[21] reported the successful, sequential, cyclooligomerisation and hydroformylation of butadiene. One polystyrene resin provided the support for both a nickel carbonyl catalyst and a rhodium hydridocarbonyl catalyst. Butadiene was transformed into 3-(cyclohex-3-enyl)propanal and 2-(cyclohex-3-enyl)propanal in a ratio of 4.3:1. Separate studies[22]

using single step reactions (i.e. solely hydroformylation) showed that increases in the polymer bound PPh_2 to rhodium ratio led to increases in normal to branched product ratios but at the cost of overall yields. This effect has obvious parallels in homogeneous catalysis.

More recently the mode of ligand replacement, that the phosphines are replaced, assumed by the foregoing studies on $[HRh(CO)(PPh_3)_2]$ has been called into question. Paetzold[23] *et al.* studied phosphinated styrene-divinylbenzene copolymers using infra-red spectroscopic techniques. Polymer granules were stirred with $[HRh(CO)(PPh_3)_2]$ in toluene under an atmosphere of 1:1 H_2:CO and samples removed periodically for infra-red spectroscopy. The progressive changing of the band pattern allowed the authors to conclude that, in the early stages no hydrido or carbonyl bands could be seen and that under the influence of the atmosphere new carbonyl bands appeared but not Rh-H bands. The new bands were assigned to a polymer bound carbonyl cluster species. Assymetric hydroformylation has also been accomplished using supported catalysis[24]. The ligand system (Scheme 5.9) was functionalised with a vinyl group at either R_1 or R_2 to allow subsequent polymerisation.



Scheme 5.9 Ligands for supported assymetric hydroformylation

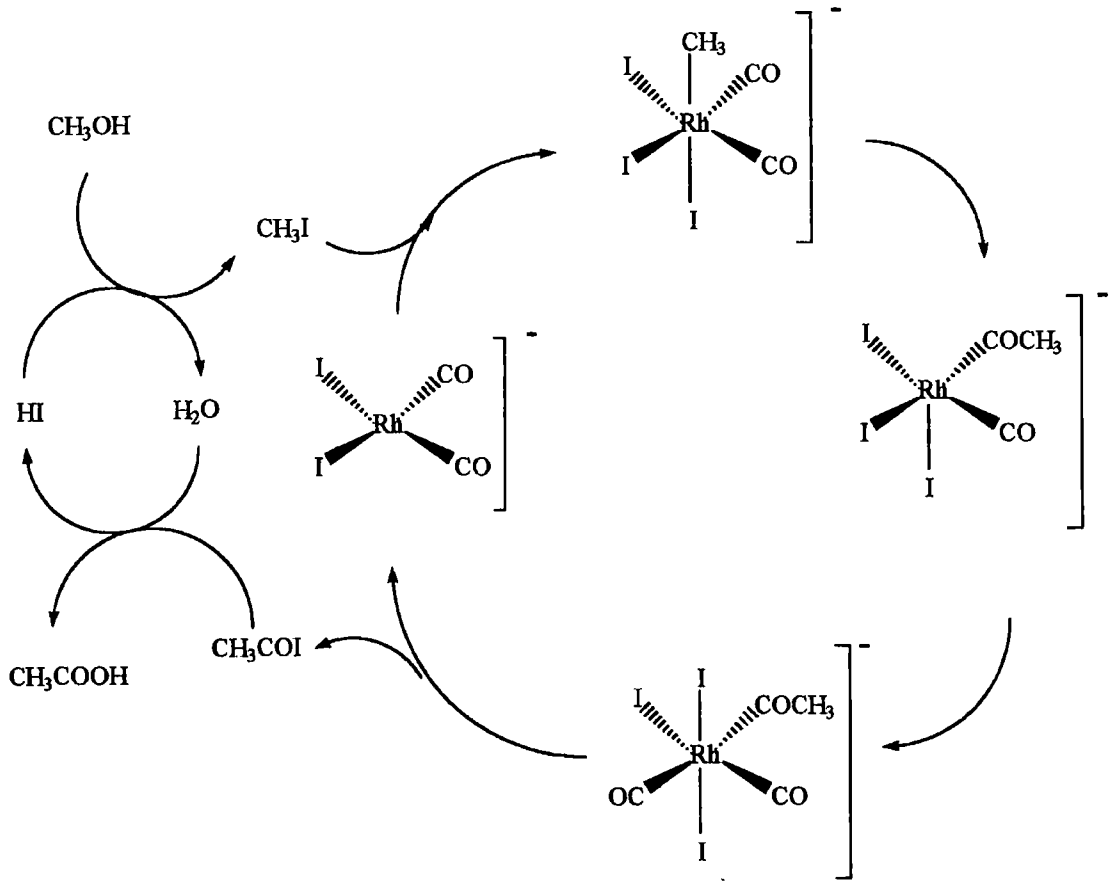
Introduction of $[Rh(acac)(CO)_2]$ afforded an active catalyst capable of 2000 turnovers in the hydroformylation of styrene. Branched products were around 80% of the total and these were in enantiomeric excesses of up to 90%.

Balue and Bayon[25] report the immobilisation of a rhodium thiolate binuclear catalyst by protonation of amine groups, pendant from the sulphur bridges, using a sulphonic acid ion-exchange resin. The products of hydroformylation were methyl acetals rather than aldehydes, formed almost quantitatively, with branched products exceeding linear products by 4:1.

5.1.4 Carbonylation of methanol

The carbonylation of methanol to acetic acid is not a hydroformylation reaction but the reporting of results for this reaction sits most comfortably in this chapter. The process known as the "Monsanto Acetic acid process" is carried out on a very large scale $\sim 10^6$ tonnes per year[26]. It follows an anionic catalytic cycle as depicted in Scheme 5.10.

For a catalytic cycle involving anionic species, an ion exchange resin is needed with positively charged fixed ions. This approach has been successfully adopted by Drago[27] *et al.* The authors copolymerised styrene with 4-vinylpyridine, then alkylated with methyl iodide, forming a methylpyridinium functionalised polymer. Two methods were employed to introduce the catalyst into the substrate. The first method entailed reaction of the polymer with solutions of $RhCl_3$ in the presence of CO and iodide, the second involved the direct reaction of $[Rh(CO)_2Cl]_2$ with the polymer. In both cases, infra-red spectroscopy revealed bands in the carbonyl stretching region, characteristic of $[Rh(CO)_2I_2]^-$. Rates of CO pressure drop using the resin supported catalyst were reported as being similar to rates measured for the analogous homogeneous system.



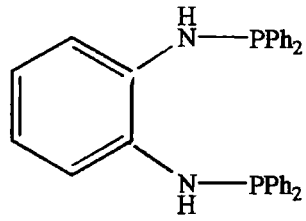
Scheme 5.10 Catalytic cycle for carbonylation of methanol

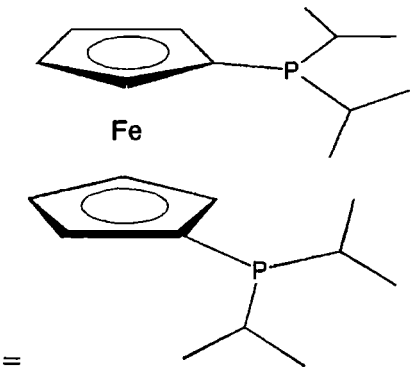
5.2 Experimental

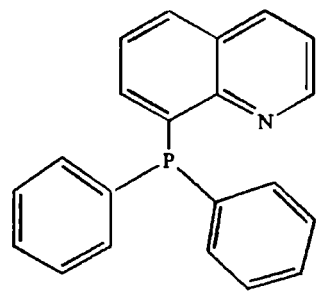
General experimental details are described in Appendix (I)

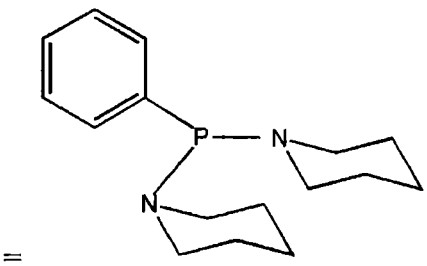
5.2.1 Ligands used for hydroformylation studies.

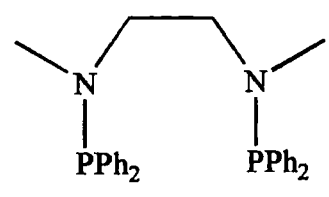
Diphenylphosphino-2-pyridine (PPh_2py) was supplied by the Aldrich chemical company.Bis (N,N'-diphenylphosphinomethyl)ethylenediamine (dppmen)[29] and bis (N,N'-diphenylphosphino)phenylenediamine (dppphn)[30] were available in the laboratory. Other ligands were synthesised as described in Chapters 3 and 4.

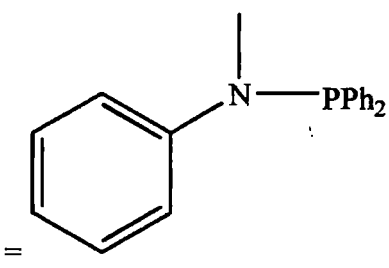
dpppphn = 

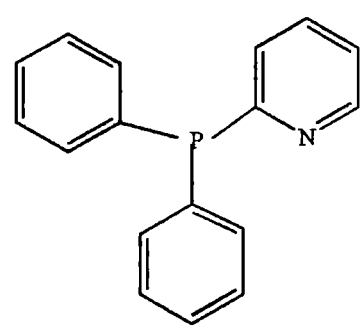
diPPFc = 

PPh_2Q = 

$PPhpip_2$ = 

dppmen = 

PPh_2Nma = 

PPh_2py = 

Scheme 5.11 Ligands used for hydroformylation with their abbreviations

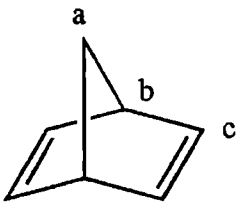
The ligands were chosen to be capable of protonation and cover a range of types, namely aliphatic/aromatic bidentate (diPPFc), aromatic P,N ligands (PPh_2py and PPh_2Q)and aminophosphines; bidentate with aliphatic nitrogen (dppmen), bidentate with aromatic nitrogen(dppphn), monodentate with aliphatic nitrogen (PPh_2pip) and monodentate with aromatic nitrogen (PPh_2Nma). Structures are drawn above in Scheme 5.11.

5.2.2 The synthesis of $[Rh(C_2H_4)_2Cl]_2$

The method described in Inorganic Synthesis (XV) p14 was followed.
$RhCl_3.3H_2O$ (5.0g, 19mmols) was dissolved in water (7.5 mls). To this was added methanol (125 mls). Ethene was bubbled through the solution for three days. Gradually, over this time the colour changed from deep red to orange and a rust coloured solid precipitated. At the end of the reaction the solid, $[Rh(C_2H_4)_2Cl]_2$ was collected by filtration, washed with methanol ($20cm^3$),and then dried *in vacuo* (2.1g, 54 %).

5.2.3 The synthesis of $[Rh(NBD)_2][BF_4]$

The method described by Schenk[31] *et al* was followed.
In a 100 ml Schlenk tube, $[Rh(C_2H_4)_2Cl]_2$, (0.7g, 1.78 mmol), was suspended in CH_2Cl_2 (30mls) and cooled in an ice-bath. A second similar tube was prepared with norbornadiene (NBD), (0.93 ml, 10 mmol), in CH_2Cl_2 (15 mls). The NBD solution was added to the rhodium solution and stirred for 30 minutes before the addition of an excess of $AgBF_4$ (1g) against a stream of nitrogen. After a further 45 minutes, the solution was filtered and THF (10 ml) added. The volume was reduced to about 5 mls and the resultant residue washed twice with THF. On drying *in vacuo* the yellow solid turned red. Yield 0.65g (1.74 mmol, 49%). (Found: C, 43.82; H, 4.35) $C_{14}H_{16}BF_4Rh$ requires C, 44.96; H, 4.31%). ^{13}C NMR, ($CDCl_3$) : $\delta = 93.09$ (s, 4C, C_c), $\delta = 69.64$ (d, $^1J_{C\text{-}H}$ 4.7 Hz, 1C, C_a), $\delta = 55.50$ (s, 2C, C_b)-ppm.

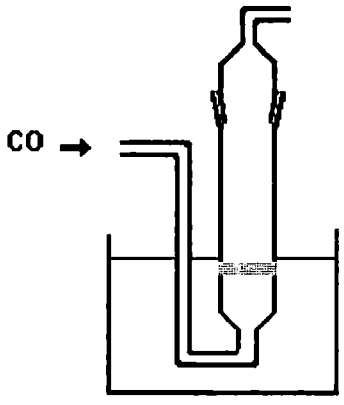


Scheme 5.12 ^{13}C assignments for NBD

5.2.4 The synthesis of $[Rh(CO)_2Cl]_2$

The method described in Inorganic Synthesis v5 p 211 was followed.

$$2\ RhCl_3.3H_2O + 6\ CO \rightarrow [Rh(CO)_2Cl]_2 + 6\ H_2O + 2\ COCl_2$$



Scheme 5.13

$RhCl_3.3H_2O$, (0.4g, 1.52 mmol) was weighed into the apparatus in Scheme 5.13 suspended on the no.3 sinter. The apparatus was heated in an oil bath to exactly 100°C and CO gas was passed through. Orange-red crystals of $[Rh(CO)_2Cl]_2$ condensed higher up the tube. The reaction continued over 3 days, with several stops to remove product by dissolution in hexane. Careful evaporation of the hexane solution led to reappearance of the crystals which were stored in a desiccator. Yield 0.22g (75%) IR: ν(C=O) ($CHCl_3$); 2106(m), 2090 (s), 2035 (s), 2006 (w). Lit.[28] 2105(m), 2089 (s), 2080 (vw), 2035 (s), 2003 (w) cm^{-1}.

5.2.5 The synthesis of $HRh(CO)(PPh_3)_3$

The method described in Inorganic Synthesis v15 p59 was followed.

$RhCl_3.3H_2O$ (0.26g , 1.0 mmol) in ethanol (20mls) was added to a stirred , boiling solution of triphenylphosphine (2.64 g, 10 mmol) in ethanol (100 mls). Aqueous formaldehyde (10 ml , 40% w/v soln.) was added followed immediately by KOH (0.8g) in hot ethanol (20mls). The solution was refluxed for a further 10 minutes

before being allowed to cool to room temperature. A bright yellow crystalline product was formed. This was removed by filtration and washed with aqueous ethanol and hexane and dried *in vacuo*.

Yield 0.85 g , (94%). m.pt. 120-122°C with decomposition. (Found: C, 69.11; H, 4.90, $C_{55}H_{46}OP_3Rh$ requires C, 71.90; H 5.05%). IR (KBr): ν(CO) =1920 cm^{-1} , ν(M-H) = 2035 cm^{-1} (lit. 1918, 2041 cm^{-1})

5.2.6 The synthesis of $RhCl(CO)(PPh_3)_2$

The method described in Inorganic Synthesis v11, p99 was followed.

$RhCl_3.3H_2O$ (0.52g , 2.0 mmol) in ethanol (18 mls) was added slowly to a stirred, boiling solution of triphenylphosphine (1.8 g, 6.9mmol) in ethanol (75 mls). Sufficient HCHO (37% aqueous soln.) was added to turn the red solution bright yellow (about 6 mls.). The solution was allowed to cool overnight. The yellow crystalline solid which precipitated was removed by filtration, washed with ethanol and diethyl ether and dried *in vacuo*. Yield 0.94g. (Found: C,.63.99; H, 4.35; N, 0; $C_{37}H_{30}OClP_2Rh$ requires C, 64.32; H, 4.38; N 0%). IR: (KBr), ν(C=O) 1962 cm^{-1} (vs) (lit., 1960 cm^{-1}) ; ν (P-Ph) 1434 cm^{-1}. $^{31}P\{^1H\}$NMR ($CDCl_3$) : δ = 30.05 (d, J_{Rh-P} = 127 Hz.) ppm.

5.2.7 The synthesis of diphenylphosphino-N-methyl aniline (PPh_2Nma)

Freshly vacuum distilled N-methyl aniline (4.3g ,0.040 mol) was added to toluene (40 mls) followed by the addition of triethylamine (4.06g , 0.040 mol). Into a second flask PPh_2Cl (8.85g , 0.040 mol) was added to toluene (10 mls). The flask containing the amines was cooled to -78°C and the chlorophosphine solution slowly added by syringe. The temperature was maintained at -78°C for 30 minutes with stirring and then the solution was allowed to warm to room temperature and stirring continued overnight. The white precipitate of $Et_3NH^+Cl^-$ was filtered off using a sintered glass filter and washed with 3 portions of warm toluene (20 mls). The filtrate

was reduced to dryness and redissolved in CH_2Cl_2. Hexane was added in 1 ml portions and the flask stored in the freezer. A white crystalline solid appeared which was removed by filtration and pumped to dryness.
(Found C, 76.88; H, 6.57; N, 4.50 $C_{19}H_{18}NP$ requires C, 78.36; H, 6.18; N, 4.81%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.45 (s) ppm. ^1H NMR ($CDCl_3$): δ = 7.0- 7.38 (m, 15H); 6.76 (t, 1H); 2.71 (s, 3H) ppm. IR: ν (P-Ph) 1431 cm^{-1}; ν(N-H) absent.

5.2.8 The addition of $[Co_2(CO)_8]$ to Nafion-$P(Bu^t)_2$

Beads of Nafion-$P(Bu^t)_2$ (0.5g, batch 1), (section 2.17), were stirred for 4 days in a toluene solution (10 mls) of $Co_2(CO)_8$, (0.068g, 0.4 mmol), at room temperature under an atmosphere of nitrogen. The initial white, opaque beads took on a slight reddish colouration. The cobalt carbonyl was not fully absorbed. The beads were used for hydroformylation reaction no.HF17.

5.2.9 The addition of $HRh(CO)(PPh_3)_3$ to Nafion-PPh_2

Beads of Nafion-PPh_2 (0.7g, batch 1), (section 2.16), were stirred for 7 days in toluene (10 mls) containing $[HRh(CO)(PPh_3)_3]$(138 mg, 0.2 mmol) at room temperature under an atmosphere of nitrogen. The complex was completely absorbed. The beads were used for hydroformylation reaction no.HF22.

5.2.10 The addition of $[Rh(CO)_2Cl]_2$ to Nafion-NR_3

Beads of Nafion-N^+R_3 (1.78g, batch 1), (section 2.15), were stirred in a THF solution containing $[Rh(CO)_2Cl]_2$ (0.01g, 0.0257 mmol) for 7 days under an atmosphere of nitrogen. The initially white, opaque beads took on a slight orange colour.The complex was only partly absorbed. The beads were used in catalytic run Carbon 3.

5.2.11 The addition of $[RhCl(CO)(PPh_3)_2]$ to Nafion-Ag

Nafion-H, (1g), was stirred overnight with $AgNO_3$ in an aqueous/methanolic solution with the light excluded. The beads were drained and washed with methanol (3 x 25 mls). The beads were then added to a solution of $[RhCl(CO)(PPh_3)_2]$(0.006g,

0.016 mmol) in 50:50 CH_2Cl_2/MeOH and stirring commenced. The solution lost its faint colour and the beads became pale yellow. The beads were used in catalytic run HF23.

5.3 Catalytic Studies

High pressure catalytic runs were carried out in a manner analogous to that described in Appendix (I). All homogeneous runs and runs using Nafion-H were based on cationic rhodium complexes formed by the replacement of norbornadiene from $[Rh(NBD)_2]BF_4$ by either two monodentate ligands or one bidentate ligand. Two initial trials using the complex $[Rh(NBD)(dcpe)]BF_4$ showed that hydroformylation had taken place in the presence of Nafion but that very serious leaching had occurred. It was likely that during catalysis a neutral intermediate, perhaps of the form $[HRhL_2(CO)]$, had formed and had leached out from the beads. Since species of this nature are also highly active catalysts for hydroformylation, the results obtained were very ambiguous, in that catalysis could have taken place in the solution as well as in the beads. Henceforth it was decided to adopt a "belt and braces" approach, in which the catalyst precursor would be ionic and would also contain ligands capable of protonation to prevent leaching of any neutral intermediates. The ligands used are described in section 5.2.1 in the text and in Scheme 5.11. A series of high pressure reactions was performed using a set of standardised conditions, described in section 5.3.2. The results of these reactions are reported in Table 5.1. Additionally some catalytic runs were carried out in which the conditions do not conform to the standard series and where modified forms of Nafion have been used. These results are gathered together in Table 5.2. In each standard case, the catalyst system was formed *in situ* by addition of the ligand to $[Rh(NBD)_2]BF_4$ and in each case the substrate used was hex-1-ene. For each Nafion supported run, the ligand was allowed to react with $[Rh(NBD)_2]BF_4$ and the reaction solution monitored using phosphorus NMR spectroscopy to establish that ligand replacement had indeed occurred and was complete before the resultant solution was stirred with Nafion beads.

5.3.2 Standard conditions used for catalysis reactions

i/ homogeneous case

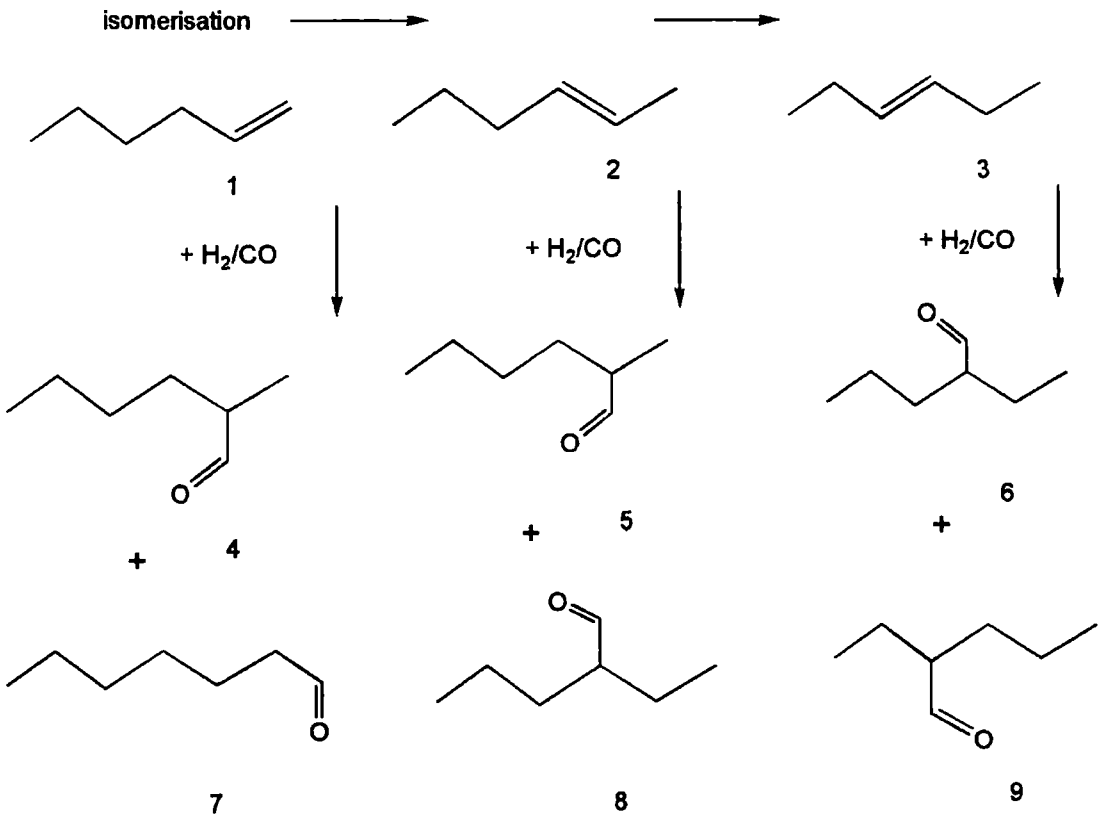
$[Rh(NBD)_2]BF_4$(0.01g, 2.7 x 10^{-5}mol) was added to a slight molar excess of ligand in the glass sleeve of the reaction vessel. To this was added 10 mls each of 1-hexene, methanol and N-methylpyrrolidinone (NMP). The sleeve was fitted to the autoclave and the autoclave flushed with nitrogen. The autoclave was pressurised to 40 bar of H_2/CO (50:50) and heated to 120°C for 5 hours.

ii/ supported case

$[Rh(NBD)_2]BF_4$ (0.01g, 2.7 x 10^{-5}mol) was added to a slight molar excess of ligand in a 100 mls round bottomed flask and dissolved in degassed methanol. The mixture was stirred for 2-3 hours before a sample was removed for ^{31}P NMR studies. In all cases the signal for free ligand could no longer be detected and a new pattern for the complex had been generated. To the flask was added 1g of vacuum dried Nafion-H beads and stirring continued overnight under nitrogen. The solution was removed by syringe from the beads which were rinsed in methanol before being transferred to the reaction vessel sleeve. The procedure then continued as described in (i) above.

5.3.3 Products of Hydroformylation of Hex-1-ene

The catalysts used for the hydroformylation of hex-1-ene also result in its isomerisation. Hex-1-ene can be isomerised to *cis* and *trans* hex-2-ene and *cis* and *trans* hex-3-ene. In theory, each of these can undergo hydroformylation to produce both linear and branched aldehyde isomers. However, as can be seen from Scheme 5.13, the loss of the double bond during hydroformylation ensures that the stereoisomerism possible for the starting material is lost in the products, and symmetry in the structure means that there are only actually three products. However a chiral centre is introduced into the molecule to give two more possible branched products.



Scheme 5.14 Products from isomerisation and hydroformylation of hex-1-ene.

Reaction solutions were distilled and analysed by gas liquid chromatography. Peaks were identified by GC-MS in the first instance and thereafter by retention times. In some cases only three isomers of hexene were seen and in some cases four isomers were seen (internal alkenes can be *cis* or *trans*). Their peaks were assigned on the basis of literature values for their boiling points on the assumption that the lowest boiling fraction elutes first. This is not sufficiently unambiguous to allow identification of *cis* and *trans* isomers. In all cases only three aldehyde products were identified. For the purposes of establishing the percentage normal product, the area produced by the normal isomer is divided by the areas generated by all isomers added together. There was no evidence for the production of alcohols or alkanes.

run no	phosphine	support	leaching	% Yield hexene isomers	Yield mol /mol Rh	% Yield aldehyde	aldehyde n:b ratio
hf5	none	Nafion H	complete	73.3	296	9.3	0.36
hf8	dppphn	none	n/a	66.4	1045	13.1	1.33
hf3	dppphn	Nafion H	no	70.5	1195	12.9	0.75
hf9	PPh_2py	none	n/a	45.8	1083	36.3	1.91
hf10	PPh_2py	Nafion H	yes	75.3	208	7.0	1.65
hf11	$PPhpip_2$	none	n/a	59.3	610	20.4	1.37
hf12	$PPhpip_2$	Nafion H	yes (15%)	76.3	253	8.5	0.59
hf14	PPh_2Q	none	n/a	63.4	412	13.8	1.10
hf13	PPh_2Q	Nafion H	complete	71.9	454	15.2	0.52
hf15	dppmen	none	n/a	41.0	1754	44.4	2.28
hf16	dppmen	Nafion H	complete	54.7	1158	29.3	0.94
hf18	PPh_2Nma	none	n/a	53.4	1303	43.6	1.29*
hf19	PPh_2Nma	Nafion H	heavy	64.3	801	26.8	0.62
hf21	diPPFc	none	n/a	79.8	1696	11.2	0.74
hf20	diPPFc	Nafion H	yes (20%)	73.4	1428	9.5	0.55
blank†	none	Nafion H	n/a	15.3	nil	nil	n/a

* 2.12 has been obtained[43] for $RhCl(CO)L_2$. † No rhodium used.

Table 5.1 Standardised high pressure results comparing homogeneous to Nafion supported hydroformylation of hex-1-ene.

The data from Table 5.1 were used to generate Charts 5.1 to 5.3.

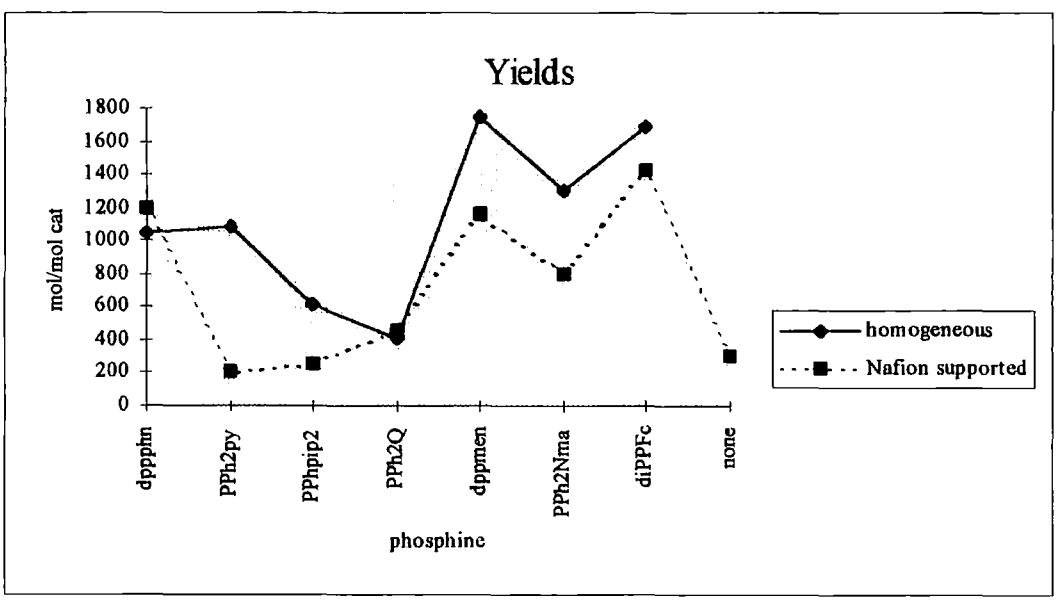


Chart 5.1 Effect of Nafion on yields of aldehydes for each ligand studied

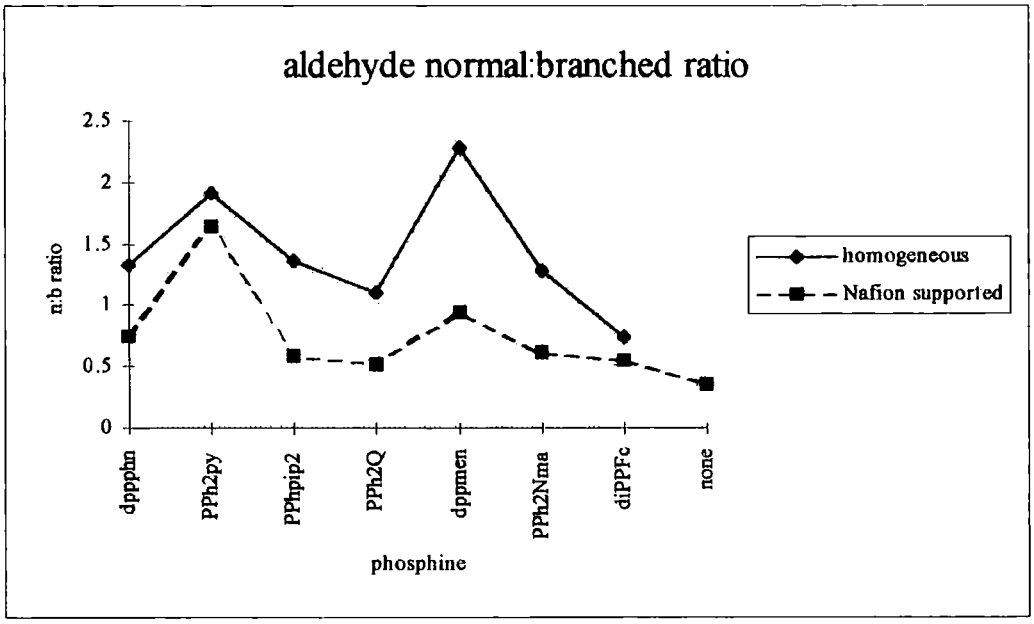


Chart 5.2 **Effect of Nafion on the normal to branched aldehyde ratio produced for each ligand studied.**

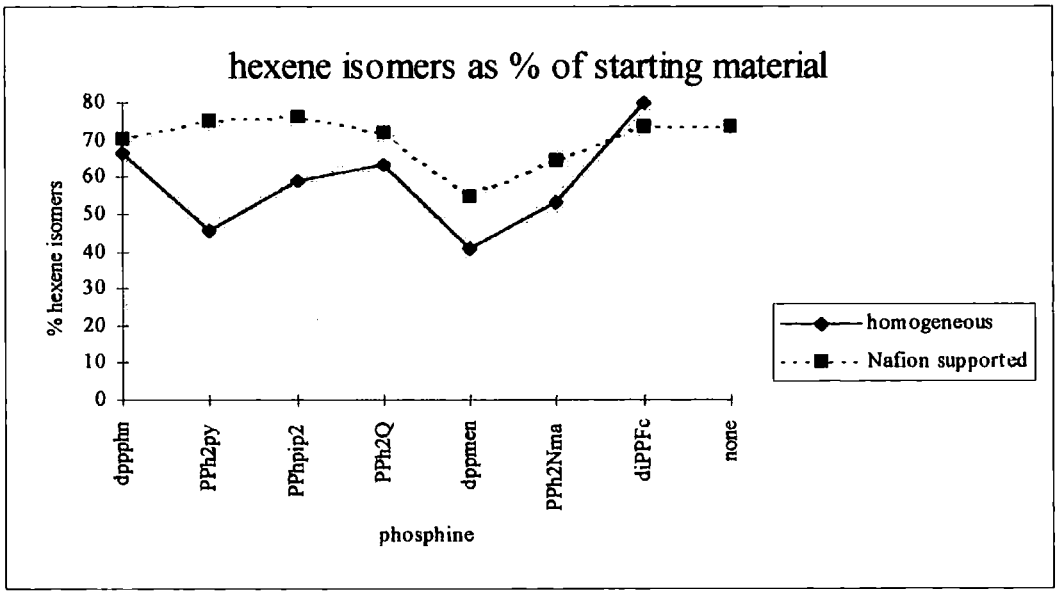


Chart 5.3 **Effect of Nafion on percentage isomerisation of hex-1-ene for each ligand studied**

In addition to the catalytic runs reported in Table 5.1, the following hydroformylation runs were performed:

Run hf4: The beads used in run hf3 were re-used in a repeat run.

Run hf6: Standard conditions except the solvent was 10 mls hexene and 20 mls water.

Run hf7: Standard conditions except the solvent was 20 mls hexene and 1 ml water.

Run hf17: Beads described in 5.2.7 were used at 170°C for 12 hrs. P = 40 bar.

Run hf22: Beads described in 5.2.8 were used at 120°C for 5 hrs. P = 40 bar

Run hf23: Beads described in 5.2.10 were used. 120°C for 5 hrs. P = 40 bar

Run hf24: Nafion-H (0.2g) was stirred overnight with $RhCl(CO)(PPh_3)_2$,(0.0035g , 9.16μmol), in CH_2Cl_2/MeOH (50:50). The beads were rinsed with MeOH and used under standard conditions.

run no	catalyst system	support	leaching	hexene isomers 1:3:2	Yield mol/mol Rh	n:b ratio
hf4	$Rh(NBD)_2BF_4$ + dppphn	hf3 reused beads	no	100:21:4	0	n/a
hf6	$Rh(NBD)_2BF_4$ + dppphn in water	Nafion H	no	no reaction	0	n/a
hf7	$Rh(NBD)_2BF_4$ + dppphn in 1ml water	Nafion H	no	100:96:46	84	1.31
hf17	Co_2CO_8	Nafion PBu_2	no*	52:100:38	4	0.96
hf22	$HRh(CO)(PPh_3)_3$	NafionPPh_2	1%**	48:31:100:39	180	0.71
hf23	$RhCl(CO)(PPh_3)_2$	Nafion-Ag	metal†	none	none	n/a
hf24	$RhCl(CO)(PPh_3)_2$	Nafion-H	yes‡	100:10:4	none	n/a

Table 5.2 Non-standard and modified Nafion high pressure results for the hydroformylation of hex-1-ene.

5.3.4 Observations relating to Table 5.2

* reaction hf17: The initial appearance of the beads was opaque and white. Their post-run appearance was orange-brown and clear.

** reaction hf22: The initial appearance of the beads was opaque and white. After reaction they were very swollen and clear with an orange colour.

[†] reaction hf23: The initial appearance of the beads was faintly yellow and clear. After reaction the beads were opaque and china clay coloured. The reaction solution contained much suspended solids.

[‡] reaction hf 24: The beads absorb the complex readily to become faintly yellow coloured. After the reaction, the beads are darker and the solution is bright yellow, turning to green then turquoise on standing. Metal carbonyl species are present in the solution, showing absorbances in the infra-red at 2061 cm^{-1} (vs) and 1887 cm^{-1} (s).

5.4 The carbonylation of methanol

A sample of modified Nafion beads (0.2g) produced as reported in section 2.15 together with Nafion-H (0.2g) as an acid catalyst were added to MeOH (20 mls) with water (10mls) containing I_2 (1.0g) and $RhCl_3.3H_2O$ (0.025g, 0.095 mol). NaI cannot be used in place of HI, CH_3I or I_2 as a promoter for methyl iodide formation from methanol[27]. The autoclave containing this mixture was heated to 120°C for 5 hrs under an atmosphere of 20 bar CO and the run designated as Carbon 1. After the reaction, the beads retained some colouration. Analysis of the solution by GC revealed a peak with the retention time of methyl acetate. Using methanol as internal standard allows the yield to be calculated as 41 turnovers. The beads were recovered and used again in a run as Carbon 2, with the same starting materials but no added rhodium. Only a trace of product was detected from this run, indicating that catalysis had been confined to the solution in Carbon 1.

Adopting the second approach used by Drago[27], a sample of Nafion-amine beads were exchanged with $[Rh(CO)_2Cl]_2$, described in section 5.2.9. These beads were suspended in a solution of I_2 (0.5g) in 20 mls MeOH/ 10 mls water in an autoclave liner. The liner was transferred to the autoclave and heated to 120°C for 5 hours under an atmosphere of 30 bar CO. Initially, the beads had a slight orange colouration and were opaque. After reaction the beads were clear and golden in

appearance. Analysis of the solution by GC showed acetic acid had been produced. Calculating yield based on a standard solution of acetic acid in methanol gives a turnover figure of 188 mol/mol catalyst. The solution was slightly cloudy but not visibly coloured.

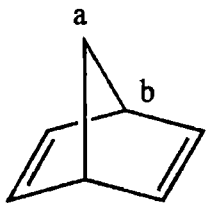
5.5 Spectroscopic studies of the ligands used in hydroformylation

Three separate approaches were made, to try to gain insight into the electronic effect each ligand has on the metal centre. The first method compared the chemical shifts of the vinylic carbons of the coordinated NBD for the series of compounds $Rh(NBD)L_2$ and Rh(NBD)(L-L) . The second method compared the stretching frequencies for ν(CO) in the compound $HRh(CO)(PPh_3)_3$ as the PPh_3 groups are replaced by the chelating ligands (L-L) and finally the third method also involved monitoring carbonyl stretches as L or L-L replaced carbonyl groups from $Mn(CO)_5Br$.

5.5.1 NMR studies

Diolefins coordinated to a transition metal centre can be sensitive indicators to electronic changes at the metal caused by other ligands[32]. A series of NMR scale reactions were carried out in which $[Rh(NBD)_2]BF_4$ (0.01g, 2.67×10^{-5}M) was dissolved in $CDCl_3$ together with a slight molar excess of the ligand to be tested. The phosphorus NMR spectrum was recorded to establish that the ligand had been coordinated, as with the catalytic experiments described earlier. Then the proton coupled carbon NMR spectrum was recorded. The results are tabulated below (in Table 5.3). The phosphorus coupling to rhodium could not be detected in all cases. The ^{13}C NMR spectra clearly showed free NBD in each case but the signals for the coordinated NBD were broader and considerably weaker. In two cases, (PPh_2Q and

$PPhpip_2$), the signals could not be seen, even when more concentrated solutions were made in CD_3OD.



Norbornadiene[33]. ^{13}C NMR: $\delta_a = 75.5$ ppm. $\delta_b = 50.9$ ppm. $\delta_c = 143.5$ ppm.

$[Rh(NBD)_2]BF_4$ ^{13}C NMR: $\delta_c = 93.09$ ppm. (section 5.2.2)

ligand	^{31}P NMR δ (ppm) free	^{31}P NMR δ (ppm) coordinated	J_{Rh-P} (Hz)	^{13}C NMR δ (ppm) coordinated
dppmen	65	82	169	83/85
dppphn	33	70	169	91/93
PPh_2Nma	56	134 129	158 145	114/115
PPh_2py	-3	26	-	149/151
PPh_2Q	-13	34	-	-
diPPFc	38	59	-	-
$PPhpip_2$	97	29	-	-

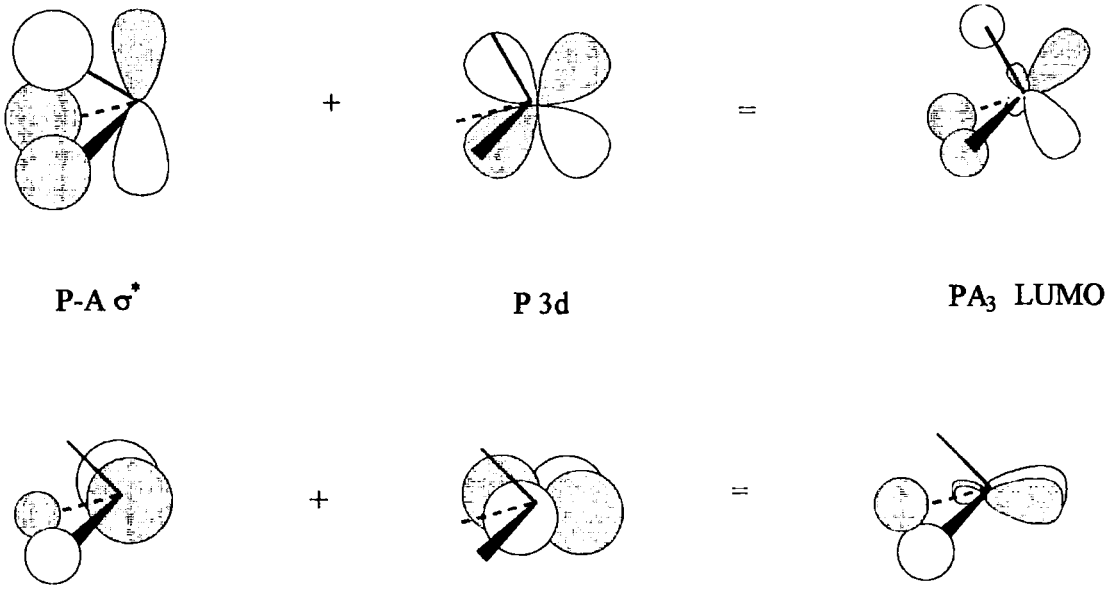
Table 5.3 NMR results.

The difficulty in locating the peaks due to coordinated NBD, in contrast to the sharp peaks for the free ligand released during the complexation, shows the fluxional nature of the dienes' coordination. Similar observations were made by Kostas and Screttas[16] concerning the behaviour of COD vinylic carbons in $Rh(COD)L_2BF_4$.

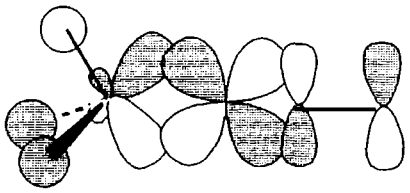
5.5.2 Infra-red studies

The bonding between a carbonyl group and a metal consists of contributions from a metal-carbon σ bond in which electron density is transferred from the ligand to the metal and a π-acceptor interaction in which electron density is transferred from the metal to anti-bonding orbitals ($2\pi^*$) on the ligand. It is this second interaction, known

as backbonding, which is the most relevant in metal phosphine carbonyl complexes because the metal d-orbital, which is involved , is also involved in bonding to phosphorus in the *trans* position. Metal to phosphorus bonding is also supplemented by backbonding, this time to orbitals on phosphorus which are the result of hybridisation between 3d orbitals and σ^* orbitals formed between phosphorus and its substituents (Scheme 5.15). Therefore the π-acidity of the phosphorus ligand influences the strength of the metal-carbon bond and subsequently the strength of the C=O bond (Scheme 5.16). This change is reflected in the ν(C=O) stretching frequency and is a general result applicable to any transition metal.



Scheme 5.15. Mixing of phosphine P-A σ^* and P 3d orbitals leading to well hybridised π-acceptor LUMOs on phosphorus taken from Orpen[34] *et al*



PA_3 LUMO M 3d CO π^*

Scheme 5.16 Phosphorus-metal-carbonyl orbital interactions

On coordination to the metal the C=O bond order is reduced compared to free carbon monoxide as reflected in the lower frequency of metal carbonyl ν(C=O) stretching. If the substituent *trans* to the carbonyl group is a strong π-acceptor due to its electron withdrawing properties then the M-C bond is weakened and the C=O bond strengthened leading to higher frequency stretches. A systematic study of the electron donor-acceptor properties of a range of phosphines has been carried out by Tolman[35] based on changes in the ν(C=O) stretching frequency of substituted $Ni(CO)_4$ when CO is replaced by a monophosphine. This study enabled predictions of carbonyl stretching frequencies to be made for a given phosphine based on the known effects of each substituent present in that phosphine. The degree to which subsequent carbonyl groups would be substituted by a given phosphine was shown by Tolman in a following paper[36] to be more strongly influenced by steric effects than electronic ones.

5.5.2.1 IR studies of reactions between bidentate ligands and $HRh(CO)(PPh_3)_3$

This exercise was limited to the bidentate ligands used for hydroformylation. Infra-red data for ν(CO) has been tabulated by L.van der Veen *et al.* for a range of diphosphine complexes with similar structures but different electron withdrawing or donating characteristics[11], allowing a comparison to be made.

$HRh(CO)(PPh_3)_3$ (0.084g, 0.09 mmol) was dissolved in 30 mls CH_2Cl_2 . From this solution, 5 mls was transferred by syringe to a Schlenk tube containing a slight molar excess of ligand under nitrogen. The solution was stirred at room temperature

overnight and then heated to reflux temperature for 10 minutes. Samples were transferred by syringe to an infra-red liquid cell for measurement.

$HRh(CO)(PPh_3)_3$: $\nu(CO)$ =1920 cm^{-1} , $\nu(M-H)$ = 2035 cm^{-1}

ligand	ν_1 cm^{-1}	ν_2 cm^{-1}
dppphn	1961	1890
PPh_2Q	1962	1922
dppmen	1971	1900
diPPFc	2054	1968

Table 5.4 Carbonyl stretching frequencies (I)

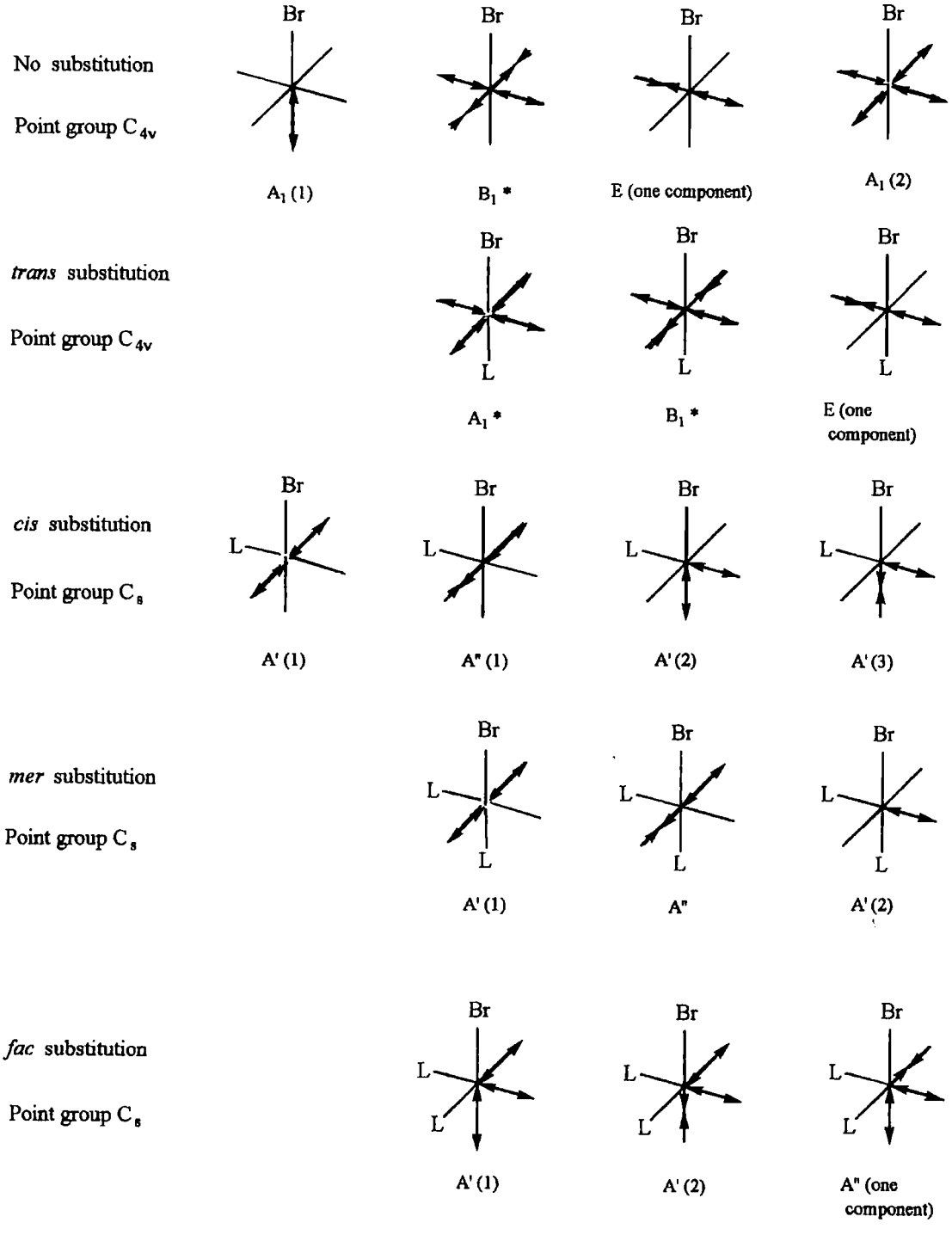
ν_1 and ν_2 are considered[11] to be the respective symmetric and anti-symmetric combinations of $\nu(CO)$ and $\nu(M-H)$.

5.5.2.2 Reactions between ligands and $Mn(CO)_5Br$

$Ni(CO)_4$ is highly toxic due to its labile carbonyl groups; a safer alternative for substitution experiments is to use $Mn(CO)_5Br$. For a series of monodentate group 5 ligands, Angelici and Basolo[37] have shown the ranking of bonding strength to be the same as that determined with the nickel studies. Displacement of one CO group from $Mn(CO)_5Br$ occurs preferentially *cis* to the bromine ligand. This is due to the decreased lability of the *trans* CO since it has no competition from bromine for metal d-electrons and hence the M-C bond is stronger. Displacement of two CO groups leads

to the formation of two possible isomers. These are shown below in Scheme 5.18 along with the symmetry information for each complex. The five CO groups in $Mn(CO)_5Br$ give rise to 3 IR active fundamental CO stretching vibrations separated into the symmetry classes of the C_{4v} point group: A_1 (axial and radial), B_1 radial and E (two degenerate radial vibrations).[38]

A description of the various vibrational modes is given below in Scheme 5.17 adapted from Adams[39] who does not always draw the distinction between L or X . The number of bands in these cases is not affected by replacing L with X or L' only the nomenclature. Symmetric stretches in *trans* substituted compounds do not have any change in dipole moment and are therefore IR inactive. Modes involving the stretching of CO *trans* to Br will be at lower frequency due to the stronger M-C bond (*vide supra*). The introduction of a bulky, asymmetric substituent as L, may split the degeneracy of some bands leading to broadening of those bands and may lift the selection rules governing the complex allowing vibration modes which are normally only Raman active to become infra-red active.



* indicates Raman active

Scheme 5.17 Fundamental Stretching Vibration modes for Carbonyl groups in subtituted Manganese Carbonyls

The bands found in the carbonyl stretching region can be assigned with varying degrees of certainty on the basis of a series of postulates put forward by Cotton and Kraihanzel[40] namely:

i/ The stretching of one CO bond increases the resistance to stretching of the remainder. Hence symmetric stretches are at higher frequency.

ii/ The interaction constant between pairs of *cis* CO groups is approximately double that for pairs of *trans* groups $k_c \approx 2k_t$ because *cis* groups share only one $d\pi$ orbital.

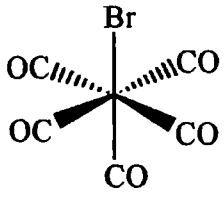
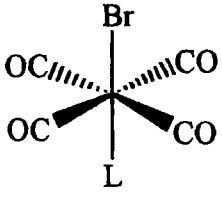
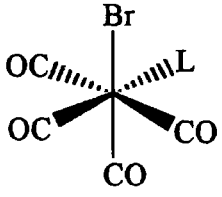
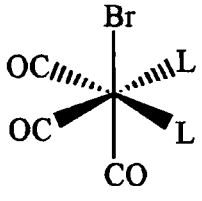
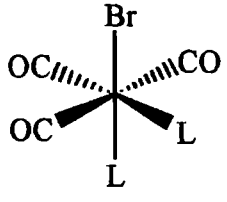
iii/ The CO stretching force constants decrease as CO groups are replaced by other, weaker π-acceptor ligands

iv/ CO groups which are *cis* to those substituents in (iii) should have higher stretching force constants than those *trans-* to such substituents.

v/ Increasing replacement of CO by ligands of lower π-acidity should increase stretch-stretch interaction constants.

Assignment of bands is helped further, by comparison with similar known compounds e.g. Atwood[41] reports $Mn(CO)_4(PPh_3)Br$ has four IR bands at 2087(m), 2022(s), 2004(vs) and 1958(s) .Angelici[37] gives data for a series of *cis* $Mn(CO)_4LBr$ complexes and a series of *fac* and *mer* $Mn(CO)_3L_2Br$ complexes[42]. In addition NMR data provide supporting evidence.

$Mn(CO)_5Br$ (0.082g, 0.3mmol) was weighed into a 100ml schlenk tube and the air replaced with nitrogen. To this was added 30 mls CH_2Cl_2 and stirring commenced to effect dissolution. A slight molar excess of ligand was added against a stream of nitrogen and stirring continued for 24 hours. A sample was taken for ^{31}P NMR and for IR measurement in a liquid cell. The remaining solution was heated to reflux temperatures and resampled for both measurements.

Complex		Number and Modes of IR active bands	Point group
		3 $2A_1 + E$	C_{4v}
	*trans*	2 $A_1 + E$	C_{4v}
	*cis*	4 3A' + A"	C_s
	*fac*	3 2A' + A''	C_s
	*mer*	3 2A' + A''	C_s

Scheme 5.18 Substituted manganese carbonyls

There is a second *mer* isomer with mutual *trans* L ligands and C_{2v} symmetry which would not be expected for bidentate ligands. It is more likely that *fac* complexes will be formed than *mer* complexes because the carbonyl groups which are mutually *trans* are more labile than those *trans* to bromine.

Phosphine	I.R. bands cm^{-1}	I.R. Assignment	^{31}P NMR data δ (ppm)
none	2136(w) 2052(s) 2006(m)	$A_1(2)$ E $A_1(1)$	n/a
PPh_2py	2136(vw) 2090(m) 2051(s) 2026(s) 2007(s) 1954(s) 1918(w)	A_1 (2){$Mn(CO)_5Br$} A' (1){*cis*-$LMn(CO)_4Br$} E {$Mn(CO)_5Br$} E_u {*trans*-$LMn(CO)_4Br$} A'(2) {*cis*-$LMn(CO)_4Br$} A' (3){*cis*-$LMn(CO)_4Br$} A''{*fac*-$(L)_2Mn(CO)_3Br$}	48, 57, 58
$PPhpip_2$	2088(m) 2052(m) 2005(vs) 1958(s)	A'(1) *cis*-$LMn(CO)_4Br$} A'' *cis*-$LMn(CO)_4Br$} A'(2) *cis*-$LMn(CO)_4Br$} A'(3) *cis*-$LMn(CO)_4Br$}	117
PPh_2Nma	2137(w) 2090(m) 2051(s) 2007(br,s) 1961(m)	A_1 {$Mn(CO)_5Br$} A' (1){*cis*-$LMn(CO)_4Br$} E {$Mn(CO)_5Br$} A'(2) *cis*-$LMn(CO)_4Br$} + $A_1(1)$ {$Mn(CO)_5Br$} A'(3) *cis*-$LMn(CO)_4Br$}	99
dppmen[29]	2093(vw) 2051(s) 2025(vs) 2010(sh) 1958(s) 1944(sh) 1919(br,s)	A'(1){*cis*-$LMn(CO)_4Br$} E{$Mn(CO)_5Br$} A'(1){*fac*-$(L)_2Mn(CO)_3Br$} A'(2){*cis*-$LMn(CO)_4Br$} A'(2){*fac*-$(L)_2Mn(CO)_3Br$} A'(3){*cis*-$LMn(CO)_4Br$} A''{*fac*-$(L)_2Mn(CO)_3Br$}	93, 38*,35*, -21,-24
dppphn	2093(vw) 2053(w,sh) 2029(vs) 1965(vs) 1919(s)	A'(1){*cis*-$LMn(CO)_4Br$} E {$Mn(CO)_5Br$} A'(1){*fac*-$(L)_2Mn(CO)_3Br$} A'(2){*fac*-$(L)_2Mn(CO)_3Br$} A''{*fac*-$(L)_2Mn(CO)_3Br$}	89, 86 32 (free ligand)
PPh_2Q	2051(m) 2024(s) 2011(sh) 1985(m) 1944(m) 1918(m)	E {$Mn(CO)_5Br$} A'(1){*fac*-$(L)_2Mn(CO)_4Br$} A'(2){*cis*-$LMn(CO)_4Br$} $(L)_2Mn(CO)_3Br$ A'(3){*cis*-$LMn(CO)_4Br$} A''{*fac*-$(L)_2Mn(CO)_3Br$}	55, 57, 59

v = very; w = weak; m = medium; s = strong; br = broad; sh = shoulder: * diminished greatly after heating

Table 5.5 Infra-red and ^{31}P NMR data of substituted $Mn(CO)_5Br$

The recurring band at around 2052 cm^{-1} could be due to unreacted starting material. This is more likely when the band was comparatively weak and other starting material bands were detected. Except where indicated, free ligand was not detected by ^{31}P NMR.

5.5.3 Molecular modelling

The bidentate ligands were modelled using the Desktop Molecular Modelling package. The fragment Rh(L-L) was drawn in each case and the most stable configuration calculated. Rhodium acts as a "dummy metal atom" to locate the ligand. The L-Rh-L bite angles were given as follows:

ligand	L-Rh-L angle	comments
dppmen	115.61°	7-membered puckered ring; 2 phenyl groups coplanar
dppphn	113.52°	7-membered puckered ring; no phenyl groups coplanar
PPh_2Q	107.08°	5-membered planar ring

Table 5.6 Bite angles calculated for the bidentate ligands used

5.6 Discussion

In order to study hydroformylation using Nafion supported complexes, the complexes chosen must be capable of being absorbed by Nafion. Initially the use of cationic rhodium phosphine complexes appeared appropriate. However, early trials using the complex $[Rh(NBD)(dcpe)]BF_4$ showed that very serious leaching had occurred. It was likely that during catalysis a neutral intermediate, perhaps of the form $[HRhL_2(CO)]$, had formed during the reaction and had leached out from the beads. The results obtained were very ambiguous, in that catalysis could have taken place in the solution as well as in the beads. In order to ensure that the rhodium complexes

were retained within the Nafion throughout the catalytic cycle, it was decided to form cationic complexes containing phosphine ligands which were themselves capable of protonation. A number of suitable phosphine ligands was readily available in the laboratory reducing the need for extra synthesis. The group of ligands included monodentate and bidentate phosphines, monodentate aliphatic and aromatic aminophosphines and bidentate aliphatic and aromatic aminophosphines.
A set of standard conditions was chosen to enable a fair comparison across the range of ligands and between the complexes used homogeneously and the complexes supported in Nafion. The complexes were allowed to form *in situ* from the reaction between $[Rh(NBD)_2]BF_4$ and the corresponding phosphine. To complete the data set, a hydroformylation reaction run was carried out using Nafion without any $[Rh(NBD)_2]BF_4$, designated as "blank" and a run was carried out using $[Rh(NBD)_2]BF_4$ without any added phosphine ligand.

From Table 5.1 and Chart 5.1 it can be seen that, in most cases, the overall yield is reduced by introduction of the catalyst into Nafion. There does not appear to be any pattern across the series of ligands with regard to yields obtained when the catalyst is used homogeneously. However, on introduction into Nafion, the three bidentate ligands consistently outperform the monodentate ligands. PPh_2Q could be considered as a bidentate ligand in homogeneous solution but in Nafion it will be protonated and can therefore be classified among the monodentate ligands. The distribution of products is clearly altered by introduction into Nafion. The ratio of normal heptanal to branched products, is reduced in all cases by supporting the catalysts. Interestingly, this remains the case despite leaching occurring in the majority of cases. The trend across the range of ligands for production of normal aldehyde using homogeneous catalysts is closely followed by the supported catalysts. Chart 5.3 shows a comparison between the homogeneous and supported catalyst reactions in terms of the percentage of 2 and 3-hexene isomers present at the end of the reaction. In most cases there are more of these isomers remaining after supported catalyst reactions. Heptanal can only be derived from hex-1-ene and assuming isomerisation occurs faster than hydroformylation then the concentration of starting material is reduced to a

greater extent in the supported case. This increase in isomerisation partly explains the decrease in normal heptanal production, displayed in Chart 5.2. The increased isomerisation seen in the supported case, can be attributed to the action of Nafion-H itself since hex-1-ene was isomerised in the "blank" experiment (Table 5.1).

Table 5.2 represents a compilation of single catalytic runs, not part of the comparative series of runs using standard conditions. The conditions used for each run are described in the text preceding Table 2. Run hf4 shows that beads recovered from a successful reaction are no longer active. The next two entries demonstrate the inhibiting effect that water can have on the reaction. The normal to branched ratio of products was almost identical whether water was present or not, leading to the conclusion that the inhibiting effect is merely the immiscibility of the the two phases and not due to water interfering in the catalytic cycle.

Runs numbered hf17 and hf22 made use of Nafion in which the sulphonic acid group had been replaced by another functional group (see Appendix (II) and Chapter 2 sections 2.13-2.16). The use of Nafion modified in this way met with modest success. Leaching was only 1% but the turnovers obtained are inferior to any achieved using the complexes supported by Nafion-H tabulated in Table 5.1..

Nafion-Ag absorbed *trans*-$RhCl(CO)(PPh_3)_2$ and the cloudy solution formed indicated the presence of AgCl. The beads were used in catalytic run hf23. It was hoped that by loss of AgCl, the Nafion sulphonic acid group would replace the chloride ion as ligand leading to a similar square planar species as that found at the start of the catalytic cycle depicted in scheme 5.1. In fact the use of silver salts was unnecessary as *trans*-$RhCl(CO)(PPh_3)_2$ absorbed readily into Nafion-H, presumably with the loss of HCl. For catalysis to occur it was necessary to use molecular hydrogen to provide a metal hydride. However, if hydrogen adds to the rhodium centre before the alkene is present then the alkene must displace either CO or L. Alternatively if alkene coordinates to rhodium first then H_2 cannot add to rhodium without loss of CO or L. The lack of catalysed reaction would seem to indicate that neither CO nor L will be displaced by either alkene or H_2. Complexes of the form $[Rh(CO)_2L_2]^+A^-$ are known[44] to be quite stable and hence inactive and to form sinks under atmospheres of

CO. Another explanation is that the coordinated polymer restricts the rotations of the complex throughout the cycle. Given the success of reactions with bidentate ligands this is a less likely explanation.

A comparison of the ligands has been made by spectroscopic techniques and computer calculations. Looking at the data collected in Tables 5.3 and 5.4, dppphn and dppmen are directly comparable, being both 7-membered ring aminophosphines. The ^{31}P NMR and ν(CO) IR data are consistent between these two, in that the phosphorus is more electron rich in the dppphn case leading to a more electron rich metal which in turn should lead to a lower (CO) stretching frequency than dppmen. This is in fact what is observed. Following the same arguments, the more electron rich metal will donate more electron density into the π^* orbitals of the NBD vinylic carbons, deshielding their nuclei. The concomitant rise of ^{13}C NMR frequency is also observed. A ranking of the four ligands for decreasing electron richness based on the ^{13}CNMR data is then as follows:

PPh_2py> PPh_2Nma> dppphn>dppmen

Scheme 5.19 Ranking of donor properties of Phosphines based on ^{13}CNMR data

A ranking of the bidentate ligands for decreasing electron richness based on the carbonyl stretches in HRh(L-L)CO is as follows:

dppphn>PPh_2Q>dppmen>diPPFc

Scheme 5.20 Ranking of donor properties of Phosphines based on ν(CO) data from HRh(L-L)CO complexes

Turning to the results obtained in the series of displacement reactions with manganese carbonyl bromide, the carbonyl stretching frequencies for the monodentate ligand substituted *cis*-L$Mn(CO)_4Br$ complexes are best compared using the A'(3) band

arising out of an asymmetric stretch involving the carbonyl group *trans* to L and hence most influenced by changes in L. The ligands PPh_2Nma and $PPhpip_2$ give only one singlet in the phosphorus NMR spectrum indicating that only one compound is formed. The ligand PPh_2py has a more complex spectrum. In addition, the IR band at 1918 cm^{-1} shows similarities with bands observed for bidentate ligands coordinated in a *fac* mode although the NMR data do not support the proposed bidentate coordination of PPh_2py. A ranking of the three monodentate ligands for decreasing electron richness is then as follows:

PPh_2py>$PPhpip_2$> PPh_2Nma

Scheme 5.21 Ranking based on ν(CO) data from A'(3) *cis*- $LMn(CO)_4Br$

The carbonyl stretching frequencies for the bidentate ligand derivatives, $L_2Mn(CO)_3Br$ can be compared using the A'(1) symmetric stretch band. This band is strong as it is caused by a large change in dipole moment. Two of the CO groups involved are *trans* to the phosphine groups under study. Using the values of the stretching frequencies for this band the following rankings for electron richness are obtained

PPh_2Q>dppmen>dppphn

Scheme 5.22 rank based on ν(CO) data from A'(1) *fac*- $(L)_2Mn(CO)_3Br$

This ranking is out of step with the results obtained for rhodium carbonyl complexes discussed above. It is worth noting a difference in the ^{31}P NMR data for $Mn(dppphn)(CO)_3Br$ and $Mn(dppmen)(CO)_3Br$. The latter has a peak at 93.2 ppm which could be assigned to bidentate coordination and a pair of peaks at -20.8 and -23.6 ppm which are not readily explained. In contrast $Mn(dppphn)(CO)_3Br$ exhibits only high frequency peaks at 85.8 and 89.2 ppm. Phosphorus shifts are often moved to lower frequency when a 4 membered chelate ring is formed, incorporating a degree of

ring strain and to higher frequency when a five-membered ring is formed. The limited data available for seven membered chelate rings suggest their effect to be roughly neutral[45]. The rigid P-N bonds in dppphn due to the direct attachment of nitrogen to the phenyl group serve to make the ring formed with manganese a "pseudo-five membered" ring which may explain the difference in chemical shifts.

The data for the bidentate ligands also include IR bands due to the presence of η^1 coordinated complexes. The A'(2) band for *cis*-$LMn(CO)_4Br$ allows comparison across the monodentate and bidentate groupings. Using data for this vibration the following rankings for electron richness are obtained:

$PPhpip_2$>PPh_2py = PPh_2NMa>dppmen = PPh_2Q

Scheme 5.23 Ranking based on ν(CO) data for A'(2) for *cis*- $LMn(CO)_4Br$ complexes

Overall there is a high degree of agreement between the various techniques used to assess the electronic donor properties of the ligands. A general ranking of decreasing electron density on phosphorus is deduced as follows:

PPh_2py>$PPhpip_2$>PPh_2Nma>dppphn>PPh_2Q>dppmen>diPPFc

Scheme 5.24 Overall combined ranking

Finally, it could be argued that this ranking should be reflected in the phosphorus NMR shifts for the free ligand or perhaps the shifts for the ligand coordinated to rhodium. There is no correlation as can be seen from the rankings given below in Scheme 5.25.

^{31}P NMR increasing frequency for free ligands

PPh_2Q<PPh_2py<dppphn<diPPFc<PPh_2Nma<dppmen<$PPhpip_2$

^{31}P NMR increasing frequency for ligands in $L_2Rh(NBD)BF_4$

PPh_2py<$PPhpip_2$<PPh_2Q<diPPFc<dppphn<dppmen<PPh_2Nma

Scheme 5.25 Ranking based on ^{31}P NMR values (Table 5.3)

Phosphorus NMR shifts are the result of shielding by all the electrons around the phosphorus atom. Only those electrons in the π-orbitals due to back donation from the metal will make their effect felt on the other metal bonded ligands (i.e. CO or NBD). The electron density around phosphorus is also affected by electronegativity differences with atoms bonded to it such as nitrogen. These effects are transmitted along σ-bonds.

Comparing the ranking obtained in Scheme 5.22 with the catalysis results it can be seen that electronic effects are only one of the influences on the results. Although there is no direct correlation it can be stated in general terms that the less electron rich ligands favour higher yields. The calculated figures for bite angles in Scheme 5.6 are in accordance with the postulate of Casey[10] that the closer a bidentate bite angle is to 120°, the more normal aldehyde should be produced.

The approach adopted to minimise leaching by choosing protonatable ligands has only met with limited success. The ligand dppphn was not leached during hydroformylation, demonstrating that, in principle, careful ligand design could lead to a useful supported catalyst system.

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Chapter 6

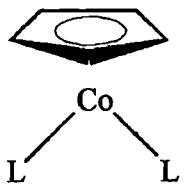
Cobalt mediated formation of pyridines

6.1 Introduction

Pyridine and its derivatives are produced on a scale of around 80,000 tons per year with a projected growth of 4% per year. The industrial process relies on vapour phase condensation of aldehydes or ketones with ammonia using doped alumina or silica-alumina as catalyst[1]. Temperatures in excess of 350°C are required and selectivity is rather poor. The principal uses of pyridines are as starting materials for the production of herbicides such as "paraquat" and related products.

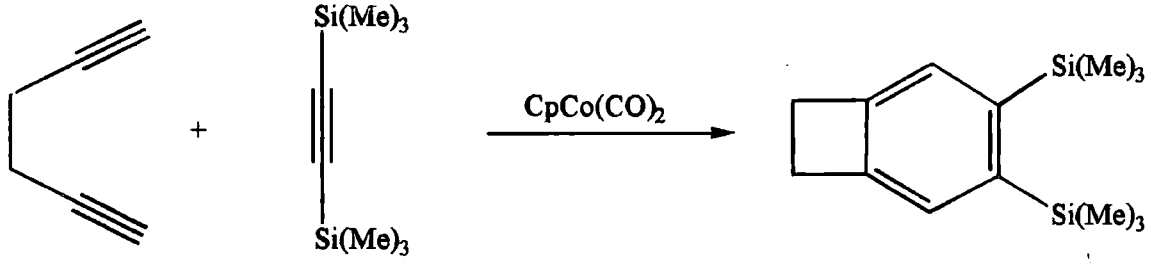
One of the earliest reports[2] of the cyclo-oligomerisation of alkynes to aromatic compounds appeared in 1960. A range of carbonyl compounds was used, including dicobalt octacarbonyl to trimerise alkynes. Diphenylacetylene required the high temperature of 280°C and the reaction was performed without the use of solvent. By using the related catalyst $[Co(CO)_4]_2Hg$, which proved capable of trimerising both mono and disubstituted acetylenes, considerably milder conditions (<100°C) could be used to obtain similar yields Use of this catalyst enabled the authors to prepare many novel benzene derivatives.

The cyclisation of alkynes is now commonly carried out by Co(I) cyclopentadienyl compounds of the form shown in Scheme 6.1, where L represents a labile ligand such as CO or alkene, loss of which generate the active 14 electron moiety CpCo.



Scheme 6.1 [CoCpL$_2$] catalyst type

Mixtures of substituted alkynes will co-cyclooligomerise to form all possible isomers thus making the reaction useless from a synthetic standpoint. In the course of developing synthetic strategies for making annelated benzenes from α,ω-diynes, Vollhardt[3] discovered that bis(trimethylsilyl)acetylene will not self condense but will react with α,ω-diynes to form annelated benzenes in high yield. For example bis(trimethylsilyl)acetylene reacts with 1,5 -hexadiyne in the presence of [CpCo(CO)$_2$] to give 4,5-bis(trimethylsilyl)benzocyclobutene (Scheme 6.2)



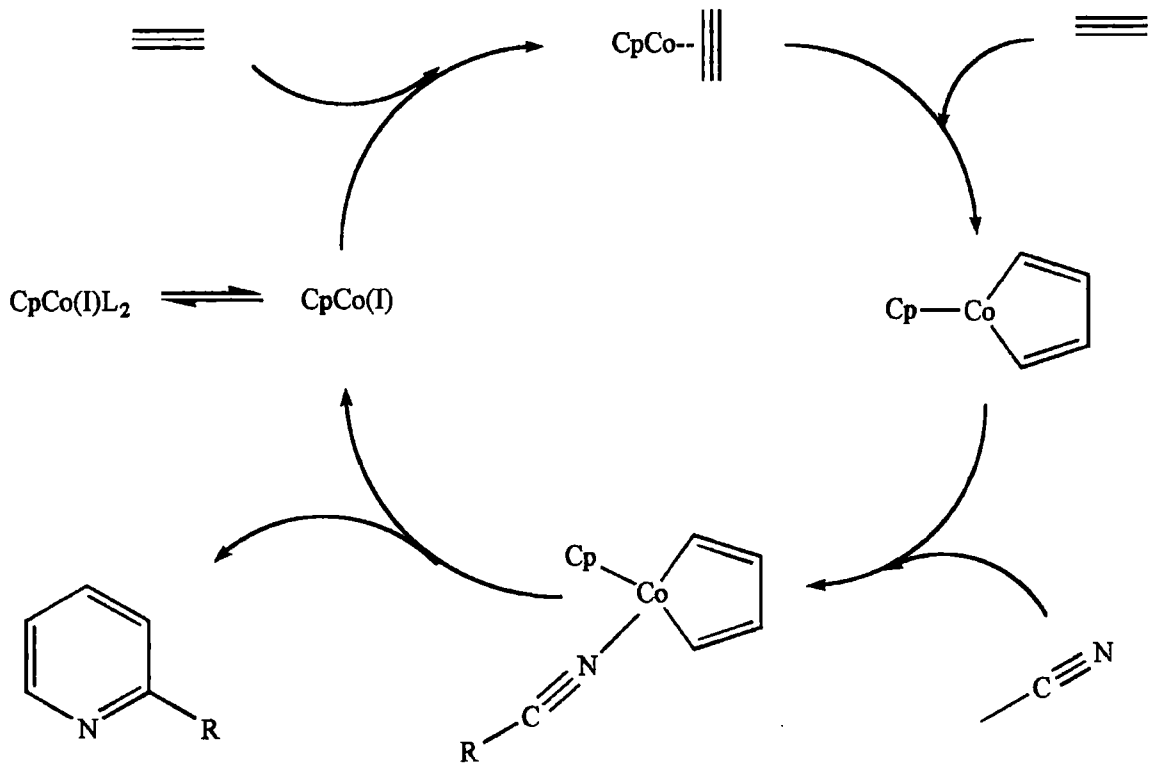
Scheme 6.2 Synthesis of benzocyclobutenes

Yamazaki[4] first reported the formation of pyridines from the cyclisation of acetylenes in the presence of nitriles. The catalyst precursor used was [Cp(Co)(PPh$_3$)$_2$], although PPh$_3$ has subsequently been found to inhibit the reaction. Acetylene reacted with a range of nitriles to form the corresponding 2-pyridines (Scheme 6.3) and the use of substituted alkynes resulted in a mixture of the substituted pyridines.

Scheme 6.3 Formation of 2-substituted pyridine

Nitriles have the same property as the silyl substituted alkynes in that they do not self condense. Bönneman subsequently showed[5] that these reactions could be achieved using catalysts formed *in situ* from $CoCl_2$ or [$Co(acac)_3$] reduced by an alkali metal, metal hydride or Grignard reagent. The most generally useful catalyst system was identified as $CoCl_2$/ $NaBH_4$. Catalysts formed *in situ* or catalysts with labile alkene groups gave turnovers of the order of 500 for the conversion of acetylene and acetonitrile to substituted pyridines with yields of 90% based on nitrile. In contrast, under the same conditions (130°C, 13 bar acetylene) [$CpCo(CO)_2$] gave only 2 turnovers and a yield of 40%. Although a wide range of transition metals is capable of the trimerisation of alkynes, only cobalt shows any activity for the synthesis of pyridines[1]. In the knowledge that the loss of labile alkene ligands forms the catalytically active fragment, CpCo, Bönneman[6] *et al* studied the catalytic activity of a range of compounds of the form [Co(COD)CpR] in which the cyclopentadiene ring was substituted on one position. The complexes were ranked for activity, based on the temperature required to convert 65% of the propyne starting material, using a continuous flow reactor with provision for on-line sampling and GC chromatography. Interestingly, there are correlations between NMR data and catalytic activity. The chemical shifts of the vinylic carbons on coordinated COD showed a linear relationship with reactivity for R = alkyl. The relationship broke down for other substituents. The ^{59}Co chemical shift of the central atom showed a clear linear relationship with reactivity for all substituents. A good relationship was also noted between the ^{59}Co chemical shift and regioselectivity for symmetrical or asymmetrical trialkyl pyridine products. The cobalt chemical shift provides, in this case, a good prediction of catalytic activity for unknown complexes. A high degree of $p\pi$ - $d\pi$ overlap between the metal and

the Cp ring leads to shielding of the Co nucleus and at the same time strong bonding and low catalytic activity.

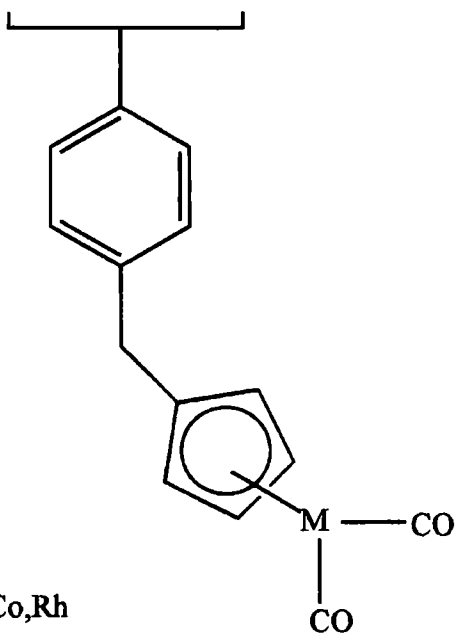


Scheme 6.4 Catalytic cycle for pyridine synthesis.

Catalysts of the forms $[CpCo(CO)_2]$ or [CpCo(COD)] are very air sensitive but are quite stable to hydrolysis. Sigman[7] *et al* describe the modification of Cp with esters and ketone groups to render cobalt complexes derived from these water soluble. They successfully trimerised 1,4-butyn-diol in aqueous solutions. The authors also conducted double isotopic crossover experiments in which [CpCo(COD)] with d_5-Cp and [CpCo(COD)] with d_8-COD groups respectively, were present in 50:50 mixtures. The mixture was used to catalyse the trimerisation of a substituted alkyne and after 60% conversion of the alkyne to product the mass spectrum of the recovered catalyst mixture was unchanged from its initial pattern. These findings led the authors to propose an alternate catalytic cycle, differing from that depicted above in Scheme 6.4 in that the COD

remains coordinated to cobalt but the Cp ring slips from η^5 to η^1 coordination to create a vacant coordination site.

Complexes of the form $[CpCo(CO)_2]$ have been heterogenised by polymerisation through the ligands. Gubitosa[8] *et al* descibe the synthesis of polystyrene modified with cyclopentadiene and subsequently coordinated to cobalt carbonyl. The authors were able to measure the characteristic infra-red absorptions of the metal carbonyl groups within the polymer. They note the absence of bands due to bridging carbonyl groups thus establishing the independence of each metal centre. No catalytic results were reported. A similar polymeric cobalt dicarbonyl catalyst was reported by Chang[9] *et al.* based on a styrene divinylbenzene (20%) copolymer (scheme 6.5). The resultant material proved to be catalytically inactive for a range of reactions including hydrogenation, hydroformylation isomerisation and disproportionation, but did show some activity towards the cyclotrimerisation of ethyl propiolate ($HC{\equiv}CCO_2C_2H_5$) . A similar catalyst based on polymeric rhodium dicarbonyl showed catalytic activity across the whole range of aforementioned reactions.



M = Co,Rh

Scheme 6.5 Metal carbonyl catalysts attached to a polymeric backbone.

Perkins and Vollhardt[10] synthesised two polymeric catalysts, based on cobalt and similar to that shown in Scheme 6.5. One polymer contained only 1% divinylbenzene and had far less

crosslinks as a result. The second polymer contained 3% divinylbenzene but was without the CH_2 link between the benzene and Cp rings. Neither polymer was active for the trimerisation reaction. However, the 3% crosslinked polymer showed unexpected catalytic activity for the Fischer-Tropsch reaction. Exposure of a suspension of this polymer in octane to CO/H_2 (3:1, 75 psi) at 190-200°C for 100 hours led to the production of a series of hydrocarbons from C_3 to C_{20}, detected by GC. This is believed to be the first example of new catalysis arising from supporting a homogeneous catalyst.

6.2 Experimental

General experimental details are described in Appendix (I)

6.2.1 Synthesis of 2-aminoethylcyclopentadiene

Sodium cyclopentadienide (NaCp, 0.226 mol) in THF was prepared as described in section 2.18. Against a stream of nitrogen, chloroethylamine hydrochloride (9g, 0.077 mol) was added over a period of 60 minutes. The solution turned pink and a white precipitate of salt appeared. Stirring was continued overnight, and then the salt removed by filtration. The THF solution was added to degassed water which was extracted with 3 X 50 ml diethyl ether. The dried combined extracts were distilled to produce a clear free flowing oil at 38-44°C (0.2mm Hg). Yield 7.5g (34.4%). Spectroscopy ^{1}H NMR δ 6.4,6.3,6.2,6.1 (lit[11]. δ 6.5, 6.3, 6.2, 6.0 ring protons for all three isomers of $C_5H_5C_3H_6NHCMe_3$) Long term storage led to dimerisation despite being under nitrogen in a freezer.

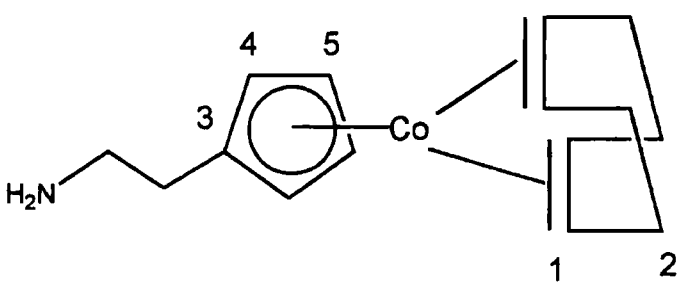
A similar synthesis was attempted using 2-chloropyridine. However no reaction took place due to the steric hindrance towards S_N2 attack of the chlorine by Cp^-. The target compound can be synthesised by another route (Jutzi *et al*)[12] but this was not pursued.

6.2.2 Attempted synthesis of [η^5-(2-aminoethylcyclopentadienyl-)η^4-(1,4-cyclooctadienyl)Cobalt (I)]

Following a procedure adapted from Bönnemann[6] *et al*, 2-aminoethylcyclopentadiene (5.05g, 50mmol) was dissolved in hexane (150mls) together with 1,4 cyclooctadiene (13.0g, 120mmol). A toluene (80 mls) solution containing triethylaluminium (150 mmol), supplied by the Aldrich Chemical company, was added by cannula.

The flask was cooled to -10°C in an ice-salt bath and while stirring under argon, cobalt(III) acetoacetanoate (17.82g, 50 mmol) was slowly added from a side-arm. The solution was allowed to warm to ambient temperature before being filtered then stored in a freezer for crystallisation.

The dark brown solid material produced was very impure. Spectroscopy: ^{13}C NMR (CD_3OD), δ 127.6, 109.1, 94.1, 78.9 (C5) , 66.9 (C1) , 28.7 (C2) , 26.9, 24.6 Tentative assignments.



Scheme 6.5 [η^5-(2-aminoethylcyclopentadienyl-)η^4-(1,4-cyclooctadienyl)Cobalt (I)]

The poor spectrum and lack of signal using ^{59}Co NMR spectroscopy suggest paramagnetic impurities. Triethyl aluminium has been succesfully used[6] in "one-pot" syntheses of cobalt cyclooctadiene complexes containing substituted Cp rings. However, in this case, its use is considered inappropriate since although the removal of a proton from cyclopentadiene is

thermodynamically favoured based on pK_a values, the removal of NH_2 protons could be faster. This may explain the formation of impure product.

6.2.3 Attempted synthesis of [η^5-(2-aminoethylcyclopentadienyl-)(dicarbonyl)-Cobalt I]

Following a procedure used by Phillipopolous[13] *et al*, 2-aminoethylcyclopentadiene (3.5g , 32.0 mmol) was dissolved in dichloromethane (50 mls.) Dicobaltoctacarbonyl (5.47g ,16mmol) was taken into a dichloromethane solution together with 3.5mls (36 mmol) 1,3-cyclohexadiene. The 2-aminoethylcyclopentadiene solution was added by cannula to the cobalt complex solution and the mixture heated to reflux for 6 hours. After reflux, the CH_2Cl_2 was removed by pumping and the oily residue extracted into diethyl ether. To the ether solution, $HBF_4.Me_2O$ (4.1g, 32 mmol) was added dropwise, with stirring at 0°C. The solid formed was separated by filtration, washed with diethyl ether and dried *in vacuo*.

Crude yield 5.76 g (57.9%). Spectroscopy: IR(KBr): ν(CO) 2013, 1949 cm^{-1}, $\nu(BF_4^-)$ 1062 cm^{-1}. ^1H NMR (CD_3OD): δ = 4.87 (ring), 3.28 ppm.

6.2.4 Synthesis of N-dimethylaminopropyl-3-cyclopentadiene

In a manner analogous to the synthesis of 2-aminoethylcyclopentadiene (*vide infra*), sodium cyclopentadienide (0.2 moles) was reacted with chloropropyldimethylamine hydrochloride (0.1 mol,15.65g) in THF.

$$2\ NaCp + Cl(CH_2)_3N(CH_3)_2.HCl = C_5H_5(CH_2)_3N(CH_3)_2 + 2\ NaCl + C_5H_6$$

The THF solution was added to degassed water which was extracted with 3 X 50 ml diethyl ether. The ether extracts were distilled to produce a clear free-flowing pale yellow oil (b.pt. 120°C, 20 mmHg). Yield 3.46 g , 22.8%. (Found: C, 79.15; H, 11.61; N, 9.18; $C_{10}H_{17}N$ requires C, 79.41; H, 11.33; N, 9.26%) IR (neat): ν 3053(=CH), 2940 (vs),

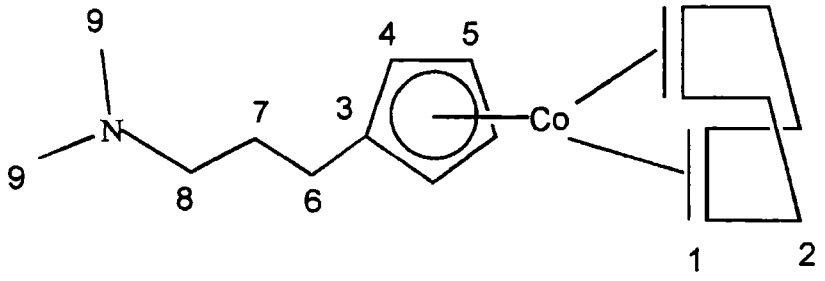
2856(s), 2761(s), 1459(m), 1373(w), 1299(w), 1261(m), 1096 (w,C-H bend), 1066(w), 1041(m), 897(w), 808 (m, C-H bend). ^{1}H NMR ($CDCl_3$): δ = 6.33, 6.15, 6.08, 5.93, 5.4 (m, CH=CH all 3 isomers); δ = 3.47(m, CpCH_2, 2H); δ = 2.85, 2.79 (s, 2 isomers, ring CH_2, 2H); δ = 2.32 (m, NCH_2, 2H); δ = 2.13 (s, NCH_3, 6H); δ = 1.829 (quin, $CpCH_2CH_2$, 2H) ppm; $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 149,147 (*ipso*); 135,134,133,131,127,126, (ring *C*H); 60, 57, (2 x s, ring CH_2); 46 (NCH_3, 2C) ppm.

6.2.5 Synthesis of N-dimethylaminopropyl-η^5-(cyclopentadienyl)(dicarbonyl) Cobalt (I)

Dicobalt octacarbonyl (8 mmol) together with $C_5H_5(CH_2)_3N(CH_3)_2$ (16 mmol) in CH_2Cl_2 and1,3 cyclohexadiene (2.38 mls, 24 mmol) were refluxed together for 6 hrs. The resulting solution was reduced in volume and diethyl ether (20 mls) added. The mixture was filtered through a pad of neutral alumina in a filter stick. The alumina was washed with 4 x 20 mls of ether and the combined solutions pumped to remove the ether. The resultant red-brown oil was estimated from proton NMR to be a 17.6% solution of product in toluene and was not further purified. IR : ν(C=O) 2019, 1955 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.94, 4.81 (C_5H_4,4H). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 84.9, 82.7, (C_5H_4,4C, *ipso* missing). 45.4 (NCH_3, 2C) ppm. Mass spectrometry EI: *m/z* = 237 (M- CO)$^+$, 209 (M- 2CO)$^+$, 151 $(CpC_3H_6NMe_2H)^+$.

6.2.6 Synthesis of N-dimethylaminopropyl -η^5-(cyclopentadienyl)(η^4-(cyclooctadiene)Cobalt (I)

1.0 ml of a toluene solution of N-dimethylaminopropyl-η^5-(cyclopentadienyl)-(dicarbonyl) Cobalt (I) from section 6.2.5 was dissolved in 100 mls COD, previously degassed with 3 freeze-pump-thaw cycles. The solution was irradiated with a 'Hanovia'medium pressure mercury arc lamp whilst nitrogen gas was bubbled through. Over the course of the reaction the solution was monitored by IR spectroscopy noting the loss of ν(CO) at 2019 and 1957 cm^{-1}. COD was removed *in vacuo* and the solid residue extracted with 1:1 hexane/ether mixture.



Scheme 6.6 N-dimethylaminopropyl -η^5-(cyclopentadienyl)-η^4-(cyclooctadiene)Cobalt (I)

^{1}H NMR: (C_6D_6): δ = 4.1, 3.94 (2 x s, C_5H_4, 4H); 3.05 (s,C^1H, 4H); 1.85 (s, C^9H_3, 9H); 1.06 (s, C^2H_2, 8H). ^{13}C{^{1}H}NMR (CD_3OD): δ = 100.84 (C^3); 83.91, 82.86 (C^4, C^5); 64.35 (C^1); 59.31 (C^8); 44.33 (C^9); 31.87 (C^2); 28.15, 25.4 (C^6, C^7) ppm.
A sample was submitted for ^{59}Co NMR and a singlet found at δ = -1222.3 ppm relative to $K_3[Co(CN)_6]$ in D_2O.

6.2.7 Synthesis of sodium carbomethoxycyclopentadienide

The syntheses described in sections 6.2.7-9 were adapted from a procedure by Hart[14] *et al.* Sodium cyclopentadienide, (0.08 mol in THF), was prepared as described in section 2.18. To this solution was added by syringe dimethyl carbonate (7.7 mls, 0.08 mol) forming directly a pink-white precipitate of sodium carbomethoxycyclopentadienide. The hygroscopic solid was removed by filtration and washed with diethyl ether (5 x 20 mls) and transferred to the glovebox for storage.
^{1}H NMR (D_2O): δ = 6.61, 6.11 (2 x s, C_5H_4, 2 x 2H); 3.77(CH_3) ppm.

6.2.8 Synthesis of η^5-carboxycyclopentadienyl(dicarbonyl)Cobalt (I)

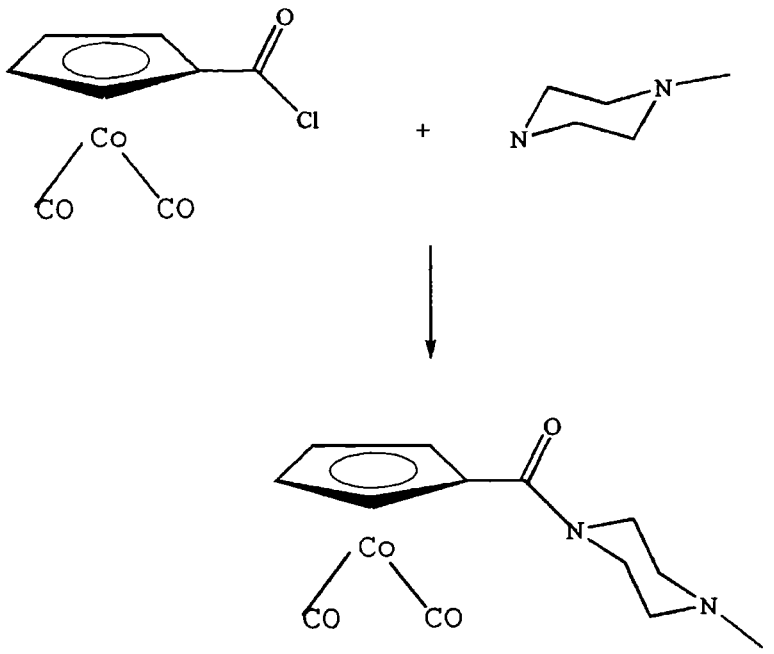
Dicobalt octacarbonyl (3.53g, 10.3 mmol) was dissolved in 200 mls THF together with I_2 (2.6g , 10.3 mmol) and stirred for 2 hours at room temperature. Sodium

carbomethoxycyclopentadienide (3.04g, 20.1 mmol) was added from a side-arm and stirring continued for 48 hours, the solution turning from green to red. The red solution was concentrated *in vacuo* to *ca.* 30 mls and diethyl ether was added. The resultant slurry was filtered through neutral alumina. The solvent was removed *in vacuo* and 100 mls of 95% aqueous ethanol, previously degassed by nitrogen bubbling through, was added. Degassed potassium hydroxide solution (25 mls, 10%) was added and the red solution stirred for 15 hours. To the mixture was added 400 mls of degassed ice-cold water, followed by the dropwise addition of concentrated HCl until the solution attained pH 4. The resulting precipitate was filtered and washed with degassed water and hexane and dried to yield the acid. M pt. 133°C (lit. 135°C)[14]. IR (KBr): 3116(m), 2031(vs), 1979(vs), 1677(br,vs), 1492 (s), 1294 (s). (lit. 3100(w), 2035(s), 1970(s), 1670(br,s), 1490(s), 1290(s))[14] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.43, 5.34 (ring) ppm; lit (acetone-d_6) 5.64, 5.52 ppm[14].

6.2.9 Synthesis of η^5-chloroformylcyclopentadienyl(dicarbonyl)Cobalt (I)

η^5-carboxycyclopentadienyl(dicarbonyl)Cobalt (I), (2g, 9 mmol), was dissolved in 100 mls toluene. To this solution was added 1.6 mls (18.3 mmol) degassed oxalyl chloride and the mixture stirred overnight. The toluene was removed *in vacuo* and the residue extracted into 2 x 25 mls hexane. The product was not further purified but used for the next stage. IR(liquid cell in hexane): $\nu(CO)_{metal}$; 2047, 1993 cm^{-1}, $\nu(CO)_{org}$; 1770, 1753 cm^{-1}. (lit.neat: 2035, 1980, 1750 (br,s)) cm^{-1}.

6.2.10 Attempted synthesis of η^5-cyclopentadienyl-N-methylpiperazinamide (dicarbonyl)Cobalt (I)



Scheme 6.7 Synthesis of piperazine derivativatised catalyst

Pyridine was dried overnight with KOH and distilled from KOH under nitrogen. 1-methylpiperazine (0.5 mls, 5.5 mmol) was dissolved in 25 mls distilled pyridine and the solution degassed by three freeze-thaw pump cycles. To this solution was added, slowly by cannula, the hexane solution of η^5-chloroformylcyclopentadienyl(dicarbonyl)cobalt (I) from section 6.2.9 above and the mixture was stirred at room temperature overnight. The pyridine hydrochloride was removed by filtration, the solution reduced in volume and hexane added producing a dark brown precipitate. The solution was removed by cannula filter and the precipitate washed with diethyl ether (2 x 25 mls).

IR (KBr): 3420 cm^{-1}, $\nu(CO)_{metal}$; 2021, 1958 cm^{-1} (m), $\nu(CO)_{org}$; 1617 cm^{-1} (vs).

(Found: C, 45.92; H, 7.1; N, 12.94; $C_{13}H_{15}N_2O_3Co$ requires C, 50.99; H, 4.94; N, 9.15%).

The product was thought to be contaminated with starting amine. ^1H NMR (CD_3OD): δ =

4.93 (s, C_5H_4, 4H); δ = 3.34, 3.2 (2 x s, (CO)N(CH_2)$_2$, 4H); δ = 2.67 (s, $CH_3N(CH_2)_2$, 4H); δ = 2.38 (s,NCH_3, 3H) ppm.

An attempt was made to convert a portion of the amide to the COD derivative in the manner of section 6.2.6. However the compound was completely insoluble in COD.

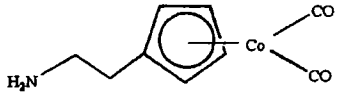
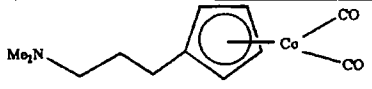
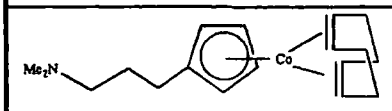
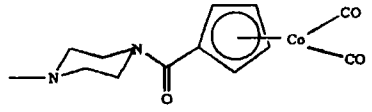
6.2.11 Synthesis of Nafion-η^5-cyclopentadienyl(dicarbonyl)Co (I)

Nafion cyclopentadienide was prepared as described in section.2.18. One gram of this was suspended in 30 mls CH_2Cl_2 containing [$Co_2(CO)_8$](0.82g, 2.4 mmol) and 1,3 - cyclohexadiene (0.64g, 8 mmol) and stirred for 3 days at room temperature under nitrogen before bringing to reflux temperature for 15 minutes. The CH_2Cl_2 was removed by cannula and the beads were washed with further portions of the same solvent until the washings were clear with periods of standing allowed for diffusion during each washing cycle.
The supernatant solution was stored for later testing for catalytic activity (none observed).
The supernatant solution was also added to Nafion-H with no apparent absorption.

6.3 Catalytic Studies

Compounds of the general formula [$CpCoL_2$] which act as catalysts for the cyclisation reaction to pyridine do not immediately lend themselves to absorption into Nafion by any of the mechanisms described in chapter 2. They are neither charged species, nor are they protonatable and replacement of the ligands by the Nafion sulphonic acid groups would interfere with the catalytic cycle. The approach adopted was to modify the cyclopentadiene ring by addition of a side chain with an amine group enabling the molecule to be protonated by Nafion. Bönnemann[6] had shown that compounds with modified cyclopentadiene rings were still active as catalysts. In fact the catalytic activity could be enhanced by suitable groups attached to the ring. The results of attempts to catalyse the formation of pyridine from propyne and acetonitrile are described in the text.

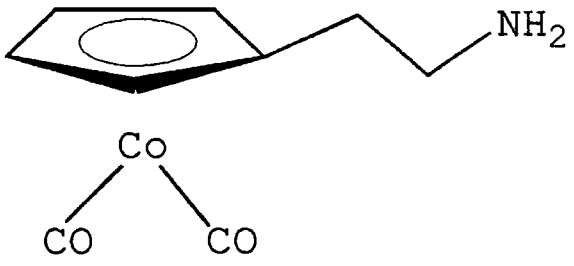
An overview of the complexes synthesised for this purpose and the conditions used is presented as Table 6.1 below.

Complex	Reaction conditions	Production of collidine*	Absorption by Nafion
	12 h, 100°C	None	Yes
	12 h, 120°C	None	Absorbed as amine but not as HBF_4 salt.
	12 h, 140°C	Homogeneous yield 15 turnovers.	Yes
	10 h, 175°C	Homogeneous yield ~5 turnovers	Yes
	5 h, 140°C	None	Yes
	10 h, 140°C	None	N/A

* In no case was collidine produced in Nafion.

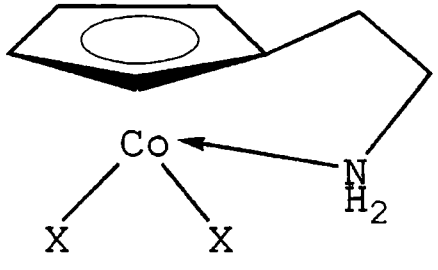
Table 6.1 Overview of complexes prepared and reaction conditions used

The first attempted synthesis was of η^5-(2-aminoethylcyclopentadienyl-)η^4-(1,4-cyclooctadienyl)Cobalt (I) (Scheme 6.5). This was known to be impure but was apparently absorbed into Nafion which took on the orange colour. The beads were added to the autoclave containing 20 mls toluene and 2 mls of but-2-yne under nitrogen. The autoclave was heated for 12 hours at 100°C. There were no cyclisation products detectable by GC. Given the doubts concerning the synthesis of the material, an alternative synthesis was attempted, of the related compound [η^5-(2-aminoethylcyclopentadienyl-)dicarbonyl Cobalt(I)] , (Scheme 6.8). This compound is a very air sensitive oil. In order to lessen the handling difficulties it was immediately converted into the tetrafluoroborate salt.



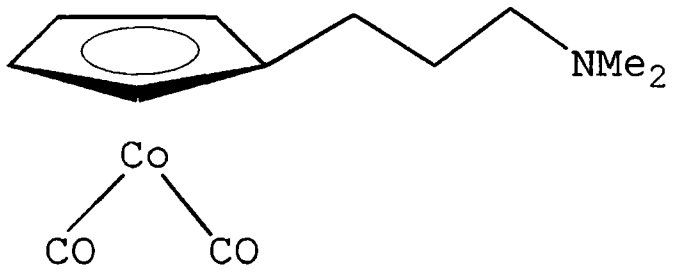
Scheme 6.8 [η^5-(2-aminoethylcyclopentadienyl-)dicarbonyl Cobalt (I)]

However, for reasons that are not fully understood, the salt was not absorbed by Nafion even after several days in either methanol, water or acetonitrile. A sample of the salt was reacted with triethylamine in degassed methanol to regenerate the amine. This was absorbed by Nafion over a period of several days. A catalytic run was performed using the beads suspended in CH_3CN. Propyne was added to the autoclave before the reaction in the manner described in section 3.5.4. and the autoclave was heated to 120°C for 10 hours. A comparative homogeneous run was also performed using 0.06g of the complex in salt form. Neither the compound in homogeneous form nor the Nafion supported form showed any catalytic activity. Cobalt (III) is known[12] to coordinate a pendant amine nitrogen to achieve 18 electrons (Scheme 6.9) though displacement of CO to form a Co(I) species was not observed. This displacement is known to occur with pendant phosphine chains[15] but of course phosphorus is a "softer", more polarisable ligand donor atom and would therefore be more likely to bond to a metal on the right hand side of the transition series than nitrogen.



Scheme 6.9 Intramolecular coordination to Co(III) where X is anionic

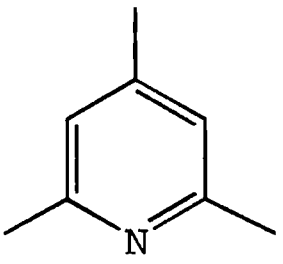
In order to eliminate completely the possibility of intramolecular coordination, a new compound was synthesised, in which the pendant chain was one carbon longer and the amine nitrogen sterically hindered with methyl groups (Scheme 6.10). Modelling studies had indicated that intramolecular coordination was virtually impossible.



Scheme 6.10 N-dimethylaminopropyl-η^5-(cyclopentadienyl)(dicarbonyl)Cobalt (I)

A catalytic run using the compound in Scheme 6.10 was then carried out as follows. To a solution of CH_3CN (4g) in toluene (19g) was added, under oxygen-free conditions, 0.2 mls of the toluene solution of catalyst leading to an approximate catalyst loading of 1.3×10^{-4} moles. Propyne was added and the autoclave was heated under nitrogen pressure for 12 hours at 120°C. The resulting solution was clear and brown with no metal deposition or precipitation. Analysis by GC revealed three peaks, identified by GC-MS as isomers of collidine (trimethyl pyridine). Comparison of peak areas from integration of the FID signal with those of a standard solution of 2,4,6-collidine allowed the calculation of yield as approximately 15 turnovers (Scheme 6.11).

Toluene solutions of catalyst were only partially absorbed into Nafion. Methanolic solutions were absorbed more readily but several catalytic runs at 120°C and 140°C failed to produce any trimerisation products.

$CH_3CN + 2\ CH_3C{\equiv}CH$ = 

Scheme 6.11 Symmetrical 2,4,6-collidine; one of 3 possible isomers

Based on the results of Bönnemann[5] it was assumed that the COD variant of the catalyst would be more reactive than the dicarbonyl complex. Conversion to the COD complex was readily achieved using photochemical techniques (section 6.2.6). However a temperature of 175°C was required before trimerisation products were detected by GC in very low yield. An attempt was made to incorporate $[Co(COD)CpC_3H_6N(CH_3)_2]$ into Nafion in a solution of methanol but the beads became green in colour, indicating the oxidation of cobalt. Alkenes coordinated to electron rich metals such as Co(I) are susceptible to attack by nucleophiles such as water or methanol[16]. However methanolic solutions of $[Co(COD)CpC_3H_6N(CH_3)_2]$ did not change in colour and the colour change was only observed within the beads of Nafion H. Alternate strategies were investigated, including the replacement of methanol with hexafluoroisopropyl alcohol as a less nucleophilic alcohol. In this case there was partial uptake of catalyst leading to brown beads and a blue solution. The beads were not catalytically active. To minimise the acidity, beads were produced in which the majority of protons were replaced by Na^+ by stirring in a solution of Na_2CO_3. The catalyst was introduced in a toluene solution containing 0.3g of methanol, that being approximately the minimum amount of methanol needed to cause the swelling of 1g of Nafion. The catalyst was partially absorbed to form pale brown beads. On transferring the remaining supernatant solution to a flask containing Nafion H, these beads turned green, confirming the observation that the acidity of the Nafion was responsible for the observed changes of the complex. The Nafion-Na^+ beads were also catalytically inactive.

The compounds produced up to this point all contained alkyl side chains with terminal amine groups for absorption into Nafion by protonation. Bönnemann[6] *et al.* had demonstrated that catalytic activity could be predicted from the ^{59}Co NMR chemical shift. The value obtained for $[Co(COD)CpC_3H_6N(CH_3)_2]$ was δ = -1222.3 ppm, which placed this compound amongst the less reactive compounds included in that study. Reactivity appeared to be enhanced by electron withdrawing groups, the most reactive compound studied by Bönnemann having an acyl substituted cyclopentadienyl ring. The compound depicted in Scheme 6.7 was synthesised to combine the features of an electron withdrawing carbonyl group adjacent to the ring with a protonatable tertiary amine function. The compound exhibited very poor solubility in acetonitrile and also failed to catalyse the cyclisation reaction at 140°C for 5 hours. It was absorbed by Nafion-H^+ but the beads were also catalytically inactive.

A completely different approach involved the modification of Nafion-H^+ to Nafion-Cp as described in sections 2.14 and 2.19, followed by its conversion to Nafion-η^5-cyclopentadienyl(dicarbonyl)Cobalt (I), described in section 6.2.11. A portion of these beads (0.9g) was suspended in degassed CH_3CN (20mls)and heated with propyne under nitrogen pressure in the autoclave for 10 hours at 140°C. The beads changed little in appearance, having a dark, opaque brown-green colour. The initially clear solution took on a faint yellow colour. The GC analysis of the products showed just a trace of product at a retention time of 9 minutes.

A second portion of the beads was suspended in hexane and exposed to 40 bar of CO/H_2 for 24 hours at 200°C. Although no Fischer-Tropsch products were detected, two new peaks appeared with retention times of 3.46 minutes and 3.97 minutes respectively. The former peak was responsible for 11% of the total integrated area and the latter peak for 0.3% with the remainder accounted for by the three skeletal isomers of n-hexane. Analysis by GC-MS showed the large peak to be 2-methyl-1-pentene and the small peak to be cyclohexane. Both products could be accounted for by dehydrogenation of the solvent hexanes.

6.4 Discussion

The strategy of attaching a protonatable side chain to the cyclopentadiene ring in order to absorb the catalyst into Nafion was ultimately vindicated. The results of catalytic trials were disappointing however. The yields obtained from homogeneous experiments were also lower than expected, leading to the possibility that lack of activity in Nafion is not necessarily just due to deactivation arising from the support but to a combination of factors including the support, the nature of the side chain and the experimental set-up. The best chance of succesfully catalysing this reaction with a Nafion supported cobalt complex would be to design a complex based on an alkene ligand (such as COD) in preference to a carbonyl compound, and to modify the cyclopentadiene group with an acyl side chain. A ketone would be more reactive than the amide made at the end of this study.

The use of Nafion-H^+ is not well suited to this class of reactions for a variety of reasons. The high temperatures used and the acid nature of Nafion preclude some substrates, such as phenyl acetylene for example, which will polymerise. Production of bulky trimers could be inhibited if Nafion is not swollen, due to steric crowding.

Modification of Nafion by addition of a Cp ring means that the polymer is no longer acidic but by the same token is no longer swollen by solvents. The use of Nafion modified in this way enabled the absorption of cobalt octacarbonyl. The resulting beads were produced at the very end of the study period and consequently only limited data were gathered concerning their properties. Their apparent ability to cleave C-H bonds in the solvent remains interesting and worthy of further investigation.

6.5 References

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Chapter 7

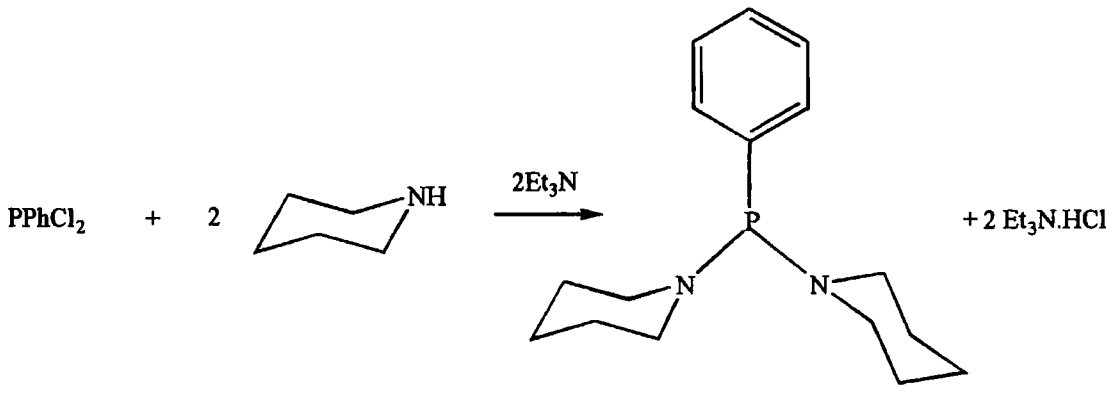
Ligands containing phosphorus and nitrogen

7.1 Introduction

In this chapter is gathered together all the supplementary information concerning the ligands containing both phosphorus and nitrogen referred to in previous chapters. The information can be further subdivided into two sections, namely, (i) aminophosphines and (ii) pyridyl and quinolyl phosphines.

7.2 Aminophosphines

Aminophosphines are that group of compounds in which a tertiary phosphine contains one or more direct P-N single bonds. They are readily obtained by the condensation of a halophosphine with a primary or secondary amine accompanied by loss of HCl. The example given in Scheme 7.1 leads to one of the compounds utilised in Chapter 5 and is a reaction dating back to the end of the last century[1].



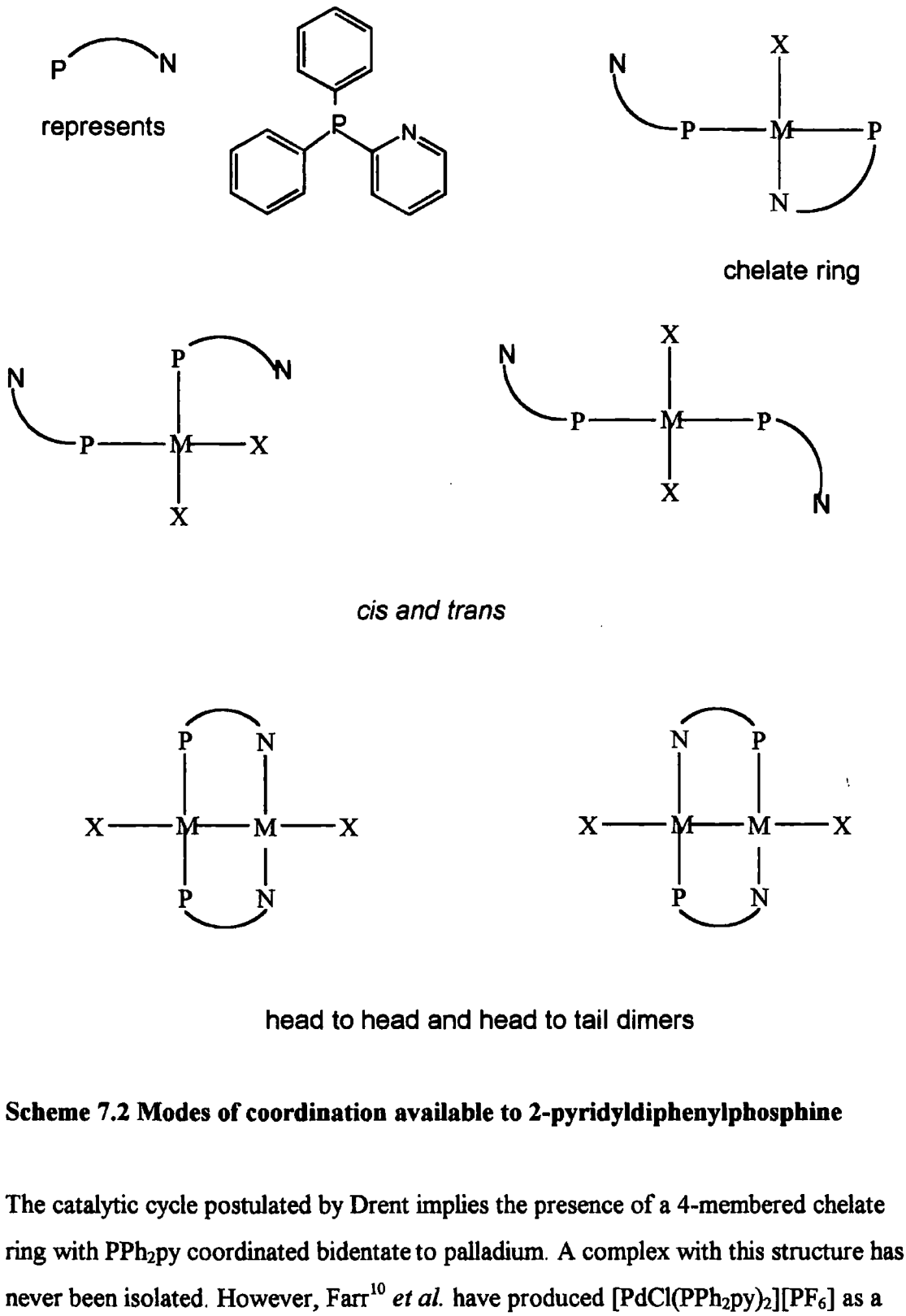
Scheme 7.1 Reaction to form an aminophosphine

The hydrogen chloride formed can be removed by a strong organic base such as triethylamine or alternatively by an excess of the amine itself if this is a strong base. In general, aminophosphines undergo reactions in a manner similar to the corresponding phosphines. Oxidation with O_3 or MnO_2 leads to the corresponding pentavalent phosphine oxides and the addition of sulphur leads to the sulphides[2] indicating that the phosphorus lone pair is available for bonding. Difficulties in assigning the P-N stretching frequencies in the infra-red spectrum were attributed to the variable nature of the bond from compound to compound. In fact P-N bonds can differ within the same compound. Romming and Songstad[3] studied the crystal structure of tris(piperidino)phosphine to discover that one of the P-N bonds was significantly longer then the other two (1.726 Å as opposed to 1.69 Å). The nitrogen atoms in the long P-N bonds are essentially sp^3 hybridised with the nitrogen lone pairs *anti* to the phosphorus lone pair. The remaining nitrogen atom is mainly sp^2 hybridised with its lone pair orthogonal to the phosphorus lone pair. Similarly, the structure of $P(NMe_2)_3$, obtained at low temperature[4], has one short and two long P-N bonds. In addition the nitrogen with the long bond to phosphorus is pyramidal whereas the remaining two are markedly flatter. *Ab initio* calculations of $P(NH_2)_3$ showed the possible structure with C_s symmetry to be 10KJ mol^{-1} more stable than the structure with C_3 symmetry, gaining the extra stability from P-N π-bonding. The structure of $[PdCl_2(PPh_2pip)_2]$ where 'pip' stands for P-N bonded piperidine shows a P-N bond length of 1.726 Å in line with sp^3 hybridisation. However the piperidine ring is noticeably flatter than free piperidine, implying some sp^2 character. Of course, the phosphorus lone pair is involved in coordination to the metal so that a direct comparison between $Ppip_3$ and PPh_2pip cannot be made. When aminophosphines coordinate to metals, the coordination takes place through the phosphorus atom. Grimblot and Bonnelle[5] studied the properties of a range of aminophosphines and were able to estimate the basicity of the phosphorus atom by using Tolman's method[6] of studying ν(C=O) for the corresponding $Ni(CO)_3L$ complex. All of the aminophosphines, (of general formula $L = PPh_n(NRR')_{3-n}$ for n = 0-2), that they studied had basicities between PBu^t_3 and PPh_3. Changing the alkyl group substituting

the nitrogen atom had very little influence on basicity, compared to changing the number of amino groups. Whilst increasing the number of amino groups led to a decrease in ν(C=O) for $Ni(CO)_3L$, it led to an increase in ν(C=O) for the series of complexes $RhCl(CO)L_2$, highlighting the pitfalls of using one system to model another. The rhodium complexes were subsequently used to hydroformylate hex-1-ene at 80°C achieving normal to branched isomer ratios in the range 0.7 - 2.3, similar to the range of data reported in chapter 5. In a subsequent study it was found that the aminophosphine becomes an increasing π-acceptor when the substituents on nitrogen are aryl as opposed to alkyl[7]. The aryl aminophosphines proved to be more selective for linear hydroformylation products with normal to branched ratios in the range 1.5 - 2.5. Asymmetric hydrogenation has been reported[8] using cationic rhodium complexes of (1S,2S)-1,2-bis(diphenylphosphinamino)cyclohexane and (2S,3S)-2,3-bis(diphenylphosphinamino)butane. The complexes contain a seven membered chelate ring which cannot lie planar but contains one nitrogen above and one below the plane of the ring. The same shape is obtained when the nitrogens are replaced by carbons or oxygens and it is this feature which is responsible for the enantioselectivity rather than any specific property conferred by nitrogen.

7.3 Pyridyl and quinolyl phosphines

In chapter 3, the role of 2-pyridyldiphenyl phosphine (PPh_2py) in the selectivity towards methyl methacrylate was described as identified by Drent[8,9] and co-workers. The catalytic cycle (scheme 3.11) shows the importance of the ability of 2-pyridyldiphenyl phosphine to coordinate in two ways, mono- or bidentate , to palladium, and in this case also to act as a carrier for a proton. A search of the Cambridge Structural database reveals a wide range of transition metals involved in bonding to PR_2py including Co, Ni, Fe, Cu, Mo, Ru, Rh, Pd, Ag, Cd, Re, Os, Pt, Au, Hg and U. Of the possible structures, depicted in scheme 7.2, only a few cases involved 4-membered chelate rings. The most common structure was of a bridged dimer.

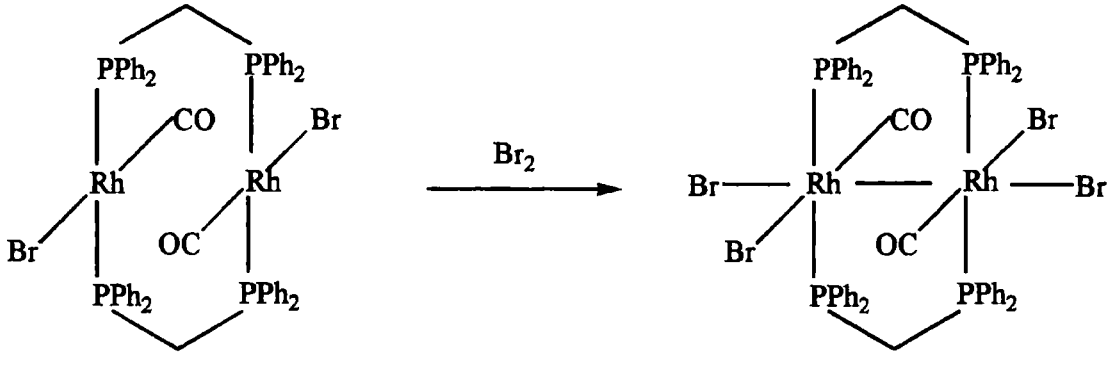


Scheme 7.2 Modes of coordination available to 2-pyridyldiphenylphosphine

The catalytic cycle postulated by Drent implies the presence of a 4-membered chelate ring with PPh_2py coordinated bidentate to palladium. A complex with this structure has never been isolated. However, Farr[10] *et al.* have produced $[PdCl(PPh_2py)_2][PF_6]$ as a

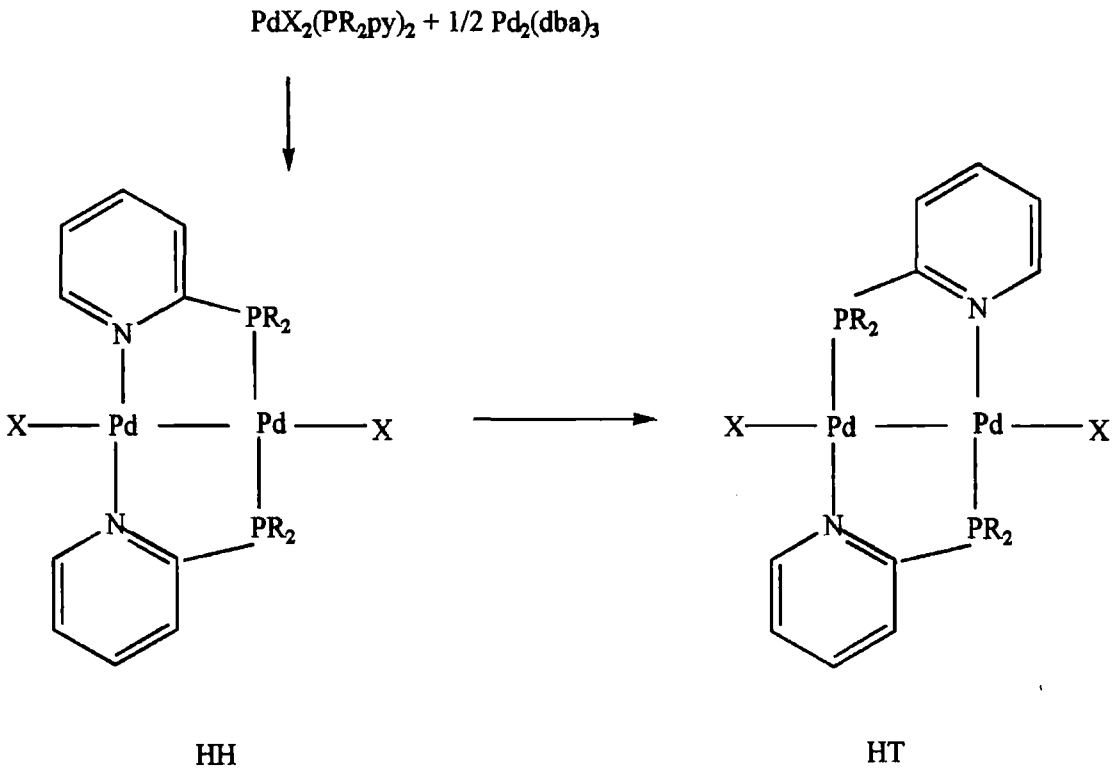
solid with correct elemental analysis and the presence of two non-equivalent phosphorus chemical shifts. An X-ray crystal structure of the analogous platinum containing compound has been determined[11]. In addition Suzuki[12] *et al* report the crystal structure of *cis*(*P,P*)-[PdCl(PMe$_2$py-*P,N*)(PMe$_2$py-*P*)]$^+$ ClO$^-_4$. In all cases the species are cationic and are formed by the removal of halogen although a neutral four membered chelate ring with ruthenium ($RuCl_2(CO)_2(PPh_2py)$ has been characterised[11]. The phosphorus chemical shift of the ring phosphorus in Suzuki's complex appears at -55 ppm compared to 17 ppm for the monodentate group. It is now well established that phosphorus chemical shifts appear at lower frequency in four membered rings[13]. More recently, a ruthenium complex containing three PPh_2py ligands, one of which was chelating, has been proposed as containing a three-centre dihydrogen bond in acid solution[14]. The deduction was made on the basis of low temperature proton NMR studies.

Short-bite bidentate ligands of this nature also allow for bridging as shown in Scheme 7.2. A metal-metal bond may form depending on the oxidation state of the metal and the distance separating the two metals. Oxidation from one state to the other can also occur as depicted for the similar dppm complex in Scheme 7.3 following work by Balch[15]. The M-P bond tends to be longer in complexes bridged by dppm than those bridged by PPh_2py due to the mutual *trans* effect experienced by the former, whereas in the latter P is *trans* to N.



Scheme 7.3 Metal-metal bond formation through oxidation

Dimeric palladium species containing a metal-metal bond are often synthesised[16] using a conproportionation reaction involving Pd(II) and Pd(O). These reactions have been shown by ^{31}P NMR to proceed in two stages[17], the initially formed head-to-head (HH) product isomerising to the more thermodynamically stable head-to-tail (HT) product (scheme 7.4). This isomerisation was noted to be more rapid for R = methyl than for R = phenyl.



Scheme 7.4 Formation and isomerisation of dimers.

This class of compounds has attracted considerable interest because of their potential as catalysts. The metal-metal bond can be broken and a small molecule can insert in the space between the two metals on one face of the dimer[18]. Examples given for a palladium dppm dimer include CO, sulphur dioxide, atomic sulphur,diazonium ions, acetylene and methyl isothiocyanate. Similarly, Xie[19] *et al* report a Ppy_3 bridged palladium dimer containing dimethylacetylenedicarboxylate. The products are complexes which have become known as molecular A-frames.

In addition to the homobinuclear metallic dimers described there are also many instances of heterobinuclear dimers and the use of PPh_2py provides a very convenient route to synthesising this type of compound because of its ability to coordinate as a monodentate or bidentate ligand. Farr[10] *et al* describe the synthesis of a rhodium-palladium dimer from *trans*-$[RhCl(CO)(PPh_2py)_2]$ and $[(COD)PdCl_2]$ with elimination of the COD. Although the initial rhodium complex is bonded to phosphorus, the product is a head-to-tail dimer with a metal-metal bond between Rh(II) and Pd(I). The same paper also describes the formation of both homonuclear (Rh-Rh, Pd-Pd, Pt-Pt) and heteronuclear dimers (Pd-Pt, Pd-Rh, Pd-Ru and Rh-Pt), all head-to-tail, as well as a head-to-head Rh-Pd cationic isomer. The reaction is quite widely applicable but does have its limitations. Attempts[20] to form an unsymmetrical Pd-Pd dimer from $[PdCl(allyl)(PPh_2py)]$ and $[PdCl_2(Bu^tNC)_2]$ led instead to a change of partners to $[Pd(\mu\text{-}Cl)(allyl)]_2$ and $[PdCl_2(PPh_2py)(Bu^tNC)]$. The steric bulk of Bu^tNC was cited as the reason for this. In all of the complexes described so far the bridging ligands have been mutually *trans*. Maisonnet[21] *et al* describe the structure of $[RuPd(PPh_2py)_2(CO)_2Cl_2]$, a head-to-tail complex in which the phosphorus and nitrogen are *trans* on the palladium but occupy mutually *cis* positions on the ruthenium. This can be synthesised by starting with either Ru(II) and Pd(O) or with Ru(O) and Pd(II). In both cases a mixture of two isomers is obtained which interconvert at above 60°C as witnessed by NMR spectroscopy. Attempts at crystallisation led to only the isomer described above however. (The second isomer was thought to be head-to-head with phosphorus atoms mutually *cis* on ruthenium and nitrogens mutually *trans* on palladium). PPh_2py can also act as a bridge in conjunction with other bridging ligands. Alcock[22] *et al.* describe the structure of the silver complex $[Ag_2Cl_2(PPh_2py)_3]$ in which two PPh_2py ligands are coordinated through phosphorus only, one on each silver atom, and the two silver atoms are bridged by both chlorines and the third PPh_2py group.

The varied chemistry displayed by the PPh_2py ligand is dependent on the pyridine being substituted in the 2 position. The use of 3 and 4-pyridylphosphines has been limited to efforts to produce water soluble phosphines[23].

The synthesis of diphenylphosphinoquinoline is described by Suggs and Pearson[24]. Use of this ligand is not widely reported in the literature, but Hudali[25] *et al.* describe the formation of $[PdCl_2(P\text{-}N)]$ and Kittaneh[26] *et al.* describe the complexes [M(P-N)(CO)Cl] for M = Rh and Ir. In each case the species is monomeric with the ligand forming a 5-membered chelate ring with the metal, which is the expected result given the stability of 5-membered rings.

7.4.Experimental

General experimental details are described in Appendix (I)

7.4.1 Dissolution of $[Pd(OAc)_2(PPh_2py)_2]$

The synthesis of $Pd(OAc)_2(PPh_2py)_2$ was attempted (section 3.3.8) using the strategy employed for the corresponding PPh_3 complex. It became apparent that, based on the elemental analysis obtained, the compound isolated was the dimer $[Pd(OAc)(PPh_2py)]_2$ The orange-red solid forms yellow solutions in acetone, green/yellow solutions in CH_2Cl_2 and orange solutions in water. Methanolic solutions are yellow until excess ligand is added when the colour changes to bright red. Nafion beads (H^+ or Na^+) take on the same bright red colour when they absorb the yellow methanolic solution. Xie[18] *et al.* also note strong colour changes for their pyridyl complexes which they explain by replacement of the chloride groups by water. The resultant ion has been isolated as a $[BF_4]^-$ salt.

$$\underset{\text{orange}}{Pd_2Cl_2(PPy_3)_2} + 2\,H_2O = \underset{\text{green}}{[Pd_2(H_2O)_2(PPy_3)_2]^{2+}} + 2\,Cl^-$$

Scheme 7.5 Colour changes noted by Xie[18] *et al*

7.4.2 $^{31}P\{^1H\}$ NMR Experiments

Palladium acetate (0.0226g) was dissolved in 10 mls toluene (0.1M solution) and PPh_2py (0.526g) was dissolved separately in 10 mls toluene (0.2M solution). Aliquots from each solution were mixed in a range of proportions and the $^{31}P\{^1H\}$ NMR spectrum of the mixture recorded. The results are presented below in Table 7.1 and are consistent with the breaking of the dimer to two monomeric species with excess ligand, based on ^{31}P NMR results for the similar complexes quoted in the

literature[21] $[Pd(PPh_2py)_2Cl_2]$, (δ = 23.8, 29.3 ppm), and $[Pd(PPh_2py)Cl]_2$, (δ = 4.4 ppm). The process is not fully understood however, since reversal of the conproportion reaction would require generation of a Pd(O) species and deposition of metal was not apparent. One possible explanation could be due to the formation of $Pd(PPh_2py)_4$:

$$[Pd(OAc)(PPh_2py)]_2 + 4\ PPh_2py = [Pd(OAc)_2(PPh_2py)_2] + Pd(PPh_2py)_4$$

Pd:P ratio	Peak values ppm (integrals %)			
assignment	monomer	monomer	dimer	ligand
1:1		16.2 (<13%)	4.0 (85%)	-5 (<13%)
1:2		16.2 (46%)	4.0 (54%)	
1:4	26 (20%)	16.2 (80%)		
1:6	26 (19%)	16.2 (81%)		

Table 7.1 NMR results at different ligand:metal ratios for the reaction of $[Pd(OAc)(PPh_2py)]_2$ with PPh_2py

Similar behaviour was noted when starting from the preformed complex in THF, i.e. the appearance of a minor peak at δ = 14.5 ppm and a major peak at δ = 5.2 ppm changing to a major peak at δ = 14.5 ppm with a minor peak at δ = 28.4 ppm plus a broad free ligand peak on the addition of excess ligand.

7.4.3 Light absorption experiment

$[Pd(OAc)(PPh_2py)]_2$ (3 mg., 3.5μmol) was dissolved in methanol (25 mls) and the light absorption measured in a 1 cm glass cuvette. An absorption maximum appeared at 452 nm with an intensity of 0.4 absorption units equivalent to a molar absorption coefficient ε = 2850 $mol^{-1}\ dm^3\ cm^{-1}$. On the addition of a threefold excess of ligand the absorption maximum moves to 526 nm and increases in intensity to

$\varepsilon = 11400$ mol^{-1} dm^3 cm^{-1}. In both cases the intensity of the absorption indicates that it is caused by a "charge transfer" transition.

7.4.4 Conductivity measurements

Palladium acetate (0.23g) was dissolved in methanol (10 mls) forming a 0.01M solution and PPh_2py (0.132g) was also dissolved separately in methanol (10 mls) forming a 0.05 M solution. The ligand solution was added in aliquots of 1ml to the palladium acetate solution and the conductivity measured after each addition. The results are presented below in Table 7.2

Added ligand (0.05M) mls.	Pd:P ratio (approx.)	conductivity μS cm^{-1}	colour
0		30	
1	2:1	130	orange
2	1:1	170	orange
3	2:3	250	red
4	1:2	330	red
5	2:5	330	red

Table 7.2 Conductivity measurements for the reaction of $[Pd(OAc)(PPh_2py)]_2$ with PPh_2py

The conductivity baseline reading for methanol was not increased by addition of PPh_2py. For comparison a solution of $[Pd(CH_3CN)_4][BF_4]_2$ in methanol (0.01 M) was measured at 1200 μS cm^{-1}. Clearly there is a significant increase in conductivity, albeit to a value less than that obtained for a known, fully ionised complex. Either the ions formed account for only a fraction of the total number of species in solution or their mobility is somewhat lower than the acetonitrile complex.

7.4.5 ^{31}P NMR studies of [RhCl(PPh$_2$py)$_3$]

In section 4.2.8 the attempted synthesis of [RhCl(PPh$_2$py)$_3$] , an anologue of Wilkinson's catalyst, is described. The product of the reaction displayed quite complex NMR behaviour, dependent on the solvent employed, as indicated below.

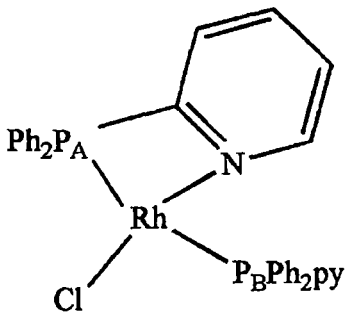
The ^{31}P{^{1}H}NMR spectrum of Wilkinson's catalyst is described in the literature[27,28] as follows: ^{31}P{^{1}H}NMR (CH_2Cl_2): δ P_1 = 48.9 (dt, 1P, J_{PP} 37.5 Hz, $J_{Rh\text{-}P}$ 192 Hz) ppm, δ P_2 = 32.2 (dd, 2P, $J_{Rh\text{-}P}$ 146 Hz) ppm. where P_1 is *trans* to Cl and $2P_2$ are mutually *trans*. The spectrum for the dimer [RhCl{P(*p*-tolyl)$_3$}$_2$]$_2$ is as follows, ^{31}P{^{1}H}NMR (toluene): δ P_1 = 49.5 (d, $J_{Rh\text{-}P}$ 196 Hz) ppm.

The ^{31}P{^{1}H}NMR spectrum of [RhCl(PPh$_2$py)$_3$] was obtained in three solvents and the data are collected below in Table 7.3.

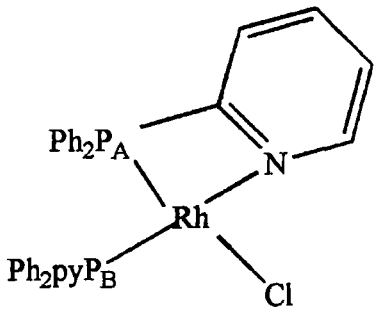
solvent	chemical shifts (ppm)	J_{PP} (Hz)	J_{RhP} (Hz)
CH_2Cl_2	(dd) -13.4	40	168
	(s) 33.1		
	(dd) 53.7	40.6	181
THF	(dd) -23.9	18	54
	(dd) -18.7	20	53
	(s) -0.5 free ligand (broad)		
	(s) 15.7		
	(s) 29.4		
	(dt) 58.9	20	134
benzene-*d6*	(s) -2.2 free ligand (broad)		
	(s) 31.8		

Table 7.3 ^{31}P{^{1}H}NMR data for [RhCl(PPh$_2$py)$_3$] in three solvents

In benzene and THF, coupling could not be seen on all peaks due to rapid ligand exchange. The peaks at δ 15.7 and 29.4 ppm are roughly in proportion 2:1 and could be due to *cis* and *trans* phosphines in the monomeric compound. The singlet at 31.8 ppm in benzene and 33.1 ppm in CH_2Cl_2 could be due to either the three coordinate $RhClL_2$ or the chlorine bridged dimer $[RhClL_2]_2$. The structures depicted in Scheme 7.6 are proposed to explain the presence of the multiplets seen in the spectra conducted in CH_2Cl_2 and THF. Structure (1) is thought to be present in CH_2Cl_2 and both isomers (structures (1) and (2)) are thought to be present in THF. Phosphorus (A) refers to the low frequency peaks in both cases, based on arguments presented in section 7.2. The metal-phosphorus couplings obtained in CH_2Cl_2 of 181Hz and 168Hz fall within the values obtained for PPh_3 in Wilkinson's catalyst. The two inequivalent phosphorus atoms would give two doublets of doublets as seen in the spectrum. In THF the two doublets of doublets are assigned to the two chelating P_A phosphorus atoms, one in structure (1) and the other in structure (2). The peak listed as a doublet of triplets in THF could be two doublets of doublets overlapping caused by the two P_B phosphorus atoms (one from each isomer). An alternative explanation for the spectrum in THF would invoke an unlikely six coordinate Rh(I) structure. Without further corroborating evidence these assignments must be regarded as tentative.



(1)



(2)

phenyl rings omitted for clarity

Scheme 7.6 Proposed solution structures of $RhClL_2$

7.4.6 Synthesis of $[PtCl_2(PPh_2py)_2]$

$[PtCl_2(PhCN)_2]$(0.059g, 0.125 mmol) and PPh_2py (0.066g, 0.25 mmol) were dissolved in toluene in a small Schlenk tube under nitrogen and stirred for 1 hr. The solution was reduced in volume *in vacuo* and hexane was added to effect precipitation. The precipitate was removed by filtration and washed with diethyl ether (3 x 3 mls) to reveal a white powder. Yield 0.1g. (Found: C, 52.41; H, 3.70; N, 3.38; $C_{34}H_{28}N_2P_2Cl_2Pt$ requires C, 51.53; H, 3.56; N, 3.53%). IR (KBr): ν(*cis* Pt-Cl) 276, 294 cm^{-1}. ν(*trans* Pt-Cl) 334 cm^{-1}.
$^{31}P\{^1H\}$NMR($CDCl_3$): δ 12.13 (t, J_{Pt-P} 3672 Hz) ppm. The data indicate that the compound is essentially in monomeric form.

7.4.7 Synthesis of $[IrCl(PPh_2py)(COD)]_2$

$[Ir(COD)Cl]_2$ (0.19g, 0.3mmol) and PPh_2py (0.22g, 0.9 mmol) were dissolved in degassed ethanol (25 mls) in a small Schlenk tube under nitrogen and stirred for 1 hr.The solution was cooled in an ice bath and the bright yellow precipitate which formed was separated by filtration. Yield 0.04g. (Found: C, 48.74; H, 4.38; N, 2.18; $C_{50}H_{52}N_2P_2Cl_2Ir_2$ requires C, 50.12; H, 4.37; N, 2.34%). $^{31}P\{^1H\}$NMR(CH_2Cl_2): δ 21.63 (100P) ppm.
(*N.B.* the reaction of $[Ir(COD)Cl]_2$ with a chelating diphosphine leads to a 5-coordinate Ir(COD)(P-P)Cl with apical chloride ligand[28].)

7.4.8 The attempted synthesis of an Iridium-Platinum dimer

$[Ir(COD)Cl]_2$ (0.082g, 0.125mmol) was dissolved in hexane (25 ml) at -30°C. Ethene gas was bubbled through the solution for five minutes leading to a white suspension of

$Ir(C_2H_4)_4Cl$ (see van der Ent and van Soest[29]). In a separate Schlenk tube, $[Pt(PPh_2py)_2Cl_2]$ (61.75mg, 0.125 mmol) together with 1.5 times excess PPh_2py (50mg) were dissolved in CH_2Cl_2 (10 mls). The platinum solution was slowly transferred by cannula under an ethene pressure to the iridium suspension. A yellow gelatinous precipitate was formed turning orange on warming to room temperature and when the ethene atmosphere was replaced with nitrogen. The solid was separated by filtration and redissolved in $CDCl_3$ for NMR study.

Phosphorus NMR revealed the presence of five phosphorus containing compounds.

1) δ 22.05 (50%) ppm, probably the iridium dimer reported in section 7.4.7.

2) δ 12.1 (4%) ppm, (satellites not visible), probably the platinum complex reported in section 7.4.6

3) δ -49.95 (17%), (J_{Pt-P} 3338 Hz) ppm, probably a Pt complex containing a *P,N*-chelate

4) δ 15.54 (20%), (J_{Pt-P} 3694 Hz) ppm.

5) δ 36.45 (7%) ppm, no satellites.

A sample of the solution was analysed by HPLC (column; Hypersil ODS reverse phase) using the following program: 90:10 H_2O/MeOH to 100% MeOH in 25 minutes to reveal six peaks. Column chromatography using neutral alumina using $CHCl_3$ then MeOH separated compounds (3) and (4) from the remainder. Attempts at obtaining crystals from this solution were unsuccessful.

7.4.9 NMR scale reaction between Wilkinson's catalyst and PPh_2Q

Equimolar quantities of $[RhCl(PPh_3)_3]$ and PPh_2Q were dissolved together in $CDCl_3$ in an NMR tube under nitrogen. A purple coloured solution resulted which gave a ^{31}PNMR spectrum with a singlet at δ 30.0 ppm (37P) and indicated the presence of free PPh_3 at δ -4.3 ppm (30P). There was no signal for free PPh_2Q at δ -13 ppm. On standing the signal for free PPh_3 disappeared. There were many smaller peaks which at -50°C were resolved into δ 47.8 (dd, J_{PP} 19Hz, J_{RhP} 142 Hz), δ 46.45 (dd, J_{PP} 22Hz,

J_{RhP} 161 Hz), δ 41.3 (dd, J_{PP} 19Hz, J_{RhP} 118 Hz), δ 38.9 (dd, J_{PP} 20Hz, J_{RhP} 108 Hz), δ 35.6 (d, J_{RhP} 118 Hz), δ 29.4 (d, J_{RhP} 126 Hz), δ 24.8 (d, J_{PP} 18 Hz), δ 23.0 (d, J_{RhP} 178 Hz) ppm.

The main peak at δ 30.0 ppm is assigned to the starting material,$[RhCl(PPh_3)_3]$, in which the PPh_3 originally *trans* to chlorine becomes detached thus giving only one phosphorus environment. The higher frequency peaks (4dd) probably arise from formation of two isomers of $RhCl(PPh_3)(PPh_2Q)$ where PPh_2Q acts as a chelating ligand. The remaining peaks show only rhodium-phosphorus coupling and therefore must contain only one phosphorus environment.

The conclusion drawn is that, despite rhodium(I) to nitrogen bonding being less favourable than rhodium(I) to phosphorus bonding, PPh_2Q nevertheless is capable of displacing two PPh_3 groups by virtue of its ability to chelate.

7.5 References

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Chapter 8

Conclusions

The principle of supporting homogeneous catalysts is now widely accepted as being potentially beneficial, in so far as the catalyst is readily separated from the products. The use of ion exchange resins as catalyst supports, as opposed to inorganic supports or catalysts with polymeric ligands, allows the supported system to be produced with great ease, obviating the need for additional synthetic steps.

Nafion has unique properties compared to other ion exchange resins, due to its fluorocarbon backbone, which is responsible for Nafion adopting its structure of cavities and channels and for it being a super acid. The strong acidity can provide an additional mechanism by which complexes are introduced into the support and can act as an acid catalyst where this is desirable. In the case that the acidity causes unwanted side reactions, then it can be easily modified by exchange with alkali metal cations.

It has been demonstrated that Nafion can absorb a wide range of complexes by one or more of three identifiable mechanisms and that these complexes will remain retained within the Nafion throughout the course of reaction. Nafion has been successfully dissolved and cast into thin films and has also been successfully modified into forms containing new functional groups. Nafion has been successfully recycled to be available again as a support without loss of performance.

The scope of reactions catalysed by Nafion supported complexes has been extended from the literature base of hydrogenation[1,2], octene isomerisation[3], ethene dimerisation[4,5], and the reduction of carbon dioxide[6] to include hydroformylation, hydroesterification and the production of polyketone polymer.

The use of Nafion as a support has a few minor limitations. Introduction of the metal complex into Nafion is most efficiently carried out in water or alcohols which cause the Nafion to swell. Similarly, these solvents are preferred as reaction media to enable high rates of diffusion of products and reactants, in and out of the cavities. In common with all

polymers, there is an upper limit to the temperature which can be used. When Nafion is present in its acid form, there is another problem encountered with the use of temperatures in excess of 120°C, namely that acid catalysis causes unwanted side reactions between substrates and solvents. Lastly, the use of Nafion is unsuitable for catalyst systems produced *in situ*. These systems comprise two or more components which may be absorbed by Nafion at different rates, leading to a change in the solution composition in the Nafion cavities compared to the bulk solution.

The hydroesterification of ethene to methyl propanoate was achieved successfully in Nafion. The palladium complex, $[Pd(PPh_3)_2(OAc)_2]$ was easily incorporated into Nafion to produce an effective catalyst system. The yields of methyl propanoate formed were higher than those obtained using homogeneous palladium complexes under comparable reaction conditions. It was found that yields of product were increased by using low loadings of metal complex in the Nafion (10^{-5} mol catalyst per gram of Nafion, roughly equivalent to one catalyst molecule within each cavity). This finding is in agreement with the findings of Seen and Cavell[5] during their studies of ethene dimerisation. A study of hydrogenation was carried out. The hydrogenation of cyclohexene, dimethyl maleate and nitrotoluene was accomplished using the complexes, $[Ir(COD)(PPh_2Me)_2]PF_6$, $[Rh(NBD)\{Fe(C_5H_4PPr_2)_2\}]BF_4$ and $[RhCl(Ph_2P\text{-}NC_5H_{10})_3]$. Yields of hydrogenation products using Nafion supported complexes were comparable or higher than yields obtained homogeneously and rates of hydrogenation of nitrotoluene were only slightly reduced, as a consequence of using low catalyst loadings. Literature reports of hydrogenation using Nafion supported complexes[2] showed rates of hydrogenation to be reduced by two orders of magnitude compared to homogeneous catalysis. These poor results were because the authors used a loading of approximately 0.08 mmol catalyst per gram of Nafion.

The hydroformylation of hexene was carried out using a series of complexes of the form $[Rh(NBD)L_2]BF_4$ where L represents a phosphine. Yields of aldehydes and normal to branched ratios were slightly lower using Nafion supported complexes in comparison with the homogeneous case. It was thought that the increase in branched products was as a result of the increased hexene isomerisation occurring within the Nafion and due to the

support itself. Hydroformylation was also achieved using rhodium complexes supported in a modified form of Nafion in which the sulphonic acid group had been replaced by ($-SO_2PPh_2$). Yields of aldehydes were modest in comparison to those obtained using Nafion-H.

The failure to produce substituted pyridines from propyne and acetonitrile using cobalt complexes incorporated into Nafion could be as a result of steric crowding within the cavities hindering the formation of the intermediate metallocycle. However, since Nafion supported complexes have been used to successfully hydrogenate oleic acid with a 18 carbon backbone and to produce polyketone, it is unlikely that steric hindrance due to the Nafion itself is a major factor. The reason for the lack of cyclisation products is more likely to be due to the overall low reactivity of these complexes, being reduced still further by the Nafion support. Notwithstanding the limitations described above and the lack of products in the aforementioned case, Nafion has proved to be of overall benefit for the support of transition metal complexes as catalysts in the majority of reactions studied. Further studies of its use for this purpose are therefore recommended.

8.1 References

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Appendix (I)

General experimental conditions

Unless otherwise stated, all syntheses were carried out under a dry, oxygen-free, nitrogen or argon atmosphere, using standard vacuum line and Schlenk techniques.

Solvents

Solvents used in syntheses were dried using the appropriate drying agents. Hydrocarbons and ethers were distilled from sodium wire, dichloromethane and acetonitrile were distilled from CaH_2 and methanol was dried with activated, Linde type 4A molecular sieves. Methanol and deionised water were deoxygenated by bubbling nitrogen gas through prior to use. The remaining solvents were deoxygenated by three freeze-pump-thaw cycles and stored in solvent pots in the dark.

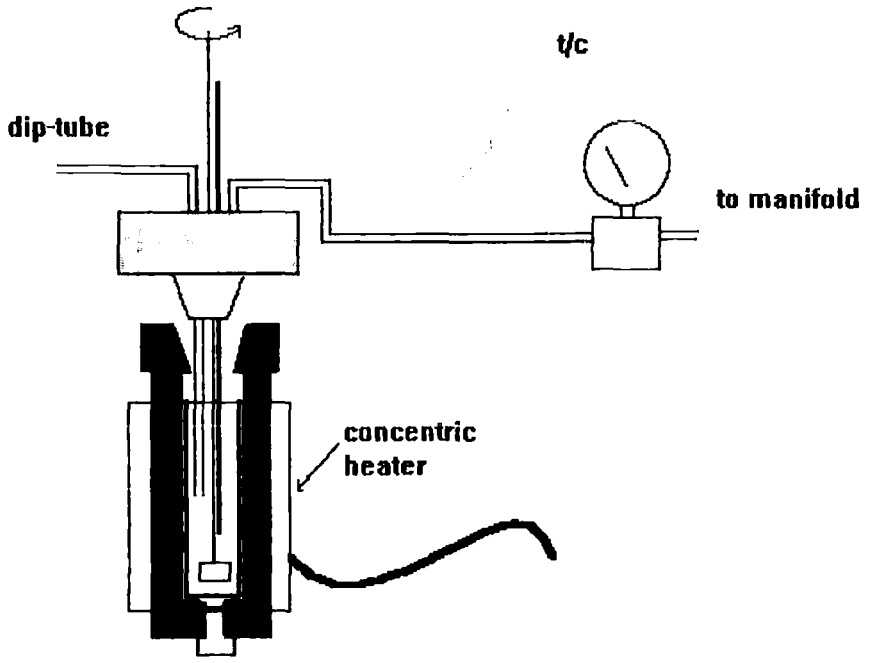
Characterisation

The complexes were characterised by observing their appearance, performing elemental analyses using a model CE-440 elemental analyser made by Exeter Analytical Inc., by infra-red spectroscopy using a Paragon 1000 series FTIR spectrometer and by nuclear magnetic resonance spectroscopy using a Varian Mercury 200 or Unity 300 MHz spectrometer. Spectra were obtained for protons and ^{13}C, referenced to the chemical shifts of the solvents and reported with respect to $SiMe_4$. Spectra were obtained for ^{31}P nuclei referenced to an external frequency lock and reported with respect to 85% H_3PO_4.

High pressure reactions

All catalytic testing was performed in the High Pressure laboratory using a stainless steel reaction vessel capable of withstanding 750 atmospheres. The vessel has

a capacity of 150 cm^3, a drain plug and is fitted with a thermocouple and dip-tube (see scheme I.1). Provision is made for continuous stirring and there are connections via 1/8" stainless steel "Swagelok" tubing to a bursting disc for emergency pressure release, an analogue pressure gauge, pressure transducer and the manifold for introduction and removal of gases. Reaction solutions are contained in a glass liner. The whole autoclave is electrically heated by a concentric band heating element.



Scheme (I).1 High pressure autoclave

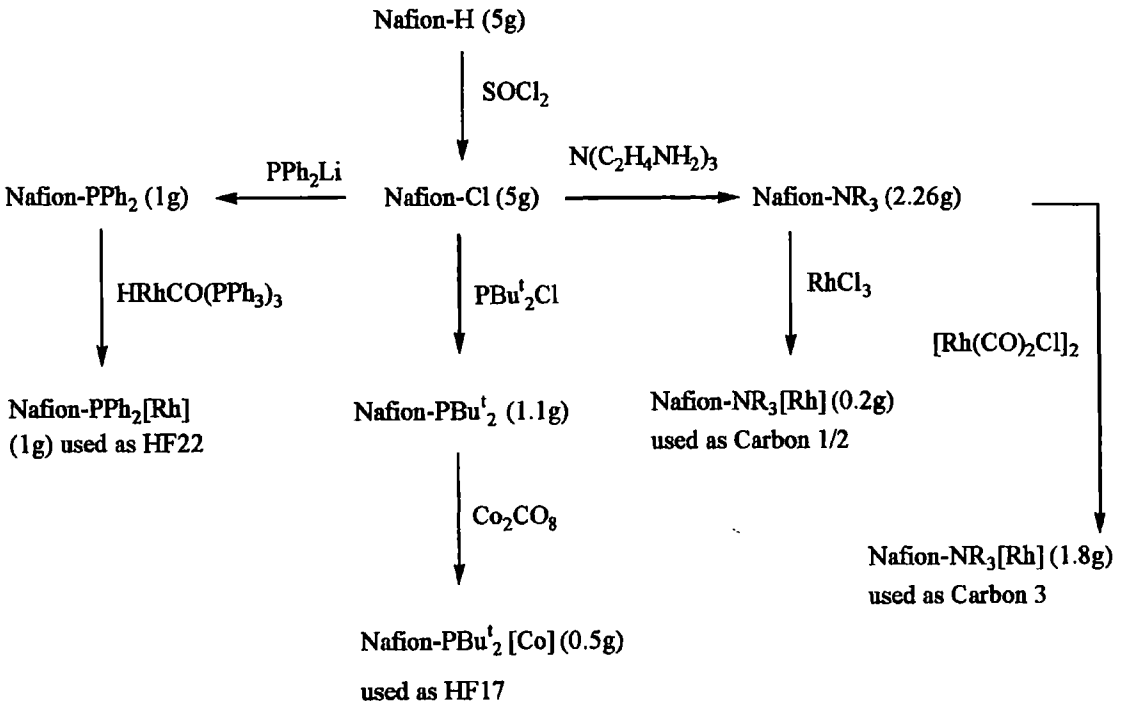
High pressure reaction product determination

Products were determined using a HP 5890 Series II gas chromatograph with flame ionisation detector, containing a SE30 capillary column and fitted with an integrator. Product peaks were identified by either a HP 5890 Series II GC coupled to a VG Analytical Trio 1000 mass spectrometer or by comparing retention times with authentic samples.

Appendix II

Overview of Modified Nafion experiments

Batch 1



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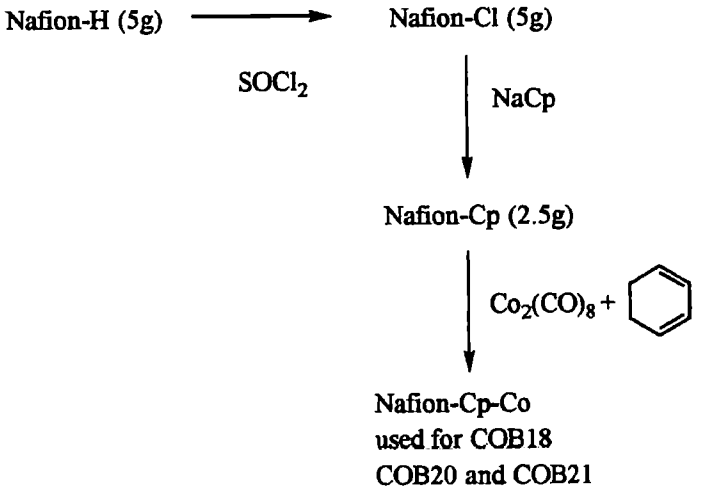

Appendix (III)

Thermodynamic calculations

i) The formation of methyl propanoate

1) $CO + CH_2{=}CH_2 + CH_3OH \rightarrow CH_3CH_2COOCH_3$

$CH_2{=}CH_2$ $\Delta H_f = 52.28$ kJ mol^{-1}, $S^\theta = 219.8$ JK^{-1} mol^{-1}

CO $\Delta H_f = -110.5$ kJ mol^{-1}, $S^\theta = 197.5$ JK^{-1} mol^{-1}

CH_3OH $\Delta H_f = -238.6$ kJ mol^{-1}, $S^\theta = 126.8$ JK^{-1} mol^{-1}

$CH_3CH_2COOCH_3$ Heat of Combustion = 2310.8 kJ mol^{-1}

Combustion reaction

2) $CH_3CH_2COOCH_3 + 5\ O_2 \rightarrow 4CO_{2(g)} + 4H_2O_{(l)}$

$4\ \Delta H_f\ CO_2 = -1572.6$ kJ mol^{-1}

$4\ \Delta H_f\ H_2O = \underline{-1143.4}$ kJ mol^{-1}

-2716

<u>+2310.8</u>

-405.2 kJ mol^{-1} $\{\Delta H_f\ CH_3CH_2COOCH_3\}$

From (1) $\Delta H_m = \Delta H_{f(products)} - \Delta H_{f(reactants)}$

$$\Delta H_m = -405.2 - \{52.28 - 110.5 - 238.6\} = -108.38\ (\Delta H_m)$$

S^θ $\{CH_3CH_2COOCH_3\}$ is not available but from similar compounds is likely to be $250\pm5\ JK^{-1}\ mol^{-1}$

$$\Delta S = S^\theta_{(products)} - S^\theta_{(reactants)} = 250 - \{219.8 + 197.5 + 126.8\}$$

$$\Delta S = -294\pm5\ JK^{-1}\ mol^{-1}$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

At 300K $\Delta G^\theta = -108 - (300 \times [-294])/1000 = -20\pm1.5\ kJ\ mol^{-1}$

At 400K $\Delta G^\theta = -108 - (400 \times [-294])/1000 = +9\pm2\ kJ\ mol^{-1}$

At $367\pm2K$ (= 94°C) ΔG^θ becomes negative.

---

ii) Ethene dimerisation

3) $2\ CH_2{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2$

$CH_2{=}CH_2$ $\Delta H_f = 52.28\ kJ\ mol^{-1}$, $S^\theta = 219.8\ JK^{-1}\ mol^{-1}$

$CH_3CH_2CH{=}CH_2$ $\Delta H_f = 1.2\ kJ\ mol^{-1}$, $S^\theta = 307\ JK^{-1}\ mol^{-1}$

$$\Delta H_m = \Delta H_{f(products)} - \Delta H_{f(reactants)}$$

$$\Delta H_m = 1.2 - 104.56 = -103.36\ kJ\ mol^{-1}$$

$\Delta S = S^{\theta}_{(products)} - S^{\theta}_{(reactants)} = 307 - (2 \times 219.8)$

$\Delta S = -132.6\ JK^{-1}\ mol^{-1}$

$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$

At 300K $\Delta G^{\theta} = -103.36 - (300 \times [-132.6])/1000 = -63.58\ kJ\ mol^{-1}$

At 400K $\Delta G^{\theta} = -103.36 - (400 \times [-132.6])/1000 = -50.32\ kJ\ mol^{-1}$

---

iii) Propyne hydroesterification

4) $CH{\equiv}C.CH_3 + CO + CH_3OH \rightarrow CH_3C(CH_2)COOCH_3$

$CH{\equiv}C.CH_3$ $\Delta H_f = 184.9\ kJ\ mol^{-1}$, $S^{\theta} = 248.1\ JK^{-1}\ mol^{-1}$

CO $\Delta H_f = -110.5\ kJ\ mol^{-1}$, $S^{\theta} = 197.5\ JK^{-1}\ mol^{-1}$

CH_3OH $\Delta H_f = -238.6\ kJ\ mol^{-1}$, $S^{\theta} = 126.8\ JK^{-1}\ mol^{-1}$

MMA $\Delta H_f = -384.8\ kJ\ mol^{-1}$, $S^{\theta} = 266.2\ JK^{-1}\ mol^{-1}$

$\Delta H_m = \Delta H_{f(products)} - \Delta H_{f(reactants)}$

$\Delta H_m = -384.8 - \{-110.5 - 238.6 + 197.5\} = -220.6\ kJ\ mol^{-1}$

$\Delta S = S^{\theta}_{(products)} - S^{\theta}_{(reactants)} = 266.2 - (248.1 + 126.8 + 197.5)$

$\Delta S = -306.2\ JK^{-1}\ mol^{-1}$

$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$

At 300K $\Delta G^{\theta} = -220.6 - (300 \times [-306.2])/1000 = -128.74\ kJ\ mol^{-1}$

At 400K $\Delta G^{\theta} = -220.6 - (400 \times [-306.2])/1000 = -98.12\ kJ\ mol^{-1}$

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iv) hydrogenation of cyclohexene

5) $C_6H_{10} + H_2 \rightarrow C_6H_{12}$ (cyclohexane)

C_6H_{10} $\Delta H_f = -38.5\ kJ\ mol^{-1}$, $S^{\theta} = 214.6\ JK^{-1}\ mol^{-1}$

C_6H_{12} (cyclohexane) $\Delta H_f = -123.1\ kJ\ mol^{-1}$, $S^{\theta} = 298.2\ JK^{-1}\ mol^{-1}$

H_2 $\Delta H_f = 0\ kJ\ mol^{-1}$, $S^{\theta} = 130.5\ JK^{-1}\ mol^{-1}$

$\Delta H_m = \Delta H_{f(products)} - \Delta H_{f(reactants)}$

$\Delta H_m = -123.1 - \{-38.5 - 0\} = -84.6\ kJ\ mol^{-1}$

$\Delta S = S^{\theta}_{(products)} - S^{\theta}_{(reactants)} = 298.2 - (214.6 + 130.5)$

$\Delta S = -46.9\ JK^{-1}\ mol^{-1}$

$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$

At 300K $\Delta G^{\theta} = -84.6 - (300 \times [-46.9])/1000 = -70.53\ kJ\ mol^{-1}$

At 400K $\Delta G^{\theta} = -84.6 - (400 \times [-46.9])/1000 = -65.84\ kJ\ mol^{-1}$

v) hydroformylation of hexene

6) $C_6H_{12} + CO + H_2 \rightarrow C_7H_{14}O$

C_6H_{12} (hex-1-ene) $\Delta H_f = -74.2$ kJ mol^{-1}, $S^\theta = 295.2$ JK^{-1} mol^{-1}

H_2 $\Delta H_f = 0$ kJ mol^{-1}, $S^\theta = 130.5$ JK^{-1} mol^{-1}

CO $\Delta H_f = -110.5$ kJ mol^{-1}, $S^\theta = 197.5$ JK^{-1} mol^{-1}

$C_7H_{14}O$ $\Delta H_f = -311.5$ kJ mol^{-1}, $S^\theta = 335.4$ JK^{-1} mol^{-1}

$\Delta H_m = \Delta H_{f(products)} - \Delta H_{f(reactants)}$

$\Delta H_m = -311.5 - \{-74.2 - 0 - 110.5\} = -126.8$ kJ mol^{-1}

$\Delta S = S^\theta_{(products)} - S^\theta_{(reactants)} = 335.4 - (295.2 + 130.5 + 197.5)$

$\Delta S = -287.8$ JK^{-1} mol^{-1}

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

At 300K $\Delta G^\theta = -126.8 - (300 \times [-287.8])/1000 = -40.46$ kJ mol^{-1}

At 400K $\Delta G^\theta = -126.8 - (400 \times [-287.8])/1000 = -11.68$ kJ mol^{-1}

$\Delta G^\theta = 0$ at 441K (168 °C)

Appendix IV

The Crystal Structure of $[PdCl_2\{PPh_2(C_9H_6N)\}] \cdot CH_2Cl_2$

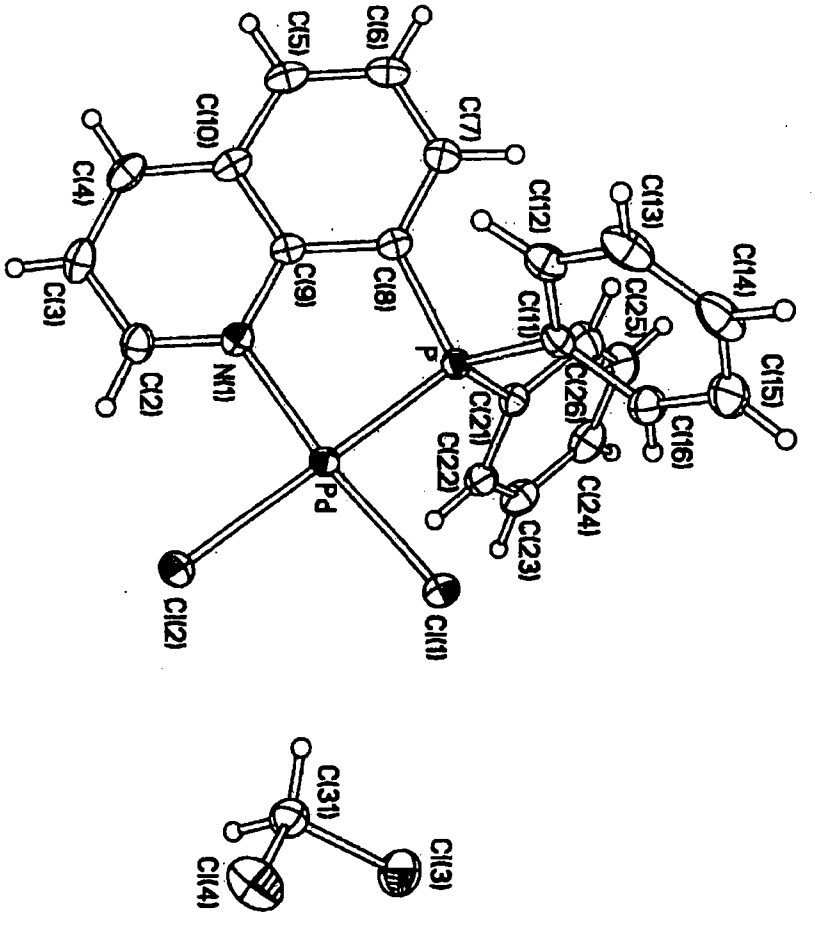

Table 1 **Crystal data and structure refinement for $[PdCl_2\{PPh_2(C_9H_6N)\}]$**

Empirical formula	$C_{21}H_{16}Cl_2NPPd \cdot CH_2Cl_2$
Formula Weight	575.54
Temperature	120(2)K
Wavelength	0.71073Å
Crystal System	Monoclinic
Space Group	$P2_1/n$ (No.14)
Unit Cell Dimensions	a = 13.3863(3) Å
	b = 9.259(1) Å
	c = 17.793(6) Å
Volume	2228.8(9) Å
Z	4
Density (Calculated)	1.715 g cm^{-3}
Absorption Coefficient	1.394 mm^{-1}
F(000)	1144
Crystal Size	0.4 x 0.4 x 0.15 mm^3
θ range for data collection	1.5 to 29°
Index ranges	$-17 \leq h < 18$, $-12 \leq k \leq 12$, $-24 \leq l \leq 22$
Reflections collected	16869
Independent reflections	5870 [R(int) = 0.0216]
Reflections with $I>2\sigma(I)$	5348
Completeness to θ = 29°	99.0%
Absorption correction	Integration
Max. and min. transmission	0.8646 and 0.7090
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5870 / 0 / 334
Largest final shift / e.s.d.ratio	0.004
Goodness-of-fit on F^2	1.122
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0236, wR_2 = 0.0535
R indices all data	R_1 = 0.0281, wR_2 = 0.0576
Largest diff. peak and hole	0.471 and -0.776 e. $Å^{-3}$

Table 2 **Selected Bond Lengths (Å) for $[PdCl_2\{PPh_2(C_9H_6N)\}] \cdot CH_2Cl_2$**

Bond length (Å)		Bond length (Å)	
Pd-N(1)	2.068(2)	Pd-P	2.2069(7)
Pd-Cl(1)	2.2962(6)	Pd-Cl(2)	2.3817(7)
P-C(11)	1.808(2)	P-C(8)	1.815(2)
P-C(21)	1.816(2)	N(1)-C(2)	1.328(2)
N(1)-C(9)	1.392(2)	C(8)-C(9)	1.416(3)

Table 3 **Selected Bond Angles (°) for $[PdCl_2\{PPh_2(C_9H_6N)\}]\cdot CH_2Cl_2$**

Bond Angle (°)		Bond Angle (°)	
N(1)-Pd-P	85.25(5)	N(1)-Pd-Cl(1)	173.10(5)
P-Pd-Cl(1)	87.86(2)	N(1)-Pd-Cl(2)	94.45(5)
P-Pd-Cl(2)	179.05(2)	Cl(1)-Pd-Cl(2)	92.44(2)
C(11)-P-C(8)	108.52(9)	C(11)-P-C(21)	107.25(9)
C(8)-P-C(21)	105.91(8)	C(11)-P-Pd	117.46(6)
C(8)-P-Pd	101.25(6)	C(21)-P-Pd	115.52(6)
C(2)-N(1)-C(9)	118.61(16)	C(2)-N(1)-Pd	123.30(13)
C(9)-N(1)-Pd	118.08(12)	C(7)-C(8)-P	125.08(15)

Crystal structure and data provided by Dr.A.S.Batsonov, University of Durham.

Appendix 5

Colloquia, Lectures and Seminars Attended

5.1 Lectures attended at Durham

1996

October 16	Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook Silylformylation and Silylcarbocyclisations in Organic Synthesis
October 22	Professor Lutz Gade, Univ. Wurzburg, Germany Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity
October 22	Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston Making Polymers for Biomedical Application - can we meet Nature's Challenge? Joint lecture with the Institute of Materials
October 23	Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany Function Based on Organisation
October 30	Dr Phillip Mountford, Nottingham University Recent Developments in Group IV Imido Chemistry
November 13	Dr G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements
November 19	Professor R. E. Grigg, University of Leeds Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes
November 27	Dr Richard Templer, Imperial College, London Molecular Tubes and Sponges
December 11	Dr Chris Richards, Cardiff University Sterochemical Games with Metallocenes

1997

January 15	Dr V. K. Aggarwal, University of Sheffield Sulfur Mediated Asymmetric Synthesis
January 16	Dr Sally Brooker, University of Otago, NZ

Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry

January 21 — Mr D. Rudge, Zeneca Pharmaceuticals
High Speed Automation of Chemical Reactions

January 22 — Dr Neil Cooley, BP Chemicals, Sunbury
Synthesis and Properties of Alternating Polyketones

February 4 — Dr A. J. Banister, University of Durham
From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur

February 5 — Dr A. Haynes, University of Sheffield
Mechanism in Homogeneous Catalytic Carbonylation

February 18 — Professor Sir James Black, Foundation/King's College London
My Dialogues with Medicinal Chemists

February 19 — Professor Brian Hayden, University of Southampton
The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts

February 25 — Professor A. G. Sykes, University of Newcastle
The Synthesis, Structures and Properties of Blue Copper Proteins

March 4 — Professor C. W. Rees, Imperial College
Some Very Heterocyclic Chemistry

March 5 — Dr J. Staunton FRS, Cambridge University
Tinkering with biosynthesis: towards a new generation of antibiotics

March 11 — Dr A. D. Taylor, ISIS Facility, Rutherford Appleton Laboratory
Expanding the Frontiers of Neutron Scattering

March 19 — Dr Katharine Reid, University of Nottingham
Probing Dynamical Processes with Photoelectrons

1997

October 8 — Professor E Atkins, Department of Physics, University of Bristol
Advances in the control of architecture for polyamides: from nylons to genetically engineered silks to monodisperse oligoamides

October 15 — Dr R M Ormerod, Department of Chemistry, Keele University
Studying catalysts in action

October 22 — Professor R J Puddephatt (RSC Endowed Lecture), University of Western Ontario
Organoplatinum chemistry and catalysis

October 23 — Professor M R Bryce, University of Durham, Inaugural Lecture
New Tetrathiafulvalene Derivatives in Molecular, Supramolecular and Macromolecular Chemistry: controlling the electronic properties of organic solids

October 28 — Professor A P de Silva, The Queen's University, Belfast

Luminescent signalling systems"

November 5 — Dr M Hii, Oxford University
Studies of the Heck reaction

November 11 — Professor V Gibson, Imperial College, London
Metallocene polymerisation

November 20 — Dr L Spiccia, Monash University, Melbourne, Australia
Polynuclear metal complexes

November 25 — Dr R Withnall, University of Greenwich
Illuminated molecules and manuscripts

November 26 — Professor R W Richards, University of Durham, Inaugural Lecture
A random walk in polymer science

December 2 — Dr C J Ludman, University of Durham
Explosions

1998

January 27 — Professor R Jordan, Dept. of Chemistry, Univ. of Iowa, USA.
Cationic transition metal and main group metal alkyl complexes in olefin polymerisation

January 28 — Dr S Rannard, Courtaulds Coatings (Coventry)
The synthesis of dendrimers using highly selective chemical reactions

February 4 — Professor P Fowler, Department of Chemistry, Exeter University
Classical and non-classical fullerenes

February 17 — Dr S Topham, ICI Chemicals and Polymers
Perception of environmental risk; The River Tees, two different rivers

February 18 — Professor G Hancock, Oxford University
Surprises in the photochemistry of tropospheric ozone

February 25 — Dr C Jones, Swansea University
Low coordination arsenic and antimony chemistry

March 4 — Professor T C B McLeish, IRC of Polymer Science Technology, Leeds University
The polymer physics of pyjama bottoms (or the novel rheological characterisation of long branching in entangled macromolecules)

March 18 — Dr J Evans, Oxford University
Materials which contract on heating (from shrinking ceramics to bullet proof vests)

October 21 — Professor P Unwin, Department of Chemistry, Warwick University
Dynamic Electrochemistry: Small is Beautiful

October 26 — Dr W Peirs, University of Calgary, Alberta, Canada

	Reactions of the Highly Electrophilic Boranes HB(C6F5)2 and B(C6F5)3 with Zirconium and Tantalum Based Metallocenes
October 27	Professor A Unsworth, University of Durham What's a joint like this doing in a nice girl like you? In association with The North East Polymer Association
October 28	Professor J P S Badyal, Department of Chemistry, University of Durham Tailoring Solid Surfaces, Inaugural Lecture
November 11	Dr M Wills, Department of Chemistry, University of Warwick New Methodology for the Asymmetric Transfer Hydrogen of Ketones
November 12	Professor S Loeb, University of Windsor, Ontario, Canada From Macrocycles to Metallo-Supramolecular Chemistry
November 17	Dr J McFarlane Nothing but Sex and Sudden Death!
November 18	Dr R Cameron, Department of Materials Science & Metallurgy, Cambridge University Biodegradable Polymers
December 1	Professor N Billingham, University of Sussex Plastics in the Environment - Boon or Bane In association with The North East Polymer Association.
January 27	Professor K Wade, Department of Chemistry, University of Durham Foresight or Hindsight? Some Borane Lessons and Loose Ends
February 9	Professor D J Cole-Hamilton, St. Andrews University Chemistry and the Future of life on Earth
March 9	Dr Michael Warhurst, Chemical Policy issues, Friends of the Earth Is the Chemical Industry Sustainable?
May 12	Dr Duncan Bruce, Exeter University The Synthesis and Characterisation of Liquid-Crystalline Transition Metal Complexes

5.2 Symposia attended

1997

8-11 July	3rd International Symposium: Supported Reagents and Catalysts in Chemistry University of Limerick
26 Sept	2nd Anglo-Dutch Symposium on Catalysis and Organometallic Chemistry The Royal Netherlands Academy of Arts and Sciences. Amsterdam

1998

6-9 April — Royal Society of Chemistry, 1998 National Congress and Young Researchers Meeting

1999

29-30 March — 3rd Anglo-Dutch Symposium on Catalysis and Organometallic Chemistry University of Sheffield. (Poster Contribution)