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Studies of Nickel (II) Diphosphine Complexes Directed Towards Carbon Monoxide/Ethene Catalysis

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Where go the Boats?

Dark brown is the river,
Golden is the sand,
It flows along forever,
With trees on either hand.

Green leaves a-floating
Castles on the foam,
Boats of mine a-boating -
Where we'll all come home.

On goes the river,
And out past the mill,
Away down the valley,
Away down the hill.

Away down the river,
A hundred miles or more,
Other little children,
Shall bring my boats ashore.

Robert Louis Stevenson

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I would like to thank my friends, especially Dan and Boo, and the girls at Durham City Rugby Football Club. I'd like to thank my family, Mum and Dad, Lou and Neil, Kez, and my little brother M. J. who I must apologise to for not having a bigger suitcase.

Thankyou Simon.

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 thesis is concerned with the synthesis, characterisation and reactivity of a variety of nickel(II) diphosphine complexes considered possible catalyst precursors for the copolymerisation of CO and ethene. [Ni(diphos)(*o*-tolyl)(py)]Y (**1**), [Ni(diphos)$_2$](Y)$_2$ (**2**), and [Ni(diphos)(S)$_2$](Y)$_2$ (**3**) {Y = OTs, OTf} are found to be catalyst precursors for the CO/ethene reaction (115°C, 1200psi, 1:1 CO:ethene) with high selectivity to polyketone formation, the activity depending on the phosphine ligand employed. However, the activity is low and attributed in part to the formation of the [Ni(diphos)(CO)$_2$] (**4**) complexes which are stable under the reaction conditions. The diphosphine ligand employed, particularly the nature of the backbone, is found to influence the synthesis and reaction chemistry of the complexes (**1**), (**2**) and (**3**).

A series of complexes of the type [Ni(R$_2$P(CH$_2$)$_n$PR$_2$)(*o*-tolyl)Br] (**5**) {n = 2; R = Ph, Cy, ^{t}Bu) have been synthesised and the complex [Ni(dppe)(*o*-tolyl)Cl] has been characterised by X-ray crystallography. The influence of the chelating diphosphine on the structural characteristics and NMR parameters of these compounds has been investigated. When n > 2, the complexes of the type [Ni(diphos)(*o*-tolyl)X] were not isolated. The reaction of type (**5**) complexes with TlY (Y = OTs, BF$_4$) in pyridine led to the formation of complexes of the type [Ni(diphos)(*o*-tolyl)(py)]Y (**1**).

A series of complexes of the type [Ni(diphos)Cl$_2$] (**6**) {diphos = dcpe, dBpe, dcpn} have been synthesised and characterised by X-ray crystallography. The influence of the chelating phosphine ligand on structural characteristics of these compounds has been investigated. Complexes of the type (**2**) and (**3**) can be synthesised from type (**6**) complexes. Detailed studies on the behaviour of a series of complexes of the type [Ni(diphos)$_2$](Y)$_2$ (**2**) and [Ni(diphos)(Y)$_2$] (**3**) {Y = OTs and OTf), and the equilibrium between them in solution have been undertaken. The complex [Ni(dppe)$_2$](OTs)$_2$ has been characterised by X-ray crystallography.

Contents

Abbreviations

r.t.	Room temperature
GC	Gas Chromatography
MS	Mass Spectroscopy
NMR	Nuclear Magnetic Resonance
VT	Variable Temperature
HFIPA	Hexafluoro*iso*propylalcohol
AIBN	2,2'-Azobis(2-methylpropionitrile)
cod	Cycloocta-1,5-diene
HOTs	*p*-toluenesulphonic acid
HOTf	Trifluorosulphonic acid (triflic acid)
HOAc	acetic acid
OTs^-	tosylate
OTf^-	triflate
OAc^-	acetate
diphos	Any Chelating Phosphine
dppm	1,1-Bis(diphenylphosphino)methane
dppe	1,2-Bis(diphenylphosphino)ethane
dcpe	1,2-Bis(dicyclohexylphosphino)ethane
dBpe	1,2-Bis(di-*tert*-butylphosphino)ethane
d*i*ppe	1,2-Bis(di*iso*propylphosphino)ethane
depe	1,2-Bis(diethylphosphino)ethane
dmpe	1,2-Bis(dimethylphosphino)ethane
dppv	1,2-Bis(diphenylphosphino)ethylene
2,2-dppp	2,2'-Bis(diphenylphosphino)propane
dppp	1,3-Bis(diphenylphosphino)propane
dcpp	1,3-Bis(dicyclohexylphosphino)propane
d*i*ppp	1,3-Bis(di*iso*propylphosphino) propane
dmpp	1,3-Bis(dimethylphosphino)propane
dcpn	1,8-Bis(dicyclohexylphosphino)naphthalene
dppn	1,8-Bis(diphenylphosphino)naphthalene
dppbut	1,4-Bis(diphenylphosphino)butane
dpppent	1,5-Bis(diphenylphosphino)pentane
Boxylyl	1,4-Bis(di-*tert*-butylphosphino)*ortho*-xylene
bpep	2,2'-biphenylylenebisdiethylphosphine

diop	4,5-Bis(diphenylpropylphosphino)methyl-2,2'dimethyl-1,3 dioxolane
np_3	tris-(2-(diphenylphosphino)ethyl)amine
pp_3	tris-(2-(diphenylphosphino)ethyl)phosphine
dpppO	2,2-bis(diphenylphosphinomethyl)-1-methoxypropane
dpppS	2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane
etriphos	1,1,1-tris(diethylphosphinomethyl)ethane
dppp-dppp	2,3-bis-(diphenylphosphinomethyl)-1,4-bis(diphenylphosphino)butane
bipy	2,2-bypyridine
DMAMN	1,8-Bis(dimethylaminomethyl)naphthalene
py	pyridine

Introduction

The development of catalytic processes to transform cheap feedstocks e.g. CO, CH_3OH and $CH_2{=}CH_2$ into value added chemicals is of great interest. Such conversions to, for example, ethanoic acid, propanoic acid, etc. are currently achieved by using a transition metal catalyst.[1,2] For example palladium phosphine complexes can be used to catalyse the carbonylation of ethene to form both polyketone (Equation 1) and methyl propanoate (Equation 2). The reaction can be tailored, depending on the steric and electronic properties of the phosphine to produce polyketone or methyl propanoate in high yields and with good selectivity.[3,4,5.]

$$nCH_2{=}CH_2 + nCO + CH_3OH \xrightarrow{[Pd]} \underset{\text{polyketone}}{H\text{-}(CH_2CH_2CO)_n\text{-}OCH_3}$$

Equation 1

$$CH_2{=}CH_2 + CO + CH_3OH \xrightarrow{[Pd]} \underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3}$$

Equation 2

Shell have recently started marketing polyketone, a perfectly alternating polymer of CO and ethene, as CARILON® which is claimed to "exhibit a unique balance of properties unlike any other engineering plastic."[6] Methyl propanoate, may itself be converted, via a base catalysed reaction with methanal, to yield methyl methacrylate (MMA) which is subsequently polymerised into perspex.[7]

Catalytic Chemistry of Nickel

Nickel has wide applications in both homogeneous and heterogeneous catalysis. A recent review has been published on the current industrial processes that utilise nickel catalysts and these will be discussed in Chapter 1.

Industrially, nickel is second, after cobalt as the most frequently used transition metal in catalytic transformations.[8] Numerous efforts are being made in industry to replace second or third row transition metals e.g. Palladium and Rhodium, with a cheaper first row transition element e.g. Nickel, but to retain the high yields and selectivities exhibited by the current catalysts.[8]

Polyketone

Nickel was the first transition metal used to catalyse the copolymerisation of CO and ethene. In the late 1940's Reppe and Magin showed that a nickel catalyst of the type $[K_2Ni(CN)_4]$, in water, produced low melting oligomers of ethene and CO in addition to diethylketone and propionic acid.[9] An improvement was made when Shryne and Holler replaced the potassium cation with two ammonium cations, $[(Bu_4N)_2Ni(CN)_4]$ and the catalysis was carried out in the presence of strong acids such as HOTf and HOTs in solvents such as HFIPA, which resulted in higher molecular weight polyketone.[10] Sen first described the use of a palladium based catalyst of the type $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ to give polyketone.[11] Drent discovered when the anion was a weakly co-ordinating anion of a strong acid e.g. $^-$OTs, a change in selectivity was observed. A stoichiometric amount of the bidentate ligand 1,3-bis(diphenylphosphino)propane (dppp), led to the production of a perfectly alternating CO/ethene copolymer with essentially 100% selectivity.[3,4] Dppp is a bidentate diphosphine ligand containing a three carbon backbone. The equivalent bidentate ligands, (dppe) containing a two carbon backbone and (dppb) a four carbon backbone, also produced polyketone but with reduced turnovers and product yield.[3,4] Dppe gave higher yields than dppb.[3,4] An excess of PPh_3 produces methyl propanoate (discussed below).[3,4] An alternative palladium system which uses alumoxanes as cocatalysts has recently been developed and produces polyketone.[12] A further example of polyketone production *via* a nickel based catalyst uses the complex $[Ni(Ph_2CH{=}C(Ph)O)(PEt_3)Ph]$ which is similar to the SHOP type catalysts, which are used to catalyse the oligomerisation of ethene.[13] However, high yields and activities were not obtained and therefore the catalyst system was not economic for commercial production.[13] A recent patent has been disclosed where the first row transition metal, copper, gives polyketone.[14] The copper catalyst is composed of; copper (II) acetate, dppp, BF_3 etherate and *p*-benzoquinone. However, the copper based system appears only to have 5% the productivity of the palladium-based systems on a metal content basis.[14]

Methyl Propanoate

Catalysts used by Drent for the production of methyl propanoate were cationic palladium phosphine systems, prepared from palladium acetate and an excess of the monodentate phosphine, triphenylphosphine (PPh_3) and a Brønsted acid of a weakly co-ordinating anion (e.g. *p*-toluene sulphonic acid, OTs); methanol was used both as a solvent and a reagent.[3,4.] ICI have patented a process that also leads selectively to methyl propanoate; the catalyst is palladium based and contains a very bulky, rigid bidentate phosphine, Boxylyl.[5] An example of methyl propanoate production using a nickel based catalyst is in the patent literature. Ethene was tested with CO in the presence of methanol and $NiI/Mo(CO)_6$/ EtI catalyst and PPh_3 promoter in EtO_2CCH_2Me solvent to give methyl propanoate.[15] However, this reaction is not selective to methyl propanoate and various other organic compounds are produced.[15]

The use of nickel as a catalyst in the formation of either polyketone or methyl propanoate has been observed previously, although the rates and selectivities were far too low for commercial production. The effects of the phosphine ligand in palladium systems have been investigated and the nature of the phosphine ligand was found to influence the product outcome. The investigation into the effect of a phosphine in a nickel system which is analogous to the palladium system is of interest due to the economic benefits which would be gained if a nickel catalyst was as active and selective as the palladium analogue.

This thesis is concerned with the chemistry of nickel-chelating phosphine compounds as alternative catalysts to those currently employed in the palladium catalysed conversion of CO and ethene to yield either polyketone or methyl propanoate.

This work consists of seven chapters. Chapter 1 contains an overview of nickel chemistry with particular emphasis on nickel-phosphine complexes, and nickel complexes that are used as catalysts both in organic synthesis and in industrial processes. Chapters

2-6 contain the experimental data collected in this work and a discussion of these results, whilst Chapter 7 contains the conclusions drawn from the experimental work. In particular, Chapter 2 contains the synthesis and structural characterisation of a series of nickel (II) diphosphine (diphos) dichloride complexes [Ni(diphos)Cl_2] (**1**). These are of interest since they provide a platform for investigating the steric and electronic influences of the diphosphine ligand about the nickel centre, and also for their synthetic utility as they may be converted into potential catalyst precursor complexes. In Chapters 3 and 4, the complexes [Ni(diphos)(*o*-tolyl)X] (**2**) and $[Ni(diphos)(o\text{-tolyl})(S)]^+$ (**3**) are synthesised; and are of interest since they are potential catalyst precursor complexes. Chapter 5 contains a solution study of the cationic nickel complexes $[Ni(diphos)_2]^{2+}$ (**4**) and $[Ni(diphos)(S)_2]^{2+}$ (**5**). Complexes of the type (**3**), (**4**) and (**5**) are designed to be phosphine complexes that are cationic and contain a weakly co-ordinating anion. This is a common feature of all of the active palladium catalysts, for the copolymerisation of CO and ethene, or formation of methyl propanoate. In Chapter 6, the effect of the phosphine ligand on activity and selectivity is investigated when the complexes of the type (**3**), (**4**) and (**5**) are tested as catalysts for the CO/ethene reaction in methanol. The carbonylation of the complexes of the type (**2**), (**3**), (**4**) and (**5**) is also investigated separately.

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Chapter 1

Nickel Phosphine Chemistry

1.1 Nickel Chemistry

The organometallic chemistry of nickel is extensive, dating back to 1890 when Mond prepared the first binary metal carbonyl compound [$Ni(CO)_4$] (**1**)[1] and comprehensive literature reviews have been published.[2,3,4.] This chapter is specifically concerned with organometallic nickel phosphine complexes, though, however, nickel complexes containing non-phosphine ligands, which are relevant to catalysis involving CO and ethene will be discussed.[5]

Nickel is in group ten of the Periodic Table and is a member of the triad, Ni, Pd, and Pt.[6] The number of ligands, and hence, the co-ordination number and structure, bound to a nickel centre is determined by the ligand's ability to stabilise the complex, and the 16/18-electron rule.[6] Nickel is a first row transition metal, and in contrast to Pd and Pt, it forms complexes of all the main structural types and main co-ordination numbers namely; four co-ordinate square-planar and tetrahedral; five co-ordinate trigonal bypyramidal and square-pyramidal; six co-ordinate octahedral.[6]

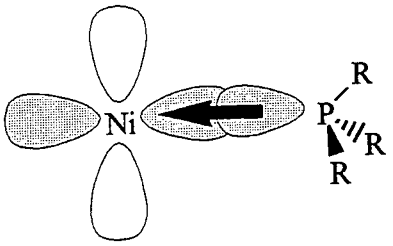
The 18-electron rule states that; a stable complex (with electron configuration of the next highest noble gas) is obtained when the sum of the metal d-electrons, electrons donated from the ligand, and the overall charge of the complex equals 18.[7] The 16-electron rule states that; a stable complex is obtained when the sum of the metal d-electrons, electrons donated from the ligand, and the overall charge of the complex equals 16, and is obeyed for d^8 metals such as Ni(II), Pd(II), Pt(II), and Rh(I).[7] The most common oxidation states in the chemistry of nickel are Ni(II) and Ni(0). There are also examples of complexes of Ni(I), Ni(III) and even Ni(IV). The interchange between Ni(II) and Ni(0) forms the basis of most of the phosphine chemistry of nickel.

Ligands are classified for electron counting purposes according to the number of electrons they formally donate to the metal centre. One electron ligands (denoted as X type ligands) are σ-donors, for example; alkyl, aryl, hydride, halide, amide and alkoxide ligands. Two electron ligands (denoted as L type ligands) may, in addition to donating two electrons to the metal, be π-acceptors, for example; CO, alkenes or phosphines, or π-donors, for example; fluoride or oxide based. Therefore, the classification of the ligands depends on their basic or acidic nature; strong field ligands such as CO, alkenes or phosphines, act as σ-base and π-acid ligands; weak field ligands, such as oxides and fluorides, act as σ- and π-base ligands.[7]

1.2 Phosphines as Ligands

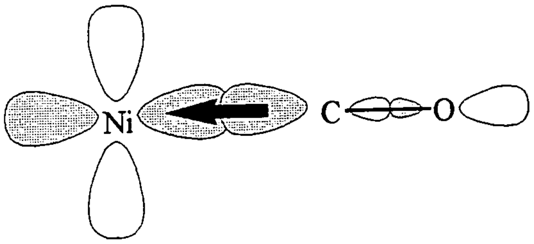
Phosphines are neutral, L type, two electron σ donors. However, in contrast to the nitrogen and oxygen σ-donors, phosphines, PR_3, are also capable of accepting electron density from the metal into the P-C σ^* orbitals (**i**). This means that phosphines exhibit π-acidity as does CO (**i**). In metal complexes containing carbonyl ligands the metal-CO bond has σ and π character. The complexes, particularly metals in a low-valent oxidation state, are stabilised by backbonding to CO in which the π^* orbital accepts electron density from the metal. The CO π^* orbital possesses the ideal symmetry for accepting electron density from an occupied metal *d*-orbital. CO is a therefore known as a strong π-acid.[7,8]

(i)



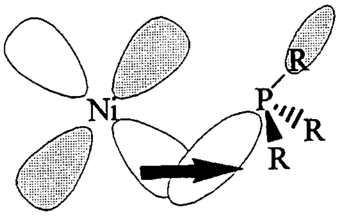
Ni (d σ-orbital) $\longleftarrow$ P(σ)

P ligand to metal σ bonding



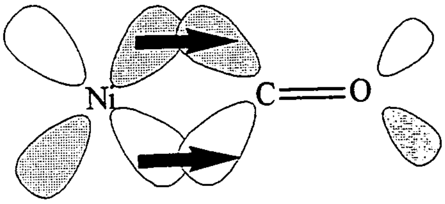
Ni (d σ-orbital) $\longleftarrow$ CO(σ)

CO ligand to metal σ bonding



Ni (d π-orbital) $\longrightarrow$ PR(σ^*)

metal to P backbonding



Ni (d π-orbital) $\longrightarrow$ CO(π^*)

metal to CO backbonding to give a π bond

Phosphines are important because, by changing R, the electronic and steric properties of the metal complex are altered.

1.2.1 Electronic Effects

The electronic properties of a series of phosphines were investigated, by Tolman, by measuring the CO stretching frequency, ν_{CO}, in the nickel carbonyl phosphine complexes, $[Ni(PR_3)(CO)_3]$ **(2)**.[9] Back-bonding, in electron rich complexes, strengthens the metal carbon bond, and weakens the C-O bond, thereby reducing its bond order and lowering ν_{CO}. The CO stretching frequency, is therefore, found to be a sensitive probe for determining the electronic characteristics of a metal centre. Strong σ-donors, for example alkyl phosphines, increase the electron density at the nickel centre and back-bonding subsequently lowers ν_{CO}. A comparison of ν_{CO} of a complex of type **(2)** containing a strongly electron donating phosphine ligand e.g $[Ni(PBu^t_3)(CO)_3]$ **(3)**, (ν_{CO} =

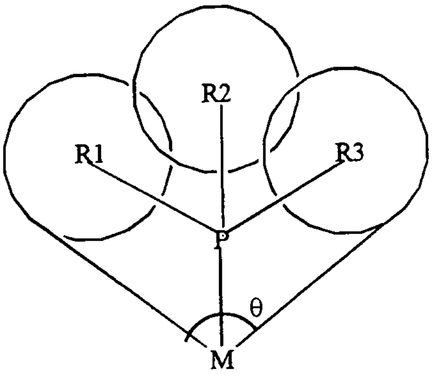
2056.1cm^{-1}) with a complex of type (**2**) containing a strongly electron withdrawing phosphine ligand e.g [Ni(PF$_3$)(CO)$_3$] (**4**), (ν_{CO} = 2110.8cm^{-1}) illustrates the effect; the ligand PF$_3$ displays π-acidity almost as that observed in CO.[8] Aryl, alkoxy and dialkylamino phosphines, respectively, are successively more effective in promoting π-acidity, they exhibit electronic behaviour in between that of an alkyl phosphine or PF$_3$ ligands.[7,8]

1.2.2 Steric Effects

Steric properties of a phosphine control the degree of co-ordinative saturation and reactivity of the complex. Tolman has defined the steric effects of phosphines by the cone angle, θ, the angle at the metal atom swept out to enclose the van-der Waals radii of the groups attached to phosphorus (**ii**). It is dependent on the actual interatomic distance between M and P.[7,8,9]

Typical cone angles are PMe$_3$ (118°), PMePPh$_2$ (136°), PPh$_3$ (145°), PBu$^t_3$ (182°).

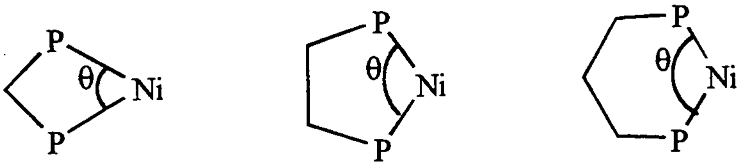
(ii)



1.2.3 Bite Angle in Diphosphine Complexes

In chelating diphosphines the bite angle is a better diagnostic tool for defining the steric bulk of the diphosphine. The bite angle is defined as the angle between the two phosphorus atoms and the nickel atom, P-Ni-P. The magnitude of the bite angle, for the same metal, depends largely on the size of the chelate ring; steric and electronic factors have a more subtle influence. Typical bite angles in four-, five, and six-membered chelate ring nickel complexes are given (**iii**).

(iii)



4-membered ring

5-membered ring

6-membered ring

θ ~ 80 °

θ ~ 85-90 °

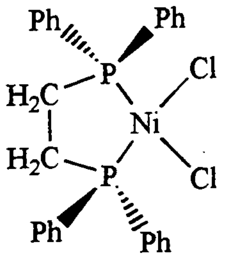
θ ~ 90-95 °

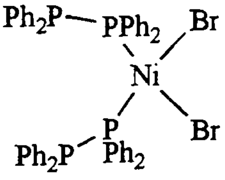
1.3 Nickel (II) Phosphine Complexes

1.3.1 Co-ordination Modes of Diphosphines in Nickel (II) Complexes

Several co-ordination modes of diphosphines in nickel complexes have been observed (**iv**). The most common form of co-ordination mode is *cis*-chelating for example $[Ni(dppe)Cl_2]$ (**5**).[10] Under certain circumstances, a bidentate phosphine can behave as a monodentate phosphine for example in the *cis* square-planar complex $[Ni(Ph_2P\text{-}PPh_2)_2Br_2]$ (**6**)[11] or in [Ni(dppm)(dppm)(CN)](CN) (**7**),[12] where one dppm ligand is functioning as a monodentate ligand and one dppm as a chelating ligand. This reflects the stereochemical flexibility of the dppm ligand. Examples of *trans*-chelating diphosphines are rare. Diphosphines that do complex in a *trans*-chelating fashion must have a backbone where the number of carbons is greater than 5, (**8**).[13]

(iv)


(5)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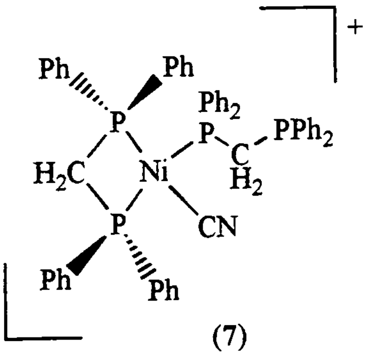
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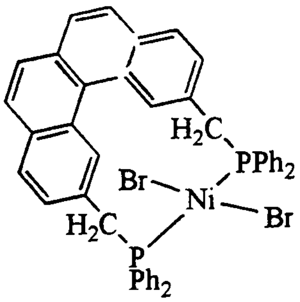

(8)

1.3.2 Synthesis of Ni(II) diphosphine dihalide complexes

Nickel (II) diphosphine dihalides of the type [Ni(P-P)X_2] **(9)**, where X = Cl, Br, I can be prepared by the simple reaction of anhydrous $NiCl_2$ with the desired phosphine in ethanol (Equation 1).[10]

$$NiCl_2 + P\text{-}P \longrightarrow [Ni(P\text{-}P)Cl_2]$$

Equation 1

When X = NO_3 only the bisdiphosphine nickel complex can be isolated. Nickel bisdiphosphine dihalide complexes of the type [Ni(P-P)$_2$](X_2) **(10)**, in solution, rapidly undergo ligand exhange reactions through disproportionation (Equation 2).[14]

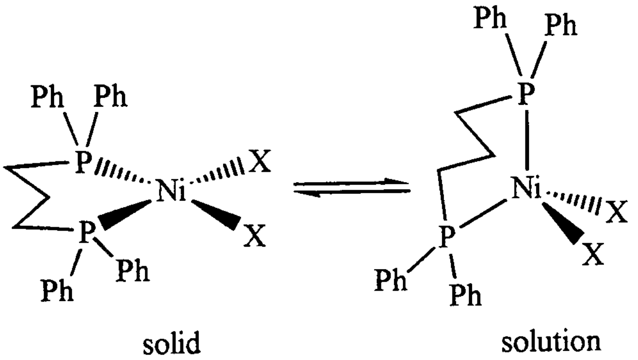
$$2[Ni(P\text{-}P)X_2] \rightleftharpoons [Ni(P\text{-}P)_2]X_2 + NiX_2$$

Equation 2

1.3.3 Four Co-ordinate Nickel (II) Diphosphine Complexes

Ni(II) diphosphine and monophosphine complexes generally obey a 16-electron rule. When the series of phosphine complexes [Ni(dppm)X_2] **(11)**,[10] [Ni(dppe)X_2] **(12)**,[10] [Ni(dppp)X_2] **(13)**,[10] and [Ni(dppb)X_2] **(14)**[15] are compared, in the solid state, differences in their stereochemistry are observed. Steric interactions between the co-ordinated ligands in four co-ordinate Ni (II) complexes can result in distortions from the square-planar towards a tetrahedral configuration. The lowest energy complex is formed in preference. The ligands dppm, dppe and dppp all form square-planar diamagnetic, low-spin, complexes of the type [Ni(P-P)X_2], where X = Cl, Br, I. Complexes of the type [Ni(dppb)X_2] **(14)** are all tetrahedral except when X =NCS which is square-planar. Complexes of type **(14)** show similarities to the monophosphine complexes of the type [Ni(PPh_3)$_2$$X_2$] **(15)**[16] which are all tetrahedral and paramagnetic in both the solid and solution states. The variation of structure between complexes; **(11)**, **(12)**, **(13)**, and **(14)** occurs with the increase in the number of carbons in the backbone and is due to the larger steric crowding in a square-planar configuration around the nickel atom making the square-planar configuration less favourable.[10]

In solution, complexes of the type [Ni(dppp)X_2] **(13)** exhibit an equilibrium between the square-planar and tetrahedral forms (Equation 3).[10]



Equation 3

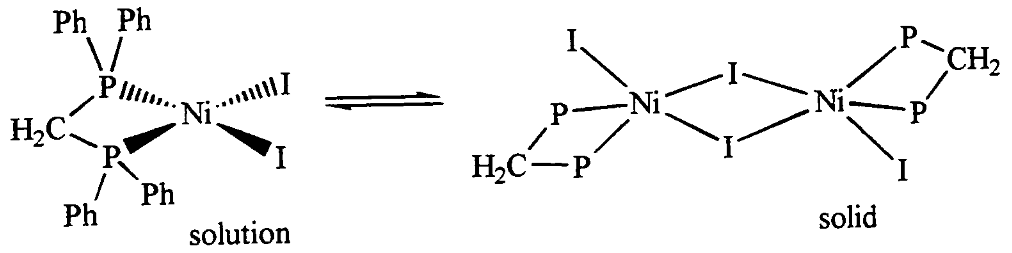
The square-planar - tetrahedral equilibrium is dependent on the van der Waals radius of the halide ion, the amount of tetrahedral isomer decreases in the order of decreasing Van der Waals radius, I>Br>Cl.[17] The increased chain length and flexibility of dppp, compared to dppe, allows the PPh_2 groups to spread out and interact more strongly with the X atoms in the planar form and therefore the tetrahedral configuration becomes more favourable.[17] The equilibrium observed in solution for **(13)** is not observed for $[Ni(dmpp)X_2]$ **(16)** i.e. when methyl groups replace the phenyl group on the dppp.[18] The small steric size of the methyl group, compared to the bulkier phenyl group, favours a square-planar configuration for which the interactions between the methyl and the X group are minimal.[18] However, if the steric bulk of the ligand is increased, for example from phenyl groups to the bulkier cyclohexyl group to give the ligand, dcpp, the increased steric interactions in both the square-planar and tetrahedral forms renders the isomerism to the tetrahedral form less favourable. The complex $[Ni(dcpp)Cl_2]$ **(17)** is consequently square-planar in solution and in the solid state.[19]

In a similar manner to the diphosphine complexes, the nickel (II) monophosphine dihalide complexes $[Ni(PR_3)_2X_2]$ **(15)** exhibit a square-planar - tetrahedral equilibrium in solution.[16] The equilibrium is dependent on both steric and electronic factors. Triaryl monophosphine complexes, for example, where R is a bulky phenyl group, are all tetrahedral in both the solid and solution state, whereas, trialkyl monophosphine complexes are square-planar in both the solid and solution state. However, the intermediate complex $[Ni(Bu^nPPh_2)_2X_2]$ **(18)** (where R is a diphenylalkyl monophosphine) is tetrahedral in the solid state, but in solution a square-planar - tetrahedral equilibrium is observed.[16]

The effect of the relationship between the bite-angle of a diphosphine ligand and tetrahedral distortions in predominantly square-planar complexes has been studied for the bisdiphosphine complexes of the type $[Ni(P\text{-}P)_2](BF_4)_2$ **(19)**, where it was found that increasing the bite angle of the diphosphine ligand results in an increasingly large distortion of the complexes from a square-planar to a tetrahedral geometry, the R substituents of the diphosphine are phenyls.[20]

1.3.4 Five Co-ordinate Nickel (II) Diphosphine Complexes

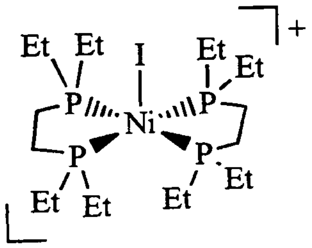
In five co-ordinate Ni(II) diphosphine complexes the 18 electron rule is obeyed. Complexes containing the dppm ligand have a tendency to become five co-ordinate. When the square-planar, four co-ordinate cationic complex, $[Ni(dppm)_2](PF_6)_2$ **(20)** is recrystallised from an acetonitrile/toluene mixture then crystals of the five co-ordinate, square-pyramidal, cationic complex $[Ni(dppm)_2(CH_3CN)](PF_6)_2$ **(21)** are obtained.[20] Dppm is unique in its formation of diamagnetic five co-ordinate dimeric complexes of nickel halides. The dimeric complex **(22)** is stable in the solid state but in solution it reverts to the monomer **(23)** (Equation 4)[21].



(23) **(22)**

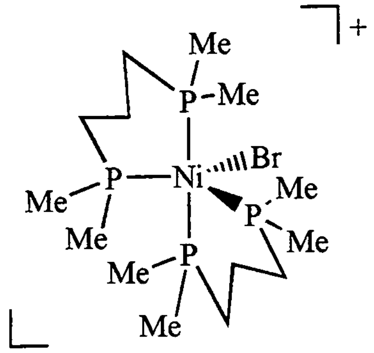
Equation 4

The ligand depe, forms five co-ordinate diamagnetic $[Ni(depe)_2X](BPh_4)$ **(24)** complexes as well as the four co-ordinate $[Ni(depe)X_2]$ **(25)** complexes {X = Cl, Br, I, NCS, CN}. The complex $[Ni(depe)_2I](BPh_4)$ **(26)** was characterised by X-ray crystallography and was assigned a square-pyramidal struture.[22]



(26)

The flexible ligand, dmpp, forms five co-ordinate complexes $[Ni(dmpp)_2X]^+$ (**27**), as well as the four co-ordinate square-planar $[Ni(dmpp)X_2]$ (**28**) {X = Cl, Br, I, NCS}. The five co-ordinate complexes $[Ni(dmpp)_2X]^+$ possess trigonal bypyramidal structures for $[Ni(dmpp)_2Br]^+$ (**29**) and X = I, whereas when X = Cl or NCS the structures are distorted with approximately C_s microsymmetry.[18]



(**29**)

In contrast to the diphosphine ligand dppe, the unsaturated analogue dppv, forms five co-ordinate $[Ni(dppv)_2X]^+$ (**30**) complexes as well as four co-ordinate $[Ni(dppv)X_2]$ complexes. The $[Ni(dppv)_2X]^+$ (**30**) complexes are assigned a square-pyramidal structure.[23] The nearly coplanar backbone in nickel diphosphine complexes containing the dppv ligand, appears to aid the formation of five co-ordinate complexes. The inability of the dppe ligand to form five co-ordinate complexes may be steric in origin. In dppe, the twist of the $-CH_2-CH_2-$ backbone would result in the blocking of the co-ordination sites above and below the plane of the Ni atom by the *o*-phenyl protons or methylene protons and consequently a five co-ordinate complex is not formed. The planar backbone of dppv leaves these sites open for co-ordination.[23]

The various electronic and steric properties of the phosphine ligands influence the formation of either 16- or 18 electron complexes and therefore result in nickel (II) forming complexes with all possible geometries for four and five co-ordination.

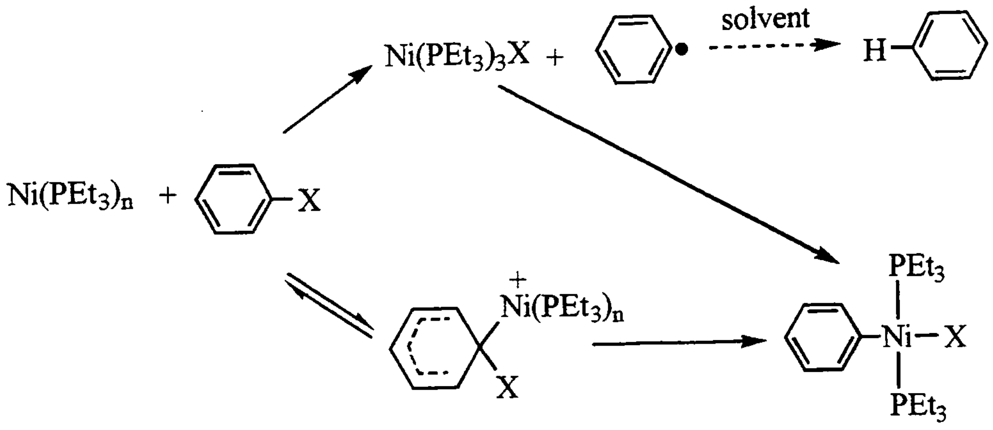
1.4 Organometallic Chemistry

The nature of the ligand influences the organometallic nickel diphosphine chemistry. Aryl, alkyl and hydride ligands form predominantly Ni(II) diphosphine complexes. Carbonyl and alkene ligands stabilise low oxidation states and form predominantly Ni(0) diphosphine complexes.[2,3,4] The transformation between these oxidation states *via* processes such as oxidative addition, reductive elimination, and migratory insertion, are relevant to the synthetic and catalytic organometallic chemistry of nickel.

1.4.1 Oxidative Addition and Reductive Elimination

Oxidative addition to Ni(0) complexes to form Ni(II) complexes, and the reverse reductive elimination are often facile. Isolation of an organonickel complex requires a careful choice of phosphine ligand to impart a high reactivity to the nickel(0) complex and a good stability to the organonickel product.[24] The nature of the organohalide molecule also determines the reactivity of the oxidative addition and the stability of the organonickel complex to reductive elimination.[24] The oxidative addition of alkyl halides to Ni(0) complexes proceeds via an S_N2 mechanism, the order of reactivity being $Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PR_3)_2(alkene) > Ni(PAr_3)_2(alkene) > Ni(cod)_2$; the more nucleophilic the metal, the greater its reactivity.[25] In a similar fashion to S_N2 reactions studied in organic chemistry, steric hindrance at the carbon slows the reaction, the order of reactivity of the RX group being MeI > EtI > *i*-PrI.[25] The order of reactivity $ROSO_2(C_6H_4Me) > RI > RBr > RCl$ illustrates the dependence of the reactivity on the nature of the leaving group.[25]

The oxidative addition of aryl halides can proceed *via* a radical mechanism or a competing aromatic nucleophilic substitution mechanism, which is activated by electron withdrawing substituents (Equation 5).[24]



Equation 5 Oxidative addition of an aryl halide to Ni(0)

The Ni(I) complex [Ni(PEt$_3$)$_3$X], formed in the first step *via* a radical mechanism is stable enough to be observed. Both mechanisms can provide the aryl nickel product but collapse of the radical pair is unfavourable for sterically hindered aryl adducts. Thus, 2-bromo-*m*-xylene and hexachlorobenzene did not produce aryl nickel products and the Ar radical abstracts a hydrogen atom from the solvent to give ArH.[24]

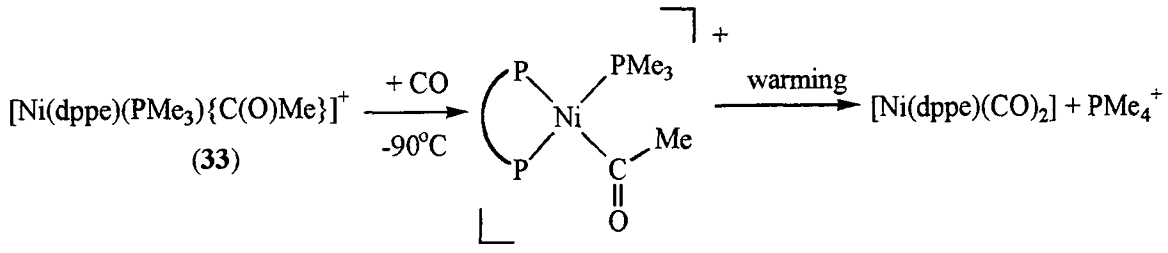
The oxidative addition of RX {R = *o*-substituted aryl, X = Br, I) to the complex [Ni(dcpe)(CH$_2$=CH$_2$)] resulted in the isolation of the complex [Ni(dcpe)RX].[26] Such diphosphine complexes isolated from an oxidative addition reaction are very rare. The enforced *cis* conformation results in less stability than the monophosphine complexes with respect to reductive elimination.[7] The presence of the *o*-substituent on the aryl ligand imparts extra stability to the complex and a similar observation has been found in the monophosphine complexes *trans*-[Ni(PR$_3$)$_2$RX].[27,28,29] However, the monophosphine complexes are additionally stabilised, with respect to reductive elimination, by the *trans*-orientation of their ligands.[7,27]

The complex [Ni(dppe)(2,3-$Cl_2C_6H_3$)Br] was prepared *via* a ligand displacement reaction of dppe in the complex *trans*-[Ni(PR_3)$_2$(2,3-$Cl_2C_6H_3$)Br].[30] The complex *trans*-[Ni(PR_3)$_2$(2,3-$Cl_2C_6H_3$)Br] was prepared by the reaction of the [Ni(PR_3)$_2$$Br_2$] complex with the relevant Grignard reagent.[28] Other complexes of the type *trans*-[Ni(PR_3)$_2$RX] have been prepared *via* a similar Grignard route[27,28] or *via* the *in situ* reduction of the [Ni(PR_3)$_2$$Br_2$] complex and oxidative addition reaction of an aryl halide in the presence of zinc metal.[31,32] However, a similar *in situ* reduction - oxidative addition reaction of an aryl halide in the presence of zinc metal for the complex [Ni(dppe)Cl_2] does not occur.[31]

The oxidative addition of PhBr to the [Ni(dppb)$_2$] gives the complex [Ni(dppb)PhBr], whereas, the similar [Ni(dppp)$_2$] complex is completely unreactive.[33] The complex [Ni(dppe)$_2$] is also unreactive to oxidative addition of aryl halides.[34]

1.4.2 Insertion and β-Elimination

Carbonylation, or the insertion of CO, into a nickel (II) alkyl or aryl species leads to a nickel (II) acyl species. The insertion reaction is a migration of an X type, alkyl or hydride ligand, onto an adjacent carbonyl group, which generates a new X type ligand incorporating the CO group. Consequently the process is known as a migratory insertion.[7] The acyl species is often only an intermediate in an organic synthesis reaction and this is related to the ease of the reduction, by CO *via* decarbonylation/migratory deinsertion, of Ni(II) complexes, giving rise to Ni(0) species.[35] However, stable nickel acyl species [Ni(dmpe)(PMe_3){C(O)Me}] BF_4 **(31)** and [Ni(dmpe)$_2${C(O)Me}]BF_4 **(32)** are obtained from the carbonylation of [Ni(dmpe)(PMe_3)$_2$Me]BF_4 and [Ni(dmpe)$_2$Me]BF_4 respectively.[36] Complexes **(31)** and **(32)** are stabilised by the strongly electron donating chelating phosphine ligand, dmpe.[35] The analogous dppe acyl complex [Ni(dppe)(PMe_3)$_2${C(O)Me}]BF_4 **(33)** was only observed at low temperature. On warming **(33)** decomposed *via* a pathway involving decarbonylation and reductive migration of an alkyl cation from the metal centre to a trialkyl phosphine ligand; the Ni(0) complex [Ni(dppe)$(CO)_2$] and PMe_4^+ were identified (Equation 6).[36]



Equation 6

Other acyl complexes which have been isolated are the square-planar four co-ordinate complexes of the type $[Ni(PMe_3)_2(COCH_3)X]$, (X = Cl, Br, I), decarbonylation of the acyl group is reversible and the complexes are only stable in the presence of CO.[37] The carbonylation of the methyl β-methoxy complex $[Ni(PMe_3)_2(CH_2OMe)Br]$ leads to the stable acyl complex $[Ni(PMe_3)_2\{C(O)CH_2OMe\}Br]$, in contrast to the corresponding carboxyethyl complex $[Ni(PMe_3)_2(CH_2CO_2Et)Br]$, for which the corresponding acyl complex is only stable in the presence of CO.[38] Five co-ordinate cationic acyl complexes $[Ni(np_3)(COR)]BPh_4$ (R = CH_3, C_2H_5, $CH_3C_6H_4$) which contain the bulky tetradentate ligand np_3, where np_3 = tris(2-(diphenylphosphino)ethyl)amine, have also been isolated, the monocarbonyl species $[Ni(np_3)(CO)]BPh_4$ was also claimed to be present at the end of the reaction.[39]

Insertion of ethene into Ni-hydride and Ni-alkyl/aryl species is common in the nickel catalysed dimerisation, and oligomerisation of ethene.[5] The insertion of ethene into a Ni-H or Ni-R species usually generates an intermediate nickel alkyl species, which contains β-hydrogens and is consequently unstable with respect to the reverse reaction of insertion, β-H elimination, which regenerates a Ni-H species and an alkene. The complex $[Ni(dBpe)(C_2H_5)]^+$ which contains a β-agostic ethyl group, which represents an intermediate stage in the insertion/β-elimination process, has been characterised by X-ray crystallography. The complex is related to catalytic intermediates for alkene polymerisation.[40] The complex was prepared by the protonation of

[Ni(dBpe)(CH_2=CH_2)] with HBF_4 at 273K. The complexes [Ni(P-P)(C_2H_5)]$^+$ {P-P = dBpp, Boxylyl} were also prepared *via* a simiar route.[40]

The insertion of ethene can be confirmed by the recovery of 3,5-dichlorostyrene from the reaction of ethene with the complex [Ni(dppe)($Cl_2C_6H_3$)(γ-pic)]ClO_4, the insertion of ethene into the Ni-aryl bond, and subsequent β-H elimination generates the aryl vinyl organic product.[30]

The vinyl complex *trans*-[Ni(PPh_3)$_2${*cis*-C(CH_3)=C(CH_3)(Ph)Br] has been isolated from the insertion reaction of 2-butyne into the nickel-aryl bond in the complex [Ni(PPh_3)$_2$PhBr].[41]

1.4.3 Nickel(0) Phosphine Complexes

Strong field ligands such as CO, alkenes or phosphines are good electron acceptors as well as donors and Ni(0) d^{10} complexes are stabilised by backbonding to these π-acid ligands.[6]

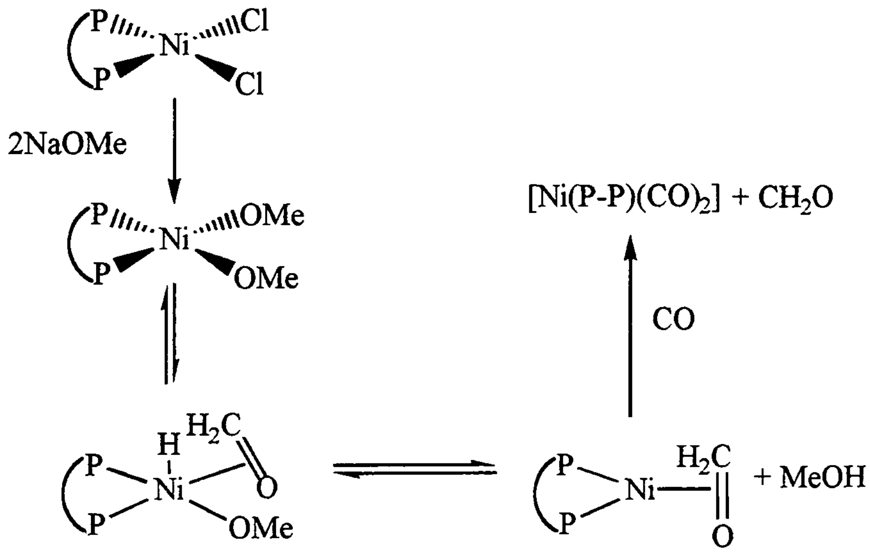
1.4.3.1 Nickel(0) Carbonyl Complexes

In 1890 Mond discovered the first binary metal carbonyl, [Ni(CO)$_4$] **(1)** by the reaction of nickel metal with CO at r.t. amd 1atm.[1] The subsequent decomposition, on heating, generates pure nickel metal and carbon monoxide. This process, still used today, is known as the Mond process for purification of nickel metal. The 18 electron rule is satisfied when four carbonyl ligands are co-ordinated to Ni(0) and therefore the complex [Ni(CO)$_4$] is tetrahedral.[1]

The carbonyl ligands, in [Ni(CO)$_4$] **(1)**, can be substituted successively with a two electron ligand, L, for example, a phosphine ligand, to give nickel carbonyl phosphine complexes of the type [Ni(CO)$_3$(PR_3)] **(2)**, [Ni(CO)$_2$(PR_3)$_2$] **(5)** and [Ni(CO)(PR_3)$_3$] **(6)**, or in the case of a bidentate diphosphine (P-P), chelating complexes of the type

$[Ni(CO)_2(P\text{-}P)]$ (7).[2,3] Carbonyl substitution in 18 valence electron complexes usually proceeds *via* a dissociative mechanism which generates a coordinatively unsaturated intermediate.[6] Complete substitution of all the carbonyl ligands is rare, successive replacement of the carbonyl ligands by more electron donating ligands i.e phosphines, stabilises the remaining CO ligands due to increased backbonding. Fully substituted $[NiL_4]$ compounds can be prepared, however, from $[Ni(CO)_4]$ (**1**) when the ligands, L, are even better π-acidic ligands, for example, L = PF_3 and PCl_3.[2]

An alternative synthesis of Ni(0) dicarbonyl phosphine complexes, $[Ni(CO)_2(PR_3)_2]$ (**5**) is the *in situ* reduction of Ni(II) phosphine halide complexes $[Ni(PR_3)_2X_2]$ (**8**) with zinc dust in the presence of CO.[42] Equally, the Ni(0) dicarbonyl diphosphine complexes $[Ni(CO)_2(P\text{-}P)]$ (7), containing a chelating diphosphine, can be obtained by an alkoxide-promoted reduction of a Ni(II) diphosphine dihalide complex, in the presence of CO, with sodium methoxide in methanol (Equation 7).[43]



Equation 7

However, this is not a general method, and for example, $[Ni(dppb)Cl_2]$ (**9**) and $[Ni(PPh_3)_2Cl_2]$ (**10**) decompose rapidly when treated with sodium methoxide in toluene-methanol solution, yielding $Ni(OMe)_2$, NaCl and free phosphine.[43]

1.4.3.2 Nickel (0) Alkene Complexes

Nickel alkene complexes are utilised as starting materials to provide a Ni(0) complex for oxidative addition reactions.[2,3] A common starting material is the biscyclooctadiene complex $[Ni(cod)_2]$. The nickel tetra phosphine complexes, $[Ni(PR_3)_4]$, which cannot be prepared *via* substitution of $[Ni(CO)_4]$, may be prepared by the reaction of the desired phosphine with a nickel alkene complex e.g. $[Ni(cod)_2]$.[2,3] The complex $[Ni(Boxylyl)(CH_2{=}CH_2)]$ was synthesised by the treatment of $[Ni(cod)_2]$ with Boxylyl under ethene.[40]

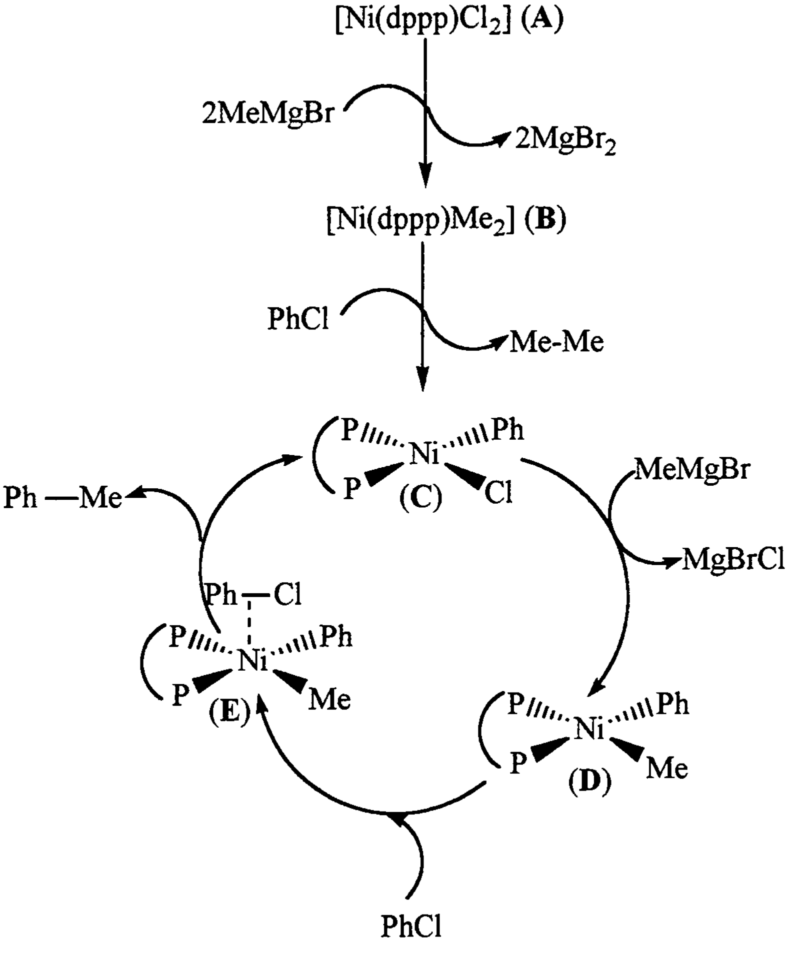
A series of nickel diphosphine alkene complexes [Ni(P-P)(alkene)] have been prepared generally by the reduction of a $[Ni(P\text{-}P)Cl_2]$ complex with a metal in the presence of the desired alkene. For example, the alkene complexes $[Ni(P\text{-}P)(CH_2{=}CH_2)]$ {P-P = dBpe, dBpp) were prepared by the reaction of $[Ni(P\text{-}P)Cl_2]$ with zinc powder under ethene,[40] and the complex $[Ni(dcpe)(CH_2{=}CH_2)]$, by the reaction of $[Ni(dcpe)Cl_2]$ with a lithium dispersion under ethene.[26] The $[Ni(P\text{-}P)(C_{10}H_8)]$ complexes of the diphosphine ligands dippe, and dippp have been prepared by reduction of $[Ni(P\text{-}P)Cl_2]$ with magnesium in the presence of naphthalene.[44]

A series of 14 electron complexes [Ni(P-P)] {P-P = dcpe, dcpp, dcpb were prepared by the reaction of $[Ni(P\text{-}P)Cl_2]$ with sodium sand in toluene.[45] These complexes were reacted with CO_2, to give the Ni(0)-CO_2 complexes.[46]

1.4.4 Nickel Diphosphine Complexes in Organic Synthesis

Complexes of the type $[Ni(P\text{-}P)X_2]$ {X = Cl, Br} show a wide range of catalytic properties for the cross coupling of alkyl, aryl and alkenyl Grignard reagents with aryl and alkenyl halides.[47] The most effective catalysts are $[Ni(dppp)Cl_2]$ for alkyl and simple aryl Grignard reagents, $[Ni(dmpe)Cl_2]$ for alkenyl and allylic Grignard reagents and

[Ni(PPh$_3$)$_2$Cl$_2$] for sterically hindered aryl Grignard reagents and halides. A specific example is shown in Equation 8. A nickel diphosphine dichloride complex of the type [Ni(P-P)Cl$_2$] (**A**), reacts with a Grignard reagent, RMgX to form a diorganonickel complex, of the type [Ni(P-P)R$_2$] (**B**) which is subsequently converted to the organo-halide nickel complex of the type [Ni(P-P)RX] (**C**) by an organic halide. The reaction with the Grignard reagent then forms a new diorganonickel complex of the type, [Ni(P-P)RR'] (**D**) from which the cross-coupling product is released by the attack of the organic halide. The pentaco-ordinated species (**E**) is possibly an intermediate formed prior to the regeneration of (**C**) which continues the catalytic cycle (Equation 8).



Equation 8

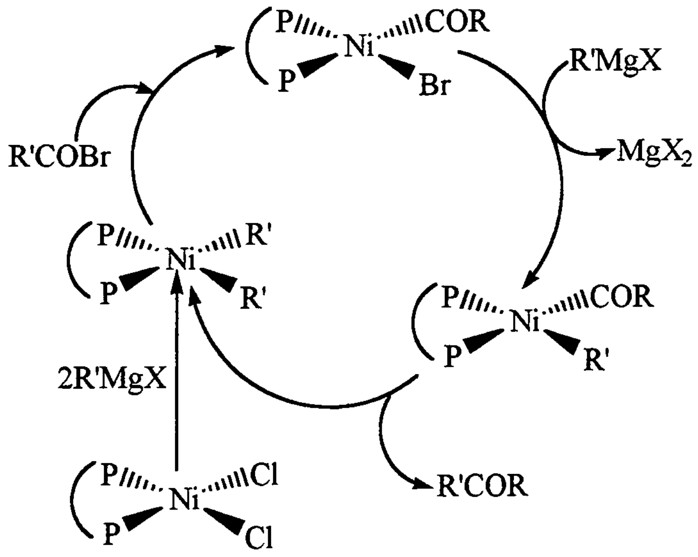
The reaction was investigated for both mono- and diphosphine ligands. Chelating bidentate diphosphines exhibited much higher catalytic activity than monodentate ligands.[47] When P-P is dppm, it was found that the nickel complex [Ni(dppm)Cl$_2$] was not an active catalyst for the cross coupling reaction.[47] However, the nickel (II) complex containing the ligand 2,2-bis(diphenylphosphino)propane, [Ni(2,2-dppp)Cl$_2$], which also contains a four-membered chelate ring, was recently found to be active for cross-coupling of a Grignard reagent with an alkyl or aryl halide.[48]

Interestingly, the complex [Ni(dppe)Cl$_2$] (**12**) catalyses the cross-coupling reaction of chlorodiphenyl phosphine with aryl halides or sulphonate esters to produce a *tertiary* phosphine (Equation 9).[49]

$$\mathrm{ArX} \xrightarrow[\text{solvent, 110°C}]{\mathrm{Ph_2PCl,\ [Ni(dppe)Cl_2],\ Zn}} \mathrm{Ar\text{-}PPh_2}$$

Equation 9

Acyl bromides are converted directly into a ketone at 0°C using a Grignard reagent in the presence of a catalytic amount of [Ni(dppe)Cl_2] (Equation 10).[50]



Equation 10

Aldehydes are obtained from acyl halides when a stoichiometric amount of tri-n-butyltin hydride and a catalytic amount of [Ni(dppe)Cl_2] are reacted at room temperature.[51]

The general lack of reports of isolated complexes of the type [Ni(P-P)RX], [Ni(P-P)RCOX], and [Ni(P-P)R_2] in the literature, may be attributed to the reactivity of these species, often intermediates in the synthesis of organic products. The enforced *cis*-orientation of the ligands in these diphosphine complexes makes them susceptible to decompositon either *via* β-hydrogen or reductive elimination depending on the nature of R and X type ligands and the reaction conditions. For example the reaction of PhCOCl with [Ni(dppe)$(Me)_2$] gives the nickel (II)-acyl complex [Ni(dppe)(PhCO)Cl] as an intermediate which reacts with a further [Ni(dppe)$(Me)_2$] to give a coupled organic product, MeCOMe, [Ni(dppe)PhCl] and "[$Ni^{(0)}$(dppe)]".[52] Whereas, the reaction of the complex [Ni(dppb)(Ph)Br] (**2**) with CO, presumably proceeding through a similar nickel

(II)-acyl complex [Ni(dppb)(PhCO)Br], gives the reductive elimination product benzoyl bromide and the dicarbonyl complex $[Ni(dppb)(CO)_2]$.[33]

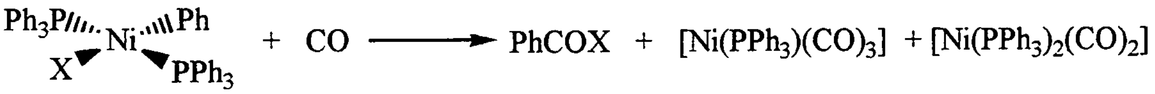
The nature of the diphosphine ligand also has an effect on the ability to isolate the organometallic nickel complex. For example a study of ligand effect on the ease of reductive elimination of C_2H_6 from complexes of the type $[Ni(P\text{-}P)Me_2]$ {P-P = dppm, dppe, dppp, dppb} has been carried out. The effect was deduced by the ligand exchange reaction of the diphosphine with the comparatively stable chelate nitrogen ligand complex $[Ni(bipy)Me_2]$ and depended on n, the number of carbon atoms in the backbone. The order of ease of reductive elimination was found to be $n = 2 < 3 << 1,4$.[53] Addition of a phosphorus ligand such as PEt_3, $P(aryl)_3$, dmpe, $P(OEt)_3$, PCy_3 to the complexes $[Ni(dmpe)(C_6H_4X)Me]$ {X = *p*-OMe, *p*-Me, *p*-F, *o*-OMe, H} which are only stable below 0°C, results in facile reductive elimination of MeC_6H_4X.[54]

1.4.5 $[Ni(P\text{-}P)R_2]$ Complexes

The complexes $[Ni(P\text{-}P)(CH_2SiMe_2Ph)_2]$ {P-P = dmpe, depe, dippe}have been prepared by a ligand substitution reaction from a chelate nitrogen ligand complex $[Ni(N\text{-}N)(CH_2SiMe_2Ph)_2]$. These complexes are stable due to the absence of β-hydrogens on the organic ligand.[55]

1.4.6 Carbonylation of Nickel Diphosphine Complexes

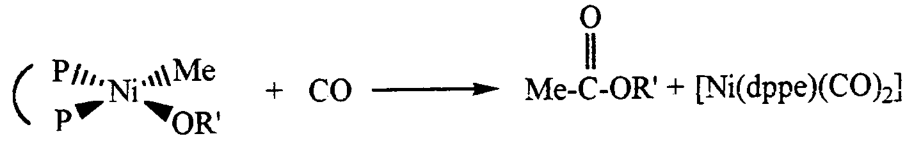
The mechanism of the carbonylation of halo(bisphosphine) organonickel(II) complexes has been investigated. The complexes of the type $[Ni(PPh_3)PhX]$ absorbed CO in pseudo first order reactions producing acyl halides and a mixture of tricarbonylmonophosphine and dicarbonylbisphosphinenickel complexes (Equation 11).[56]



Equation 11

The intermediate acyl complexes were not isolated, in contrast to those isolated from similar reactions with palladium and platinum complexes.[56]

The insertion of CO into nickel alkoxide (Ni-OR) compared with nickel alkyl (Ni-R) bonds has been investigated by Yamamoto and Komiya.[57] The complexes investigated were of the type $[Ni(L_2)(Me)(OC_6H_4\text{-}p\text{-}X)]$, {L = PEt_3, $PMePh_2$ and $PEtPh_2$, bipy; X =H or CN}. It was found that CO preferentially inserts into the nickel alkyl bond to give the acetyl(aryloxy) complex which further reductively eliminates, promoted by the CO or other π acceptor ligands, to give the aryl ester and the zerovalent nickel dicarbonyl, $[Ni(CO)_2(L_2)]$.[57] The methyl alkoxo nickel complex of the type [Ni(dppe)Me(OR')] {R' = $CH(CF_3)_2$, CH_2CF_3, $CH(CF_3)C_6H_5$} were prepared by the reaction of $[Ni(dppe)Me_2]$ with an acidic alcohol containing a fluorine substituent. Nickel alkoxide complexes tend to decompose *via* β-hydride elimination, but the presence of the fluoro- substituents results in the complex stability to β-hydride elimination.[58] The [Ni(dppe)Me(OR)] reacts with CO to give an acetate and the $[Ni(dppe)(CO)_2]$ complex (Equation 12).[58]

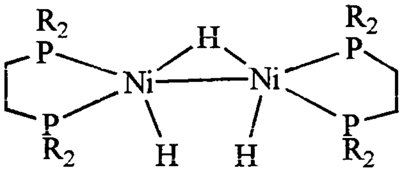


Equation 12

1.4.7 Nickel Hydrides containing Diphosphine Ligands

The novel nickel trihydride complex $[\{Ni(dippe)\}_2H_3]BPh_4$, prepared by the reaction of $[Ni(dippe)Br_2]$ with $NaBH_4$ followed by addition of $NaBPh_4$, has been characterised by X-ray crystallography. The dimeric trihydride complex contains one bridging hydride ligand and two terminal hydride ligands (one attached to each Ni atom) (v).[59]

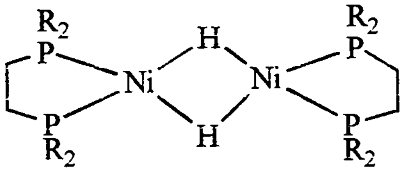
(v)



The similar $[\{Ni(dcpe)\}_2H_3]BPh_4$ complex was characterised by comparison of the ^{31}P spectra with the spectra of $[\{Ni(dippe)\}_2H_3]BPh_4$.[59] These are the first examples of nickel hydrides that contain a diphosphine ligand and a terminal hydride, although monophosphine complexes *trans*-$[Ni(PR_3)_2HX]$ {X = halide, O_2CMe, OPh, Me, Ph; R = alkyl, aryl} containing a terminal hydride ligand, are known.[60,61,62] The limited number of the former is attributed to the *cis*-stereochemistry of $[Ni(P\text{-}P)HX]^+$ which leads to reductive elimination of HX. Complexes containing the tripodal phosphine ligands $[Ni(np_3)H]^+$ and $[Ni(pp_3)H]^+$ are known.[63]

Complexes of the type $[\{Ni(R_2P(CH_2)_nPR_2)\}_2(\mu\text{-}H)_2]$ {R = Cy, Ph; n = 2-4} which contain two bridging hydride ligands have been synthesised **(vi)**.[64,65]

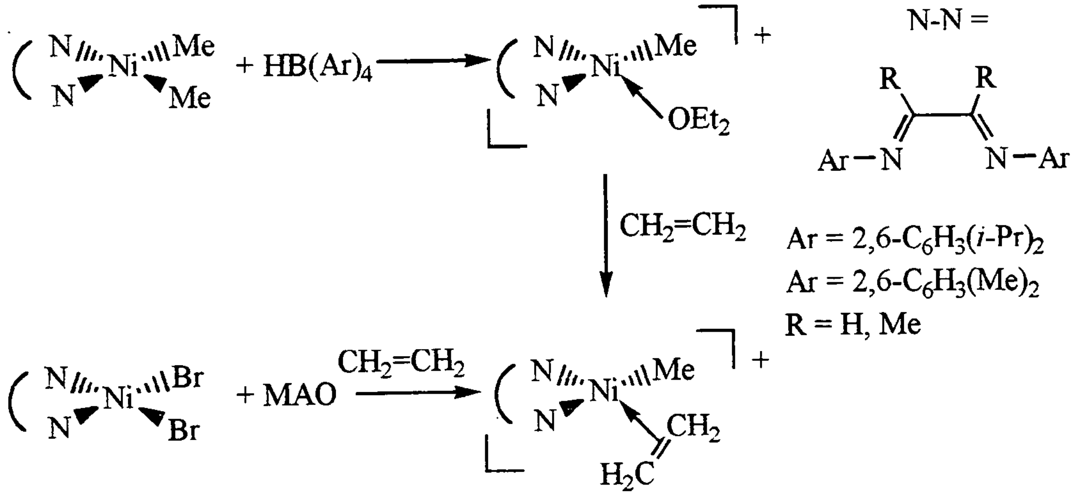
(vi)



1.4.8 Nickel Compounds used to Catalyse Reactions of Ethene and CO

Nickel(II) complexes are effective catalysts for the oligomerisation of olefins. The selectivity and controlling effects of the ligands in these homogeneous systems leads to products ranging from dimers to high-molecular weight polymers. Complexes containing monodentate phosphine ligands are known to dimerise ethene, propene, and norbornene.

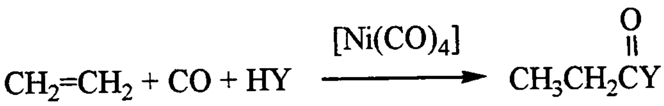
For example the cationic complex $[Ni(PR_3)_2(2,4,6\text{-}Me_3C_6H_2)(CH_3CN)]BF_4$ which contains monophosphine ligands dimerises ethene, the activity being found to increase with increasing basicity and size of the monophosphine ligand.[66] However, complexes containing diphosphine ligands, for example the complex which contains the same aryl group as above, but a diphosphine ligand, $[Ni(dppe)(2,4,6\text{-}Me_3C_6H_2)(CH_3CN)]BF_4$ are completely inactive.[30] However, nickel complexes containing bidentate ligands, which are not diphosphine ligands, catalyse the oligomerisation and polymerisation of ethene. For example Cavell and Masters developed a single component catalyst for the oligomerisation of ethene of the type [Ni(N-O)Ar(P)].[32,67] The cationic chelate nitrogen complexes $[Ni(N\text{-}N)Me(OEt)]^+$ {N-N = ArN=C(R)-C(R)=NAr; Ar = $2,6\text{-}C_6H_3(i\text{Pr})_2$, $2,6\text{-}C_6H_3(Me)_2$; R = Me, H} are effective catalysts for the polymerisation of ethene and α-olefins. The complexes can be prepared by the reaction of the $[Ni(N\text{-}N)Me_2]$ with $HB(Ar)_4$, or generated *in situ* by the reaction of $[Ni(N\text{-}N)Br_2]$ with methylalumoxane in the presence of ethene (Equation 13). The effectiveness of the catalysis was attributed to the large steric bulk of the α-arylated diimine ligands.[68,69]



Equation 13

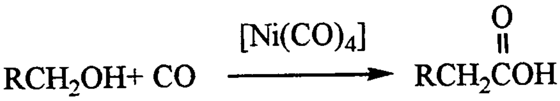
In industry, nickel catalysts are also employed for the dimerisation and oligomerisation of monoolefins for example the Shell Higher Olefin Process (SHOP) which uses a nickel catalyst of the type $[Ni(P\text{-}O)(PPh_3)(Ph)]$ to convert ethene into α-olefins.[70]

Reppe developed, over 60 years ago, nickel catalysts used in a series of homogeneous catalytic carbonylations of alkenes, alcohols and alkynes (Eq. 14-16).[5]



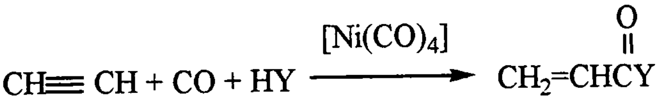
$$CH_2{=}CH_2 + CO + HY \xrightarrow{[Ni(CO)_4]} CH_3CH_2\overset{\overset{O}{\|}}{C}Y$$

Equation 14



$$RCH_2OH + CO \xrightarrow{[Ni(CO)_4]} RCH_2\overset{\overset{O}{\|}}{C}OH$$

Equation 15



$$CH{\equiv}CH + CO + HY \xrightarrow{[Ni(CO)_4]} CH_2{=}CH\overset{\overset{O}{\|}}{C}Y$$

Equation 16

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Chapter 2

The Synthesis and Characterisation of $[Ni(P\text{-}P)Cl_2]$

2.1 Introduction

A series of square-planar complexes of the type $[Ni(P\text{-}P)Cl_2]$ (**1**) containing the bidentate diphosphine ligands, P-P have been synthesised and characterised by X-ray crystallography and $^{31}P\{^1H\}$ NMR spectroscopy {P-P = 1,2-bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis(di-*tert*-butylphosphino)ethane (dBpe), and 1,8-bis(dicyclohexylphosphino)naphthalene (dcpn) (Equation 1).

$$NiCl_2 + P\text{-}P \longrightarrow [Ni(P\text{-}P)Cl_2]$$

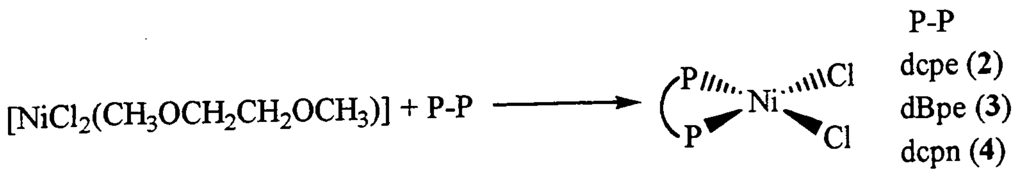
Equation 1

Nickel diphosphine dihalide complexes of the type $[Ni(P\text{-}P)Cl_2]$ (**1**) are of interest due to the their potential use *via* metathetical processes to convert them into precursors of catalytically active species.

The general ease of synthesis, the stability and ready crystallisation of the complexes (**1**) has allowed the complexes to be thoroughly studied, and their data allow structural comparisons to be made, and steric and electronic influences of diphosphine ligands about the metal in nickel (II) complexes to be assessed. Many complexes of the type $[Ni(P\text{-}P)Cl_2]$ (**1**) are reported in the literature but unfortunately most are only characterised by elemental analysis and electronic spectroscopy which makes the basis set for direct structural comparisons small.[1-16]

2.2 Discussion

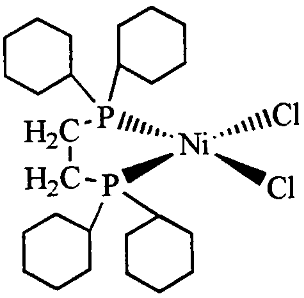
A series of complexes of type [Ni(P-P)Cl_2] (**1**) were prepared by the reaction of a slight excess of the diphosphine ligand with either $NiCl_2 \cdot 6H_2O$ or the monoglyme adduct, [$NiCl_2(CH_3OCH_2CH_2OCH_3)$].



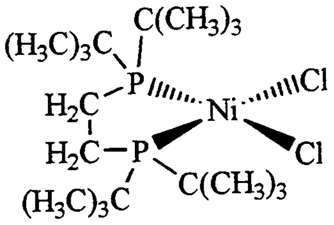
Scheme 1

Complexes (**2**) and (**3**) contain five membered chelate rings, whereas complex (**4**) contains a six membered chelate ring (see below).

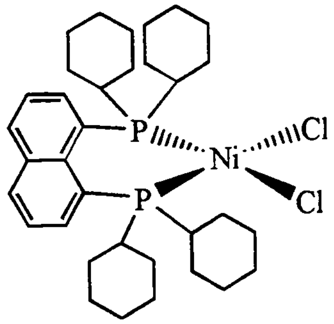
[Ni(dcpe)Cl_2] (**2**)



[Ni(dBpe)Cl_2] (**3**)



[Ni(dcpn)Cl_2] (**4**)



Addition of the diphosphine ligands dcpe and dBpe to a solution of $NiCl_2$ resulted in an immediate reaction and an instant colour change was observed. The resulting complexes, [Ni(dcpe)Cl_2] (**2**), [Ni(dBpe)Cl_2] (**3**) were orange and burgandy-red in colour, respectively. An immediate reaction was also observed in the preparation of the orange complexes [Ni(dppe)Cl_2] and [Ni(dppp)Cl_2] previously reported in the literature.[1] However, the reaction of the diphosphine ligand, dcpn, with $NiCl_2$ was very slow and was only completed after four days, resulting in a purple coloured complex [Ni(dcpn)Cl_2] (**4**).

Steric and Electronic Effects of Diphosphine Ligands in Complexes of the type [Ni(P-P)Cl$_2$] (1)

The influence of steric and electronic effects of the diphosphine ligands about the metal, in the nickel (II) complexes of the type [Ni(P-P)Cl$_2$] (**1**) was investigated by comparing solid state bond length and bond angle data obtained from X-ray crystallographic investigations, and ^{31}P{^{1}H} NMR spectroscopy solution data. The observed chemical shifts depend on the environment about the phosphorus atoms.

Solid State X-Ray Structural Comparisons

The complexes of the type [Ni(P-P)Cl$_2$] (**1**) characterised in this study, namely [Ni(dcpe)Cl$_2$] (**2**) (*Figure 1*), [Ni(dBpe)Cl$_2$] (**3**) (*Figure 2*), and [Ni(dcpn)Cl$_2$] (**4**) (*Figure 3*), were all square-planar in the solid state. Tables 1 and 2 contain selected bond lengths and angles for complex (**2**).

Table 1 Selected Bond Lengths [Å] for [Ni(dcpe)Cl$_2$] (**2**)

Bond Length [Å]		Bond Length [Å]	
Ni-P(2)	2.1598(11)	P(1)-C(21)	1.860(3)
Ni-P(1)	2.1637(10)	P(2)-C(2)	1.845(3)
Ni-Cl(2)	2.2185(11)	P(2)-C(31)	1.849(3)
Ni-Cl(1)	2.2271(10)	P(2)-C(41)	1.858(3)
P(1)-C(11)	1.843(3)	C(1)-C(2)	1.534(4)
P(1)-C(1)	1.848(3)		

Table 2 Selected Bond Angles [°] for [Ni(dcpe)Cl$_2$] (**2**)

Bond Angle [°]		Bond Angle [°]	
P(2)-Ni-P(1)	88.27(4)	C(1)-P(1)-Ni	109.84(11)
P(2)-Ni-Cl(2)	173.62(4)	C(21)-P(1)-Ni	112.70(10)
P(1)-Ni-Cl(2)	88.56(4)	C(2)-P(2)-C(31)	108.5(2)
P(2)-Ni-Cl(1)	87.99(4)	C(2)-P(2)-C(41)	101.6(2)
P(1)-Ni-Cl(1)	175.98(5)	C(31)-P(2)-C(41)	105.4(2)
Cl(2)-Ni-Cl(1)	95.31(4)	C(2)-P(2)-Ni	110.32(11)
C(11)-P(1)-C(1)	103.9(2)	C(31)-P(2)-Ni	108.05(11)
C(11)-P(1)-C(21)	104.74(14)	C(41)-P(2)-Ni	122.30(11)
C(1)-P(1)-C(21)	106.3(2)	C(2)-C(1)-P(1)	110.3(2)
C(11)-P(1)-Ni	118.39(11)	C(1)-C(2)-P(2)	110.4(2)

Complex (**3**) was crystallised from chloroform-hexane and the crystals obtained were solvated with two chloroform molecules. Tables 3 and 4 contain selected bond lengths and angles for the complex (**3**).

Table 3 Selected Bond Lengths [Å] for [Ni(dBpe)Cl$_2$].2CHCl$_3$ (**3**)

Bond Length [Å]		Bond Length [Å]	
Ni-P(1)	2.2113(10)	P(1)-C(7)	1.895(4)
Ni-Cl(1)	2.2129(10)	P(1)-C(3)	1.904(4)
Ni-P(2)	2.2129(11)	P(2)-C(2)	1.850(4)
Ni-Cl(2)	2.2285(11)	P(2)-C(15)	1.896(4)
Cl(1)-H(20)	2.574(5)	P(2)-C(11)	1.909(4)
Cl(2)-H(19)	2.74(5)	C(1)-C(2)	1.530(5)
P(1)-C(1)	1.844(4)		

Table 4 Selected Bond Angles [°] for [Ni(dBpe)Cl$_2$].2CHCl$_3$ (**3**)

Bond Angle [°]		Bond Angle [°]	
P(1)-Ni-Cl(1)	172.07(5)	C(1)-P(1)-Ni	107.21(12)
P(1)-Ni-P(2)	90.32(4)	C(7)-P(1)-Ni	110.48(12)
Cl(1)-Ni-P(2)	89.46(4)	C(3)-P(1)-Ni	119.27(13)
P(1)-Ni-Cl(2)	91.05(4)	C(2)-P(2)-C(15)	106.2(2)
Cl(1)-Ni-Cl(2)	90.23(4)	C(2)-P(2)-C(11)	102.3(2)
P(2)-Ni-Cl(2)	172.23(5)	C(15)-P(2)-C(11)	110.3(2)
Ni-Cl(1)-H(20)	91.47(12)	C(2)-P(2)-Ni	106.83(13)
Ni-Cl(2)-H(19)	158.4(10)	C(15)-P(2)-Ni	110.67(14)
C(1)-P(1)-C(7)	105.7(2)	C(11)-P(2)-Ni	119.32(13)
C(1)-P(1)-C(3)	103.2(2)	C(2)-C(1)-P(1)	112.7(3)
C(7)-P(1)-C(3)	109.9(2)		

Figure 1. **The Crystal Structure of [Ni(dcpe)Cl$_2$] (2)**

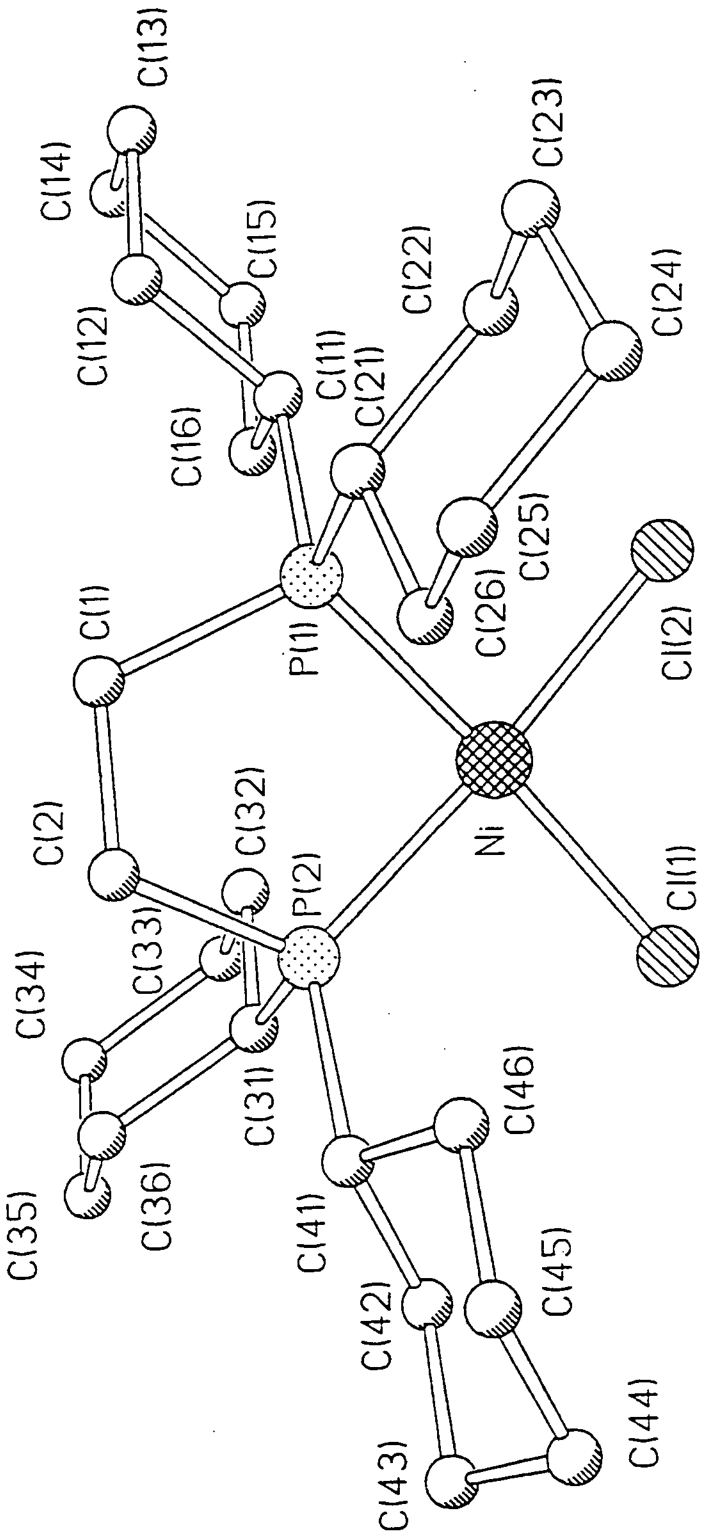
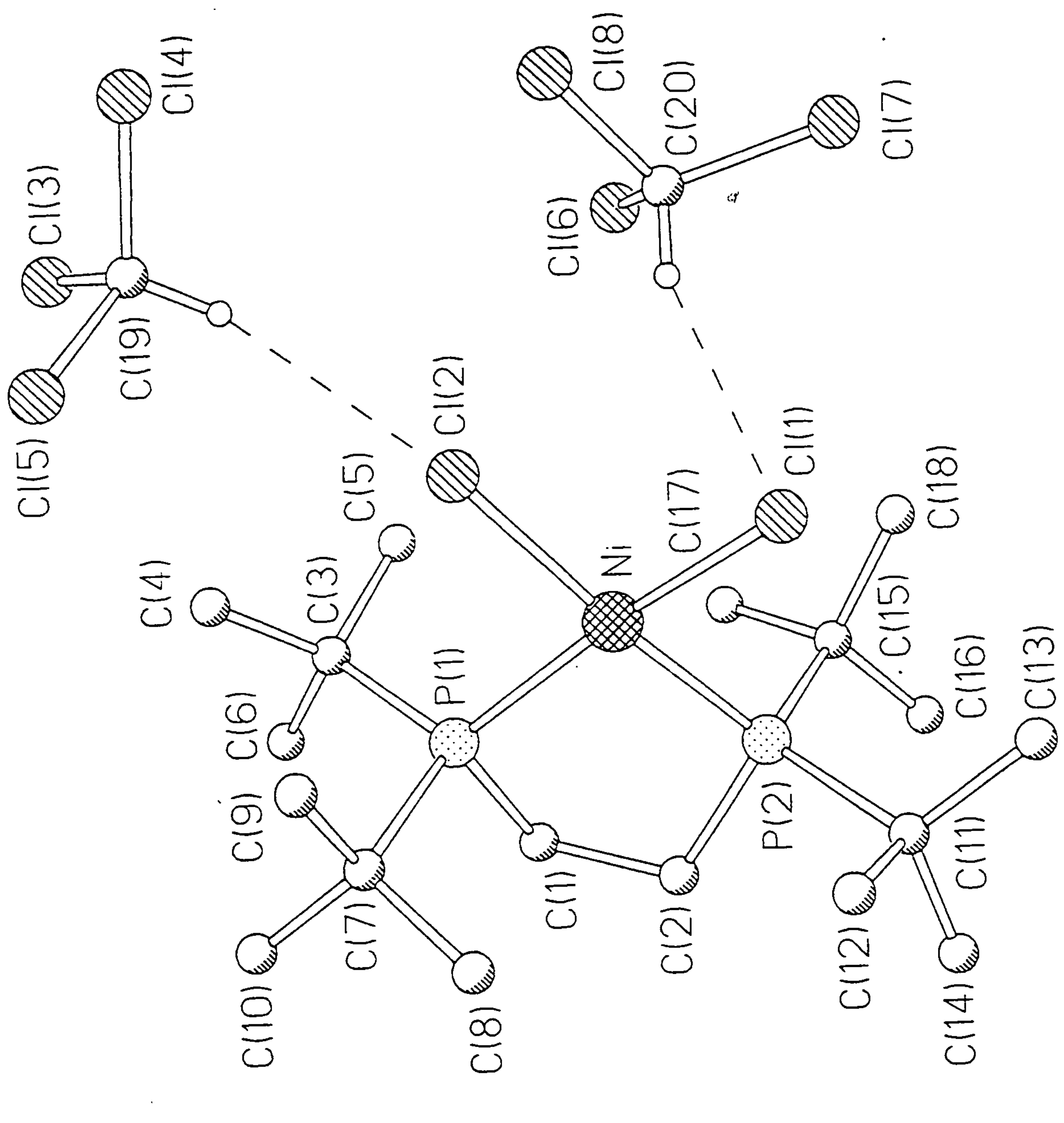


Figure 2. **The Crystal Structure of [Ni(dBpe)Cl$_2$] (3)**



In the distorted square-planar structure of [Ni(dcpn)Cl_2] (**4**), the four cyclohexyl rings were in chair conformations and the naphthalene ring was planar. The complex was purple in colour, in contrast to the usual red/orange colour of Ni(II) square-planar complexes. The complex [Ni(dppn)Cl_2] which is the Ph analogue of complex (**4**) was orange in colour. Selected bond lengths and angles are given in Tables 5 and 6.

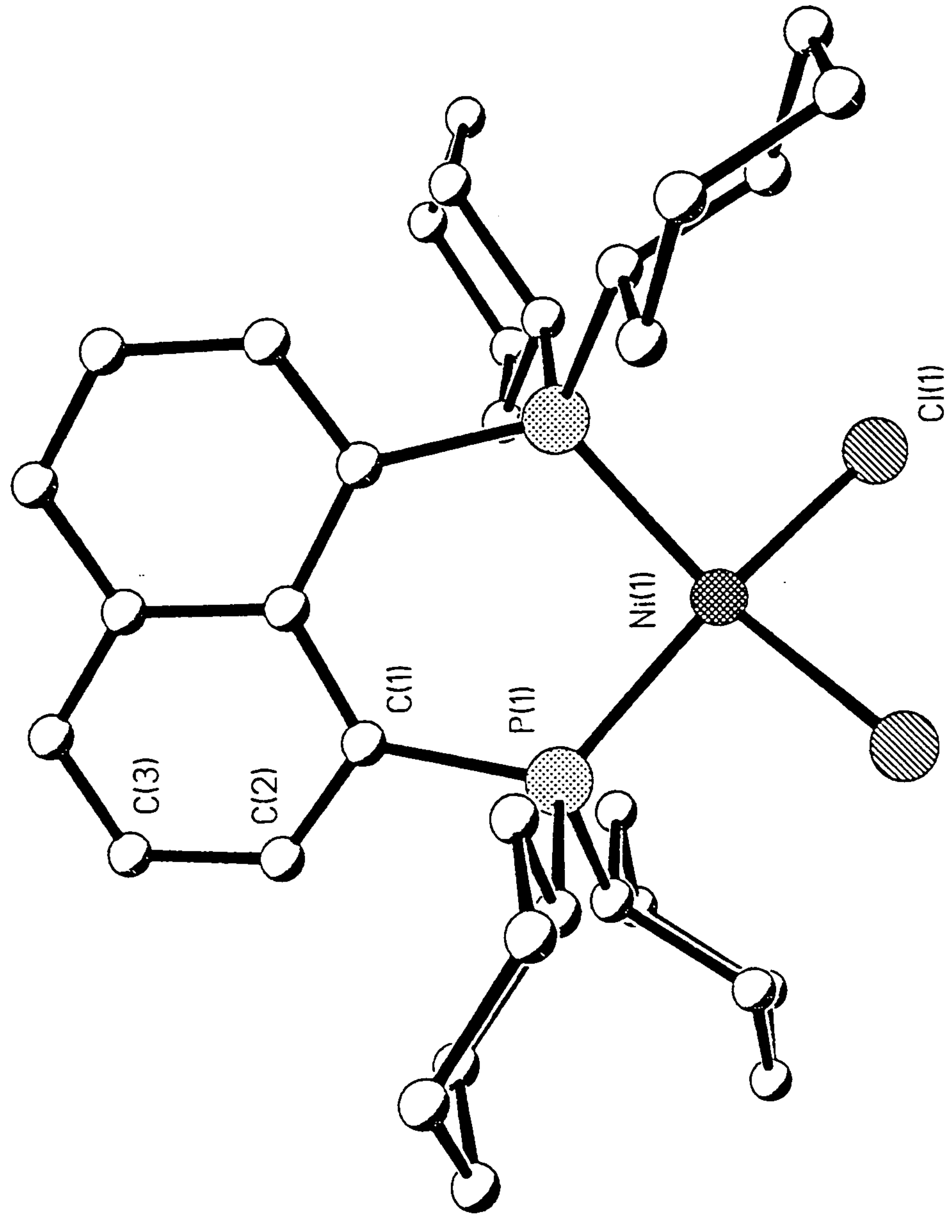
Table 5 Selected Bond Lengths [Å] for [Ni(dcpn)Cl_2] (**4**)

Bond Length [Å]		Bond Length [Å]	
Ni(1)-P(1)#1	2.1455(8)	C(3)-C(4)	1.359(5)
Ni(1)-Cl(1)	2.2017(8)	C(4)-C(4A)	1.412(4)
P(1)-C(1)	1.835(3)	C(4A)-C(4)#1	1.412(4)
C(1)-C(2)	1.388(4)	C(4A)-C(8A)	1.437(5)
C(1)-C(8A)	1.446(4)	C(8A)-C(1)#1	1.446(4)
C(2)-C(3)	1.402(4)		

Table 6 Selected Bond Angles [°] for [Ni(dcpn)Cl_2] (**4**)

Bond Angle [°]		Bond Angle [°]	
P(1)#1-Ni(1)-P(1)	96.17(5)	C(1)-C(2)-C(3)	123.0(3)
P(1)#1-Ni(1)-Cl(1)	91.15(3)	C(4)-C(3)-C(2)	119.0(3)
P(1)-Ni(1)-Cl(1)	154.10(3)	C(3)-C(4)-C(4A)	121.2(3)
Cl(1)-Ni(1)-Cl(1)#1	93.01(5)	C(4)#1-C(4A)-C(4)	119.2(4)
C(1)-P(1)-Ni(1)	119.55(11)	C(4)#1-C(4A)-C(8A)	120.4(2)
C(2)-C(1)-C(8A)	118.5(3)	C(4A)-C(8A)-C(1)	117.3(2)
C(2)-C(1)-P(1)	116.9(2)	C(1)-C(8A)-C(1)#1	125.5(4)
C(8A)-C(1)-P(1)	123.9(2)		

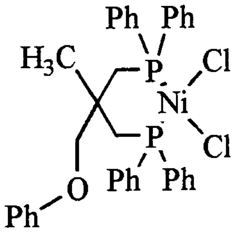
Figure 3. **The Crystal Structure of [Ni(dcpn)Cl$_2$] (4)**



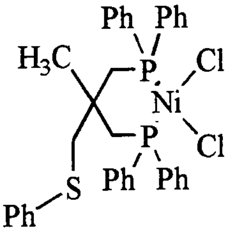
The differences in steric and electronic effects of the diphosphine ligands are reflected in the bond lengths and angles of the complexes of the type [Ni(P-P)Cl$_2$] (Tables 7 and 8).

Table 7 Comparison of Ni-P Bond lengths for complexes of the type [Ni(P-P)Cl$_2$]

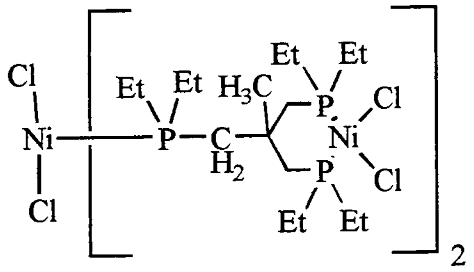
[Ni(P-P)Cl$_2$]	Ni-P$_1$ (Å)	Ni-P$_2$ (Å)
[Ni(dppe)Cl$_2$] A[14]	2.154 (4)	2.153 (4)
[Ni(dppe)Cl$_2$].CH$_2$Cl$_2$ B[14]	2.157 (2)	2.145 (2)
[Ni(dcpe)Cl$_2$] (**2**)	2.164 (10)	2.150 (11)
[Ni(dBpe)Cl$_2$] (**3**)	2.211 (10)	2.213 (11)
[Ni(dppv)Cl$_2$] [15]	2.147 (9)	2.136 (11)
cis-[Ni(Cy$_2$PH)Cl$_2$] [17]	2.14 (1)	2.16 (1)
[Ni(dcpn)Cl$_2$] (**4**)	2.146 (8)	
[Ni(dppn)Cl$_2$] [18]	2.163	2.164
[Ni(dpppO)Cl$_2$] [19]	2.164 (2)	
[Ni(dpppS)Cl$_2$] [20]	2.18 (av)	
[Ni(etriphos)Cl$_2$] [21]	2.164 (12)	2.174 (12)
[Ni(dppp-dppp)Cl$_2$] [22]	2.189 (3)	2.170 (3)



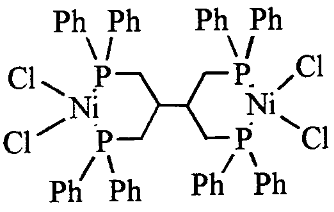
[Ni(dpppO)Cl$_2$]



[Ni(dpppS)Cl$_2$]



[Ni(etriphos)Cl$_2$]



[Ni(dppp-dppp)Cl$_2$]

Table 8 Comparison of bond angles of [Ni(P-P)Cl$_2$] complexes

[Ni(P-P)Cl$_2$]	P-Ni-P (°)	Ni-P-C$_b$ (°)	P-C$_{1b}$-C$_{2b}$ (°)
[Ni(dppe)Cl$_2$] A[14]	87.3 (2)	107.5 (3)	107.0 (6)
[Ni(dppe)Cl$_2$].CH$_2$Cl$_2$ B[14]	86.93 (6)	109.5 (2)	107.1 (3)
[Ni(dcpe)Cl$_2$] (**2**)	88.27 (4)	109.84 (11)	110.3 (2)
		110.32 (11)	110.4 (2)
[Ni(dBpe)Cl$_2$] (**3**)	90.32 (4)	107.21 (12)	112.7 (3)
		106.83 (12)	112.6 (3)
[Ni(dppv)Cl$_2$]	87.79 (4)	108.96 (12)	116.8 (3)
		108.87 (13)	117.4(3)
cis-[Ni(Cy$_2$PH)$_2$Cl$_2$][17]	90.3 (3)	115 (3)	-
[Ni(dcpn)Cl$_2$] (**4**)	96.17 (5)	119.55 (11)	123.9 (2)
[Ni(dppn)Cl$_2$] [18]	89.47		
[Ni(dpppO)Cl$_2$] [19]	95.49 (7)		
[Ni(dpppS)Cl$_2$] [20]	95.5 (4)		
[Ni(etriphos)Cl$_2$] [21]	96.3 (4)		
[Ni(dppp-dppp)Cl$_2$] [22]	96.79 (9)		
	94.52 (9)		

In the complexes which contain a diphosphine ligand in a five-membered chelate ring, increasing the σ-donor strength and steric bulk of the diphosphine, in the order Ph < Cy < ^{t}Bu, increases the Ni-P bond lengths and enlarges the bite angle P-Ni-P.

The interactions of the diphosphine ligands as shown by the Ni-P bond distances and P-Ni-P bond angles, with the chloride ligands co-ordinated to the metal centre increases as the steric bulk of the diphosphine ligand increases in the order Ph < Cy <^{t}Bu. Comparing the dppe with the dcpe complex, the bite angle of the diphosphine ligand is increased for the dcpe complex by 1° from 87.3° to 88.3° (Table 8). The Cl-Ni-Cl bond angle also increases slightly by 0.7° from 94.6° in [Ni(dppe)Cl$_2$][14] to 95.3° in [Ni(dcpe)Cl$_2$] (**2**) (Table 2). However, the small van der Waals radii of the nickel metal means that the diphosphine ligands dppe, and dcpe both behave in a similar fashion. The bulkier dcpe ligand can easily be accommodated around the nickel centre by a variation in its bond angles, which is reflected in the ligand backbone geometry where the bond angles Ni-P-C, and P-C-C, increase on average by 2° compared with the dppe complex.

The Ni-P, and Ni-Cl bond lengths in the complexes [Ni(dcpe)Cl_2] (**2**) and [Ni(dppe)Cl_2] differ only slightly (this may be due to experimental error), although the average Ni-P bond length of 2.16Å in (**2**) is longer than average Ni-P bond length of 2.15Å in [Ni(dppe)Cl_2]. This is consistent with the larger steric bulk of the dcpe ligand compared to dppe, and leads to increased steric interactions with the chloride ligands which consequently lengthens the Ni-P bond. A shortening of the Ni-P bond length, in the Ph complex would be expected if the σ*-orbitals were utilised for backbonding. The ability to accept electron density by backbonding decreases in the order Ph>>Cy~^{t}Bu. Aryl phosphine ligands have the capacity for backbonding where the P-R σ*-antibonding orbitals are of a suitable energy level to accept electron density from the metal. However, in alkyl-phosphines these P-R σ*-antibonding orbitals are much higher in energy than the d-orbitals of the metal leading to poor overlap and there is essentially no backbonding.[23] However, the effect of backbonding in Ni(II) complexes is negligible, a conclusion reached in this study, compared to that of electron rich Ni(0) complexes.[23] Thus, the relatively small increase in the Ni-P bond length between the dppe and dcpe complexes can be attributed to their different steric bulk.

The P-Ni-P bite angle increases by two degrees from 88.3° to 90.32° on replacing the R group from Cy to ^{t}Bu. The large steric bulk of the ^{t}Bu group results in increased steric interactions with the chloride ligands and is compensated by a large decrease in the Cl-Ni-Cl bond angle of 5°, from 95.3° for P-P = dcpe (Table 2) to 90.2° for P-P = dBpe (Table 4). The large deviations of the Ni-P-C (107.21, 106.83°), and P-C-C bond angles (112.7, 112.6°) from the ideal tetrahedral angles also reflect the need for compensation for the bulky ^{t}Bu group and the flexibility of the alkyl backbone. The average Ni-P bond length increases on going from the dcpe (2.157Å) to dBpe complex (2.212 Å), as expected for an increase in steric interactions. Thus, the combination of steric and electronic effects of the bulky diphosphine ligand in the complex [Ni(dBpe)Cl_2] results in increased bond lengths and angles compared to that of the similar R = Cy and R = Ph complexes.

The Ni-Cl bond lengths in the complexes [Ni(dppe)Cl_2],[14] (2), and (3) are approximately 2.22-2.23Å, which indicates that the differences between the complexes [Ni(dppe)Cl_2], (2), and (3) are mainly steric in nature.

The complex [Ni(dcpn)Cl_2] (4) is purple in colour, in contrast to the usual red/orange colour of Ni(II) square-planar complexes. The complex [Ni(dppn)Cl_2] which is the Ph analogue of complex (4) was orange in colour.[18] The bond lengths and angles of the naphthalene ring have been compared with those of the diamine ligand, 1,8-bis(dimethylaminomethyl)naphthalene (DMAMN), which is almost planar, and were found to compare closely with the napthalene ring in the complex [Ni(dcpn)Cl_2] (4).

The bite angle of 96.2° in the complex [Ni(dcpn)Cl_2] (4) is of a similar magnitude to related complexes having a diphosphine six-membered chelate ring (94.5-96.8°)[18-22.] (Table 8), although this is larger than the ideal bite angle in square-planar complexes of 90°, which is observed for the Ph analogue, dppn.[18] In contrast with complexes reported in the literature, which contain flexible backbones, the enforced rigidity of the naphthalene ring in the dcpn ligand influences the structure of the complex. In fact the complex [Ni(dpppO)Cl_2] is described as having a chair form of the six-membered chelate ring,[19] which would not be possible in the case of the ligand dcpn. The Cl-Ni-Cl bond angle of 93.01° lies between that of the complex [Ni(dcpe)Cl_2] (2) and [Ni(dBpe)Cl_2] (3) of 95.3° and 90.2° respectively. The Ni-P-C bond angle (119.5°) is considerably distorted from the tetrahedral. The unusual purple colour of the [Ni(dcpn)Cl_2] (4) may be attributed to two possibilities. In the first case the tetrahedral distortion may lead to an increase in the ligand field separation Δ, from a true square-planar conformation, and purple coloured complexes have been observed in complexes of the type [Ni(P-P)X_2] when X = Cl, Br, I, which are known to distort toward the tetrahedral isomers.[1,12,16.] Tetrahedral distortions in the [Ni(P-P)X_2] complexes increases with a decrease in ligand field strength, in the order of halide ligands Cl > Br > I.[1,12,25.] Alternatively, the purple colour may be due to orbital overlap of the metal d-orbitals with the π-orbitals of the aromatic naphthalene ring which is supported by a shortening of the Ni-P bond. In the complex [Ni(dcpn)Cl_2] (4), the Ni-P bond length is only 2.15Å whereas the average Ni-P bond length is 2.17Å for complexes which contain a diphosphine ligand in a six-membered chelate ring (R = Ph) reported in the literature (Table 7).[18-22] This π-orbital overlap has been invoked for the complex [Ni(dppv)Cl_2], which is the unsaturated analogue of the complex [Ni(dppe)Cl_2]. The unsaturated nature of the chelating diphosphine ligand leads to an enhancement of Ni to P π-bonding, and as a consequence, some degree of rehybridisation takes place at the phosphorus and the aliphatic carbon atoms, producing the observed partial coplanarities.[15,25] The Ni-P bond length was reduced in this case from 2.154Å for the saturated diphosphine ligand complex to 2.147Å for the unsaturated diphosphine ligand complex.[15]

Solution Studies - $^{31}P\{^1H\}$ NMR Spectroscopy

The complexes of the type [Ni(P-P)Cl_2] (**1**) characterised in this study, and reported in the literature, for which the diphosphine ligand co-ordinates to give a five-membered chelate, were all square-planar in solution (and the solid state).

The observed chemical shift, δ, in diphosphine complexes containing a chelate ring depends on four factors: distribution of electron density in the σ-bonds between the phosphorus atom, its substituents and the metal to which it is co-ordinated; the extent to which the phosphine participates in π-bonding; the variation in CPC bond angles; and the size of the chelate ring.[26]

The observed chemical shift, δ, in phosphine complexes can be broken into two components as follows (Equation 2):

$$\delta p = \Delta + \delta_F$$

Equation 2

δ_F = chemical shift of the non-complexed ligand

Δ = co-ordination chemical shift - the difference between the chemical shift of the complexed and non-complexed ligand.[26]

In diphosphine complexes which contain a chelate ring, variations in chelate ring size have an effect on the observed chemical shift, a new parameter Δ_R, the "ring contribution" is defined and consists of two components (Equation 3):

$$\Delta_R = \Delta_{chelating} - \Delta_{non\text{-}chelating}$$

Equation 3

$\Delta_{chelating}$ = chemical shift of a chelating phosphine complex

$\Delta_{non\text{-}chelating}$ = chemical shift of a non-chelated analogue phosphine complex, where the phosphine ligands are in a *cis*- conformation.[26]

The origin of this chelation chemical shift is not yet completely understood but probably is a consequence of the changing bond-angles at the phosphorus atom in different ways in rings of different sizes.[26] This is exemplified by the observation that the value of Δ_R, is found to depend on the size of the chelate ring. A five-membered chelate ring causes resonances to occur at ~ +35ppm, a six-membered chelate ring causes resonances to occur at ~ -15ppm, and a four-membered chelate ring causes resonances to occur at ~ -50ppm relative to a co-ordinated but non-chelating ligand having chemically similar R groups around the phosphorus atom.[26] The effect of larger ring sizes on the observed chemical shift has not been studied in as great detail. As the size of the ring increases, the bond-angles of the groups around the phosphorus atoms will more closely approach those of non-chelated complexes and the ring effect will be less obvious, although, rigidity of the diphosphine ligand may cause similar effects.

The observed chemical shifts for the complexes [Ni(dppe)Cl_2],[27] [Ni(dcpe)Cl_2] (**2**), and [Ni(dBpe)Cl_2] (**3**) increases in frequency as the σ-donation increases, in the order Ph < Cy < ^{t}Bu.

Table 9 $^{31}P\{^1H\}$ NMR data of complexes of the type [Ni(P-P)Cl_2] (**1**)

	$^{31}P\{^1H\}$ NMR δ ppm
[Ni(dppe)Cl_2][27]	57.3
[Ni(dcpe)Cl_2] (**2**)	82.8
[Ni(dBpe)Cl_2] (**3**)	88.2
[Ni(dppv)Cl_2][15]	69.7/71.2[b]

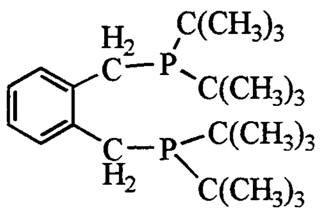
cis-[Ni($Cy_2PH)_2Cl_2$][17]	37.9
[Ni(dcpn)Cl_2] (**4**)	br (35-40)
[Ni(dppn)Cl_2][18]	31.2
[Ni(dppp)Br_2][a]	32.6
$NiCl_2$ + Boxylyl	br (45-55)

[a] The rate of exchange between the square-planar and tetrahedral isomers is faster than the NMR timescale (The complex [Ni(dppp)Cl_2] gives a broad spectrum indicative of a comparable rate of exchange)

[b] Solid-State CPMAS at 121.5 MHz

The $^{31}P\{^1H\}$ NMR spectrum of the complex [Ni(dcpn)Cl_2] (**4**) exhibits a paramagnetically broadened peak at 35-40Hz consistent with tetrahedral geometry about the nickel. The square-planar geometry in the solid state and the paramagnetism exhibited in solution are similar to those of the complex [Ni(dppp)Cl_2], which undergoes a square-planar - tetrahedral isomerisation in solution, but is square-planar in the solid state.[1] This observation is consistent with other diphosphine ligands incorporated in six membered chelate rings, in the complexes [Ni(dpppO)Cl_2],[19] [Ni(dpppS)Cl_2],[20] and [Ni(dppp-dppp)Cl_2].[22]

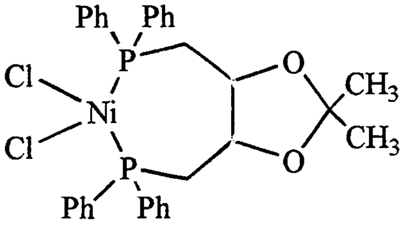
A complex of the type [Ni(P-P)Cl_2] (**1**), formed in solution, was not isolated from the reaction of the sterically demanding and strongly electron donating phosphine, Boxylyl, {1,4-bis(di-*tert*-butylphosphino)*ortho*-xylene}(i) with $NiCl_2$.



(i)

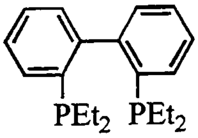
Attempts to synthesise a palladium dichloride complex containing the Boxylyl ligand were also unsuccessful, although, palladium(0) complexes have been isolated.[29] The inability to isolate the [Ni(P-P)Cl_2] (**1**) complex due to steric limitations is consistent with previous work. The nickel(0) complex [Ni(Boxylyl)(C_2H_4)] was prepared by the reaction of [Ni(cod)$_2$] with Boxylyl under an atmosphere of ethene.[30] Complexes analogous to the complex [Ni(Boxylyl)(C_2H_4)], containing the diphosphine ligands, dBpe, and dBpp, were alternatively prepared by reduction with zinc metal under an atmosphere of ethene from the complexes of the type [Ni(P-P)Cl$_2$] (**1**), indicating their reduced steric demand.[30]

The ability of four co-ordinate nickel (II) to exist in both square-planar and tetrahedral configurations, leads to the possibility of forming a tetrahedral complex in preference to square-planar complexes for ligands producing large steric interactions.[1] If the Boxylyl ligand co-ordinates in a chelating fashion a seven-membered ring complex forms. For comparison, the complexes [Ni(dppbut)Cl$_2$] and [Ni(dpppent)Cl$_2$] which contain diphosphine ligands chelating in seven-, and eight-membered rings, have been isolated, and characterised by electronic spectroscopy and are tetrahedral in the solid state.[9] The same geometry is adopted by [Ni(diop)Cl$_2$], (ii) which contains a diphosphine ligand in a seven membered chelate ring, as characterised by X-ray crystallography.[31] However, the palladium [31] and platinum[32] analogues were both found to be square-planar.



(ii)

The inability to isolate a Boxylyl complex of the type [Ni(P-P)Cl$_2$] is probably due to the fact that both the square-planar and tetrahedral forms are destabilised by steric interactions. The existence of the tetrahedral nickel(0) complex illustrates that the ligand can chelate across the tetrahedral bond distances but to a larger metal centre. The broadness observed in the $^{31}P\{^1H\}$ NMR spectrum is consistent with square-planar - tetrahedral isomerism in solution. [Ni(bpep)Cl$_2$], {bpep = 2,2'-Biphenylylenebisdiethylphosphine} (iii), which also contains a diphosphine ligand in a rigid seven membered chelate ring is found to exhibit square-planar - tetrahedral isomerism in solution.[16] Interestingly, the complex is also purple in colour.[16]



(iii)

2.3 Summary

A series of complexes of the type [Ni(P-P)Cl_2] (**1**), containing diphosphine ligands forming five membered chelate rings, particularly [Ni(dcpe)Cl_2] (**2**) and [Ni(dBpe)Cl_2] (**3**) and containing a diphosphine forming a six-membered chelate ring, namely [Ni(dcpn)Cl_2] (**4**) have been synthesised and characterised by X-ray crystallography. Complexes (**2**) and (**3**) were square-planar both in the solution and solid states. In the solid state the bite angle, P-Ni-P, of the diphosphine ligands in complexes (**2**) and (**3**) increases with increasing steric bulk of the phosphorus substituent group in the order Cy < ^{t}Bu. The bulkier diphosphine ligand, dBpe, has a greater effect than dcpe, due to larger steric interactions with the chloride ligands which reduces the Cl-Ni-Cl bond angle greatly. The flexible nature of the alkyl backbone is illustrated by the increase in Ni-P-C and P-C-C bond angles to accomodate the the bulkier Cy group.

The novel complex [Ni(dcpn)Cl_2] (**4**), is square-planar in the solid state but exhibited a square-planar - tetrahedral isomerism in solution, which is common in nickel(II) complexes containing chelating diphosphine ligands forming six-membered chelate rings.[1,19-22]

A $^{31}P\{^1H\}$ NMR spectrum obtained from a solution immediately after the reaction of $NiCl_2$ with Boxylyl, showed evidence for square-planar - tetrahedral isomerism in solution, similar to that observed in six membered ring complexes, and the seven membered ring complex [Ni(bpep)Cl_2]. The steric interactions which would occur in both a square-planar or a tetrahedral complex containing the rigid and bulky Boxylyl ligand, may prevent the isolation of the complex in the solid state.

2.4 Experimental

2.4.1 Synthesis of [Ni(dcpe)Cl_2]

Dcpe (0.30g, 0.71mmol) in warm ethanol (50ml) was added to [$NiCl_2.6H_2O$] (0.17g, 0.71mmol) in ethanol (20ml). On addition of the phosphine the solution changed colour from green to orange. After stirring for 2.5h, fine orange crystals precipitated at r.t. Cooling the solution to -20°C resulted in further precipitation of the orange solid, which after removal by filtration was dried *in vacuo* and recrystallised from dichloromethane-hexane. Yield 0.2g, (51%). Found: C, 56.3; H, 8.80. $C_{26}H_{48}Cl_2NiP_2$ requires C, 56.6, H, 8.80%. ^{1}H NMR ($CDCl_3$): δ 2.65 (d, $J_{P\text{-}H}$ 11.9Hz $PC\underline{H}_2$, 4H) 2.26 (m, PCy_2, 4H), 1.83, 1.63, 1.3 (m, m, m PCy_2, 40H)ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 82.65 (s) ppm. Crystals of [Ni(dcpe)Cl_2] (**2**) suitable for X-ray crystallography were obtained and a structure determination was performed by C. W. Lehmann.

2.4.2 Synthesis of [Ni(dBpe)Cl_2]

1,2-bis-(di*tertiary*butylphosphino)ethane (0.50g, 1.74mmol) in diethylether (30ml) was added to [$NiCl_2(CH_3OCH_2CH_2OCH_3)$] (0.35g, 1.6mmol) suspended in diethylether (20ml). An immediate colour change was observed from yellow to pink. The solution was stirred overnight and a salmon pink coloured solid precipitated. The solid was recrystallised from chloroform-hexane, to give an orange/red crystalline solid which was dried *in vacuo*. Yield 0.12g, (17%). Found: C, 48.37; H, 9.24. $C_{18}H_{40}Cl_2NiP_2$ requires C, 48.25, H, 9.00%. ^{1}H NMR ($CDCl_3$): δ 1.64 (d, br, $J_{P\text{-}H}$ 11.9Hz $CC\underline{H}_3$, 36H) 1.76 (d, br, $PC\underline{H}_2$, 4H) Hz. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 82.65 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (t, $P\underline{C}H_2$, $^2J_{P\text{-}C}$ 24.5Hz); δ 30.8 (s, $C\underline{C}H_3$); δ 38.1 (t, $P\underline{C}H_2$, $^2J_{P\text{-}C}$ 24.5Hz). Crystals of [Ni(dBpe)Cl_2] (**4**) suitable for X-ray crystallography were obtained and a structure determination was performed by C. W. Lehmann.

2.4.3 Synthesis of [Ni(dcpn)Cl_2]

1,8-bis(dicyclohexylphosphino) napthalene (0.13g, 0.27mmol) in ethanol (20ml) was added to [$NiCl_2(CH_3OCH_2CH_2OCH_3)$] (0.04g, 0.18mmol) in ethanol (10ml). There was no immediate reaction apparent and the mixture was left to stir for 4 days. A deep purple coloured solution was obtained together with a yellow solid. The solution was cannular filtered and the yellow solid was found to be the starting material by $^{31}P\{^1H\}$ spectroscopy (δ -15ppm). The volume of solvent was reduced under reduced pressure and a purple solid precipitated on cooling (-20°C). The solid was washed with aliquots of hexane (2 x 5ml) and recrystallised from dichloromethane-hexane. Crystals of [Ni(dcpn)Cl$_2$] (**4**) suitable for X-ray analysis were obtained and a structure determination was performed by C. W. Lehmann. Attempts at obtaining a $^{31}P\{^1H\}$ spectrum were unsuccessful as initial samples gave a very broad signal, δ 35-40 ppm. Unfortunately there was limited sample to obtain further analysis.

2.4.4 Reaction of Boxylyl with NiCl$_2$

Boxylyl (42mg, 1.05mmol) in diethylether (30ml) was added to [NiCl$_2$(CH$_3$OCH$_2$CH$_2$OCH$_3$)] (16mg, 0.74mmol) in diethyl ether (15ml). A colour change occurred from pale yellow to turquoise blue on addition of the phosphine solution. The ether was removed under reduced pressure and dichloromethane was added which resulted in the precipitation of NiCl$_2$ which was removed by filtration. Attempted recrystallisations from dichloromethane/hexane were unsuccessful. $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$): δ 47-54 (v. br) ppm.

2.5 References

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Chapter 3
The Synthesis and Characterisation of [Ni(P-P)RX] (1)

3.1 Introduction

As outlined in Chapter 1, complexes of the type [Ni(P-P)RX] (**1**) are important intermediates in the synthesis of catalyst precursors. However, there are relatively few examples of such aryl and alkyl complexes reported in the literature; complexes reported include [Ni(dppe)(2,3-$Cl_2C_6H_4$)Br][1] and the series of complexes [Ni(dcpe)RX] {R = *o*-chloro-, bromo-, iodo-aryls, o-tolyl; X = Cl, Br, I}.[2] The chemistry of nickel monophosphine aryl and alkyl complexes of the type [Ni(PR_3)$_2$RX] has been comprehensively studied. [3,4]

The reaction of [Ni(PPh_3)$_2$RX] (**2**) {R = *o*-tolyl; X = Cl (**3**), Br (**4**)} with a diphosphine ligand, P-P, gives square-planar type (**1**) complexes {P-P = 1,2-bis(diphenylphosphino)ethane (dppe); 1,2-bis(dicyclohexylphosphino)ethane (dcpe) or 1,2-bis(di-*tert*-butylphosphino)ethane (dBpe)}(Equation 1). The complex [Ni(dppe)(*o*-tolyl)Cl] (**5**) was characterised by X-ray crystallography.

$$[Ni(PPh_3)_2RX]\ (\mathbf{3, 4}) + P\text{-}P \longrightarrow [Ni(P\text{-}P)RX]\ (\mathbf{1}) + 2PPh_3$$

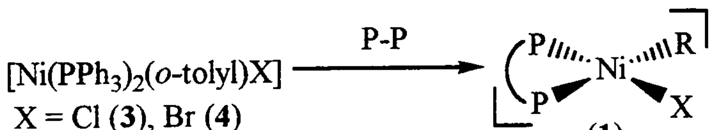
Equation 1

The reaction of complex (**4**) with a diphosphine ligand, P-P, where P-P contains three or four carbon atoms in the backbone of the diphosphine {e.g. P-P = 1,3-bis(diphenylphosphino)propane (dppp); 1,8-bis(dicyclohexylphosphino)naphthalene (dcpn) or 1,4-bis(di-*tert*-butylphosphino)*ortho*-xylene (Boxylyl) is different in each case and different to that given above. For the ligands dppp and dcpn, a displacement of PPh_3 was observed and identified by $^{31}P\{^1H\}$ NMR spectroscopy but a type (**1**) complex was not isolated. Also, a reaction was not observed on addition of the strongly electron donating and bulky diphosphine ligand, Boxylyl, to complex (**4**).

The alternative preparation of a complex of type (**1**) which contains the ligand, dppp, was attempted *via* the oxidative addition of RX to the Ni(0) complexes [Ni(dppp)$_2$] and [Ni(dppp)(PPh$_3$)$_2$] but the desired complex was not isolated.

3.2 Results and Discussion

A series of complexes of type (**1**) were prepared, in moderate yields, by the ligand displacement reaction of a monophosphine ligand by a chelating diphosphine ligand (Scheme 1).



(**1**)

Where X = Cl, P-P
(**5**) dppe,
Where X= Br, P-P
(**6**) dppe, (**7**) dcpe
(**8**) dBpe

Scheme 1

The nature of the reaction is dependent on both n, the number of carbons in the backbone of the diphosphine, $R_2P(CH_2)_nPR_2$, and the steric bulk of the diphosphine. Complexes [Ni(dppe)(*o*-tolyl)Cl] (**5**), [Ni(dppe)(*o*-tolyl)Br] (**6**), [Ni(dcpe)(*o*-tolyl)Br] (**7**) and [Ni(dBpe)(*o*-tolyl)Br] (**8**) were characterised in solution by ^{1}H, ^{31}P{^{1}H}and ^{13}C NMR spectroscopy, and complex (**5**) was characterised by X-ray crystallography.

After the reaction of complex (**4**) with the ligand dcpn, a type (**1**) complex was not isolated. During the reaction period, 2 days, a purple solid precipitated from a solution which contained free PPh$_3$, identified by ^{31}P{^{1}H} NMR spectroscopy. The purple solid, ascribed to the complex [Ni(dcpn)Br$_2$], was the same colour as the dichloride complex [Ni(dcpn)Cl$_2$].[5]

No product was isolated from the reaction of complex (**4**) with dppp, a mixture of species were observed in solution by ^{31}P{^{1}H} NMR spectroscopy. An alternative synthesis of the complex [Ni(dppp)(*o*-tolyl)Cl] was attempted *via* an oxidative addition reaction of 2-chlorotoluene to the nickel (0) bisdiphosphine complexes [Ni(dppp)$_2$] (**9**) and $[Ni(dppp)(PPh_3)_2]$ (**10**). No reaction occurred when 2-chlorotoluene was reacted with complex (**9**). Furthermore, complex (**9**) crystallised from the reaction solution containing 2-chlorotoluene and was characterised by X-ray crystallography. However, 2-chlorotoluene reacted with complex (**10**) to generate a mixture of nickel-phosphorus species which were observed in solution by $^{31}P\{^1H\}$ NMR spectroscopy, the desired complex was not isolated.

No reaction was observed on addition of the strongly electron donating and bulky diphosphine ligand, Boxylyl, to complex (**4**).

3.2.1 Synthesis of complexes of the type $[Ni(PPh_3)_2RX]$ (2)

Isolation of stable catalyst precursors is important in catalytic investigations. The presence of *o*-substituents on an aryl group, R, is known to stabilise complexes of the type *trans*-$[Ni(PR_3)_2RX]$ (**2**)[6], especially when the R substituent is electron withdrawing, for example, Cl or F[7]. However, the complex $[Ni(dppe)(2,3\text{-}Cl_2C_6H_3)Br]$[1] (synthesised by the displacement reaction of $[Ni(PPh_3)_2(2,3\text{-}Cl_2C_6H_3)Br]$ with dppe), which contains an *o*-chloro substituted aryl group, is catalytically inactive in ethylene polymerisation or dimerisation. In order to achieve relative stability, whilst maintaining potential catalytic activity, the complexes containing an *o*-tolyl group $[Ni(PPh_3)_2(o\text{-tolyl})Cl]$ (**3**) and $[Ni(PPh_3)_2(o\text{-tolyl})Br]$ (**4**) were selected as suitable precursors.

Complexes (**3**) and (**4**) were prepared by the oxidative addition of 2-chlorotoluene or 2-bromotoluene to a nickel (0) complex. The nickel (0) complexes were prepared by the *in situ* reduction, using zinc metal, of the nickel (II) complexes $[Ni(PPh_3)_2Cl_2]$ and $[Ni(PPh_3)_2Br_2]$[8] (Equation 2).

$$[Ni(PPh_3)_2X_2] \xrightarrow[\text{Zn, AIBN, Ultrasound}]{RX} [Ni(PPh_3)_2RX] \ (\mathbf{3, 4})$$

Equation 2

In order to isolate a single pure product the aryl halide must be the same as the halide in the nickel monophosphine complex. Therefore RCl was reacted with $[Ni(PPh_3)_2Cl_2]$, and RBr was reacted with $[Ni(PPh_3)_2Br_2]$.

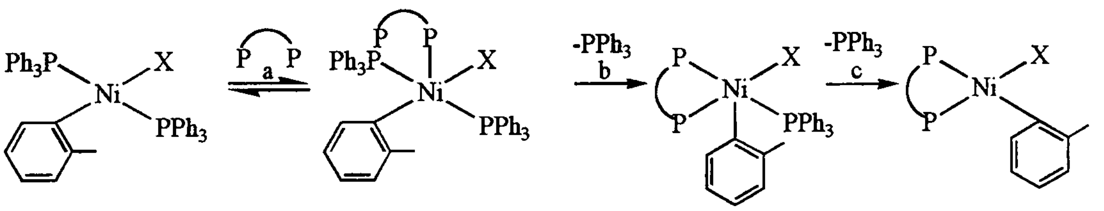
Interference of the *ortho*-substituents of the *o*-tolyl ligand with the bulky phenyl groups of the monophosphine ligands limits the rotation of the aryl group around the nickel-carbon bond.[6] Several conformational isomers exist in solution and the most stable complex is obtained when the *o*-tolyl ligand is held with its plane perpendicular to that of the complex.[6] Limited rotation occurs and is observed in the monophosphine complexes **(3)** and **(4)** by $^{31}P\{^1H\}$ NMR spectroscopy. Only one singlet is observed for the complex $[Ni(PPh_3)_2(o\text{-tolyl})Cl]$ **(3)**, but two singlets in a ratio of 5:1 (due to two isomers), are observed for the complex $[Ni(PPh_3)_2(o\text{-tolyl})Br]$ **(3)**, due to the large bromide ligands restricting the rotation about the nickel-carbon bond which is slow at r.t. on the NMR timescale at r.t.

3.2.2 Synthesis of complexes of the type [Ni(P-P)RX] (1)

Complexes of the type **(1)** were prepared *via* the ligand displacement reaction of monophosphine ligands by a chelating diphosphine ligand (Scheme 2). The uncharacterised complex [Ni(dcpe)(*o*-tolyl)Br] has been prepared previously[2] *via* the oxidative addition of 2-bromotoluene to the nickel (0) complex $[Ni(dcpe)(C_2H_4)]$, and was converted directly to the complex [Ni(dcpe)(*o*-tolyl)I][2] by addition of NaI. This literature method was not followed in these studies because a ligand displacement route allowed the synthesis of one relatively stable starting material, $[Ni(PPh_3)_2(o\text{-tolyl})Br]$ **(3)** or $[Ni(PPh_3)_2(o\text{-tolyl})Cl]$ **(4)** to react with the available diphosphine ligands.

Ligand exchange reactions of square planar complexes, for example, in the synthesis of [Ni(P-P)RX] **(1)**, generally proceed through an associative S_N2 type pathway.[9] The mechanism for the ligand exchange of the monophosphine (PPh_3) in the complexes $[Ni(PPh_3)_2(o\text{-tolyl})Cl]$ **(3)** and $[Ni(PPh_3)_2(o\text{-tolyl})Br]$ **(4)** by a chelating phosphine (P-P) is complicated by the steric effects of the *o*-tolyl group. Steric crowding at the reaction centre generally inhibits associative reaction pathways.[10]

The mechanism for an associative displacement reaction proceeds through a five co-ordinate intermediate.[9] The ability of nickel to form five co-ordinate complexes is well known, and reactions involving four co-ordinate nickel complexes often proceed through a five co-ordinate species which can often be isolated.[11] Therefore, a possible associative mechanism, to give type (**1**) complexes is: (a) initial co-ordination of P-P to nickel *via* one phosphorus atom to form a five co-ordinate intermediate, (b) simultaneous chelation of P-P and loss of one PPh_3 and (c) the facile removal of the remaining PPh_3 aided by steric interaction with the *o*-tolyl group (Scheme 2). The formation of a chelate ring (step b) is favoured as chelation imparts extra stability to the complex.



Scheme 2

Axial co-ordination is blocked sterically by the *ortho*-substituent and therefore the chelating phosphine is more likely to approach from the more accessible side which is distal to the *o*-Me. When comparing X= Cl with X=Br, a bromide ion is much larger than a chloride ion and so the first step, initial co-ordination of the diphosphine (step (a) in Scheme 2) is hindered at both possible axial sites. Also the steric bulk of the diphosphine has an effect on the rate of the reaction; the reaction is slower the larger the R group on the phosphorus atoms of the diphosphine, which is exemplifed by the increased temperature required for the reaction of dBpe with complex (**4**). The initial co-ordination of the diphosphine (step a in scheme 2) is the rate limiting step in similar displacement reactions,[12] and therefore is dependent *inter alia* on the steric bulk of the incoming ligands.

The yields of the complexes (**6**) 65%, (7) 60%, and (**8**) 19%, decrease as the steric bulk of the R group of $R_2P(CH_2)_nPR_2$, increases. The decrease in yield results from the increase in temperature required for the formation of complex (**8**) causing the decomposition of complex (**8**) to the complexes [Ni(dBpe)Br_2] and [Ni(dBpe)(*o*-tolyl)$_2$]

which were observed in solution by $^{31}P\{^1H\}$ NMR spectroscopy. The kinetic stability of the complexes of type (**1**), was dependent on the steric and electronic effects of the diphosphine. Complex (**6**) was the most stable in solution. However, over time, [Ni(dppe)Br_2] was observed in solution, and similarly [Ni(dcpe)Br_2] was observed in a solution of complex (**7**). The lability of complexes of the type [Ni(L-L)RX] {L-L = chelating ligand; R = aryl or alkyl; X = halide} has been observed previously. For example the bipyridine aryl halide complexes [Ni(bipy)RX] have not been isolated and are known to disproportionate to give [Ni(bipy)X_2] and [Ni(bipy)R_2], the latter decomposing to give the diaryl product R-R.[13] Therefore, type (**1**) complexes are related to the catalytic intermediates in aryl and alkyl cross-coupling reactions (see Chapter 1).

3.2.3 Structural comparisons between type (1) and type (2) complexes

In the crystal structure of [Ni(dppe)(2-$CH_3C_6H_4$)Cl] (**5**) (*Figure 1*) there are two, essentially square planar, isomers (**5a**) and (**5b**) which differ only by the orientation of the phenyl rings *(Figure 2)*.

The relevant bond lengths and angles of complex (**5**) are reported in Tables 1 and 2. The unit cell contains the two isomers (**5a**) and (**5b**), and a toluene solvent molecule. The phenyl groups adopt slightly differing orientations in (**5a**) and (**5b**), probably because of different steric requirements arising from the position of the toluene solvent molecule in the crystal. Complex (**5**) is the first complex of the type [Ni(P-P)RX] (**1**) to be characterised by X-ray crystallography, so direct solid-state structural comparisons with other type (**1**) complexes, or complexes containing *cis*-chelating ligands, [Ni(L-L)RX] {R = aryl, L-L = any chelating ligand} are not possible.

Figure 1. **The Crystal Structure of $[Ni(dppe)(2\text{-}CH_3C_6H_4)Cl]$ (5)**

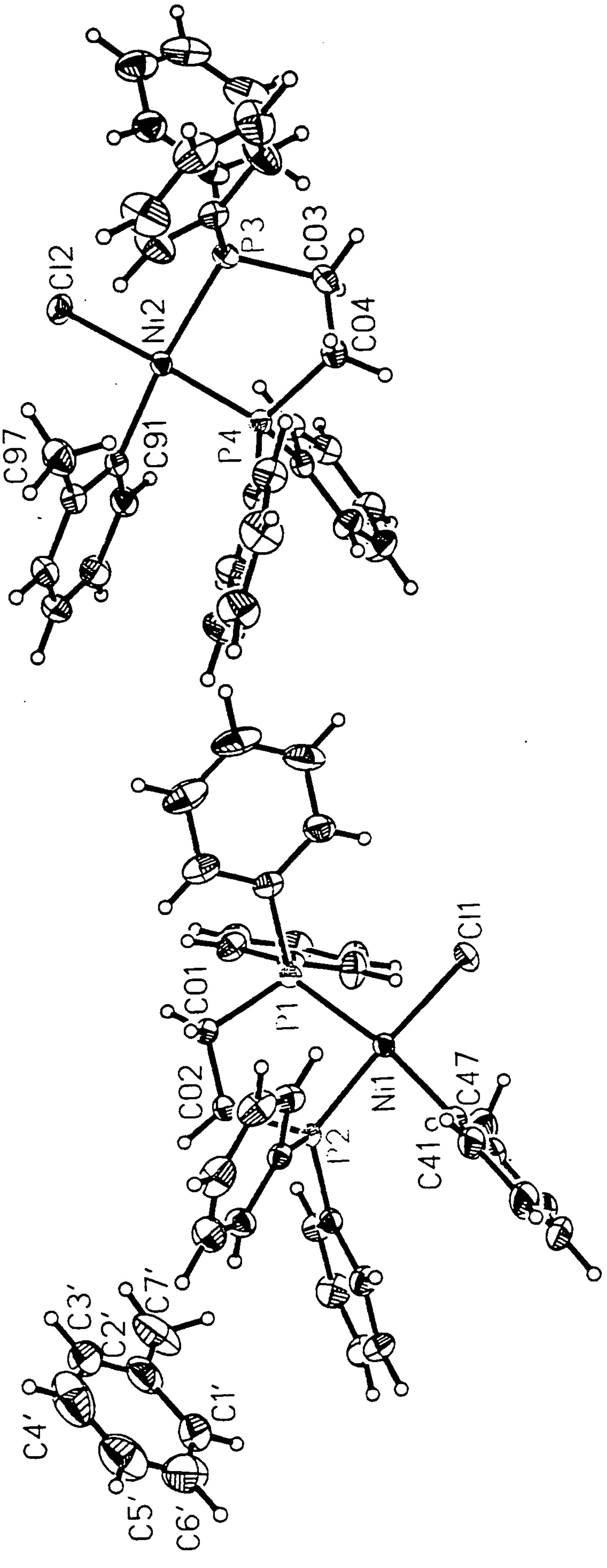
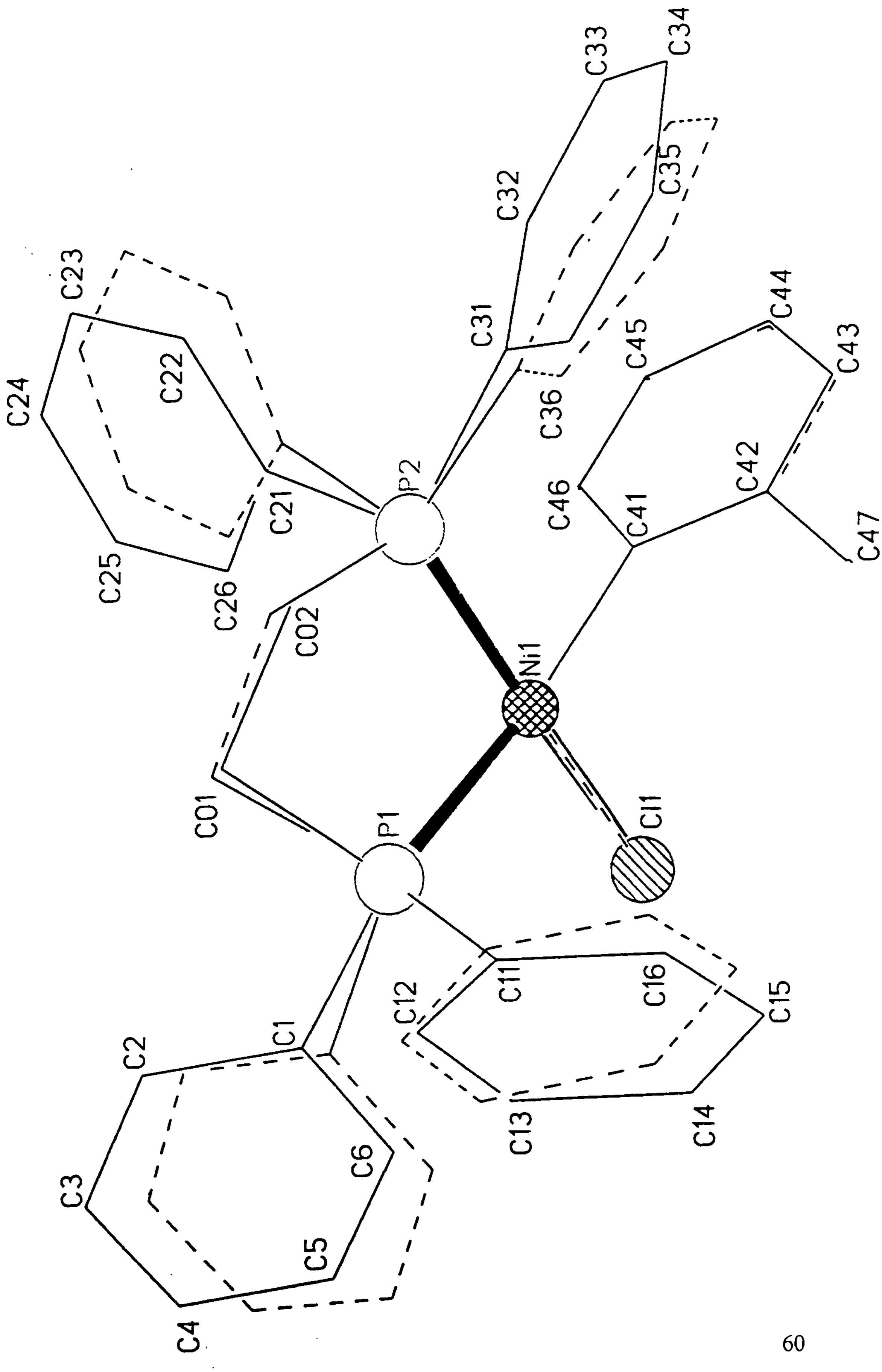
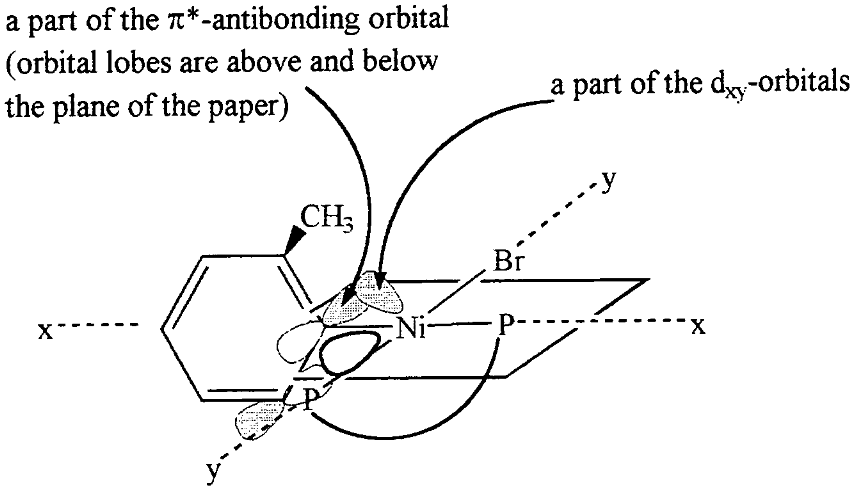


Figure 2. **The Crystal Structure of [Ni(dppe)(2-CH$_3$C$_6$H$_4$)Cl] (5) {Showing the Differing Orientations of the Phenyl Groups}**



Comparison can be made with nickel complexes in general which contain aryl, halide and phosphine ligands. In complex **(5)** the aryl ring of the *o*-tolyl group lies perpendicular to the plane of the complex **(i)**.

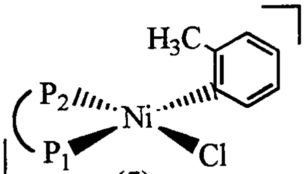
(i)



This configuration produces the most stable isomer due to minimising the steric effects of the methyl group with other ligands attached to the metal centre, and to good overlap of a π*-antibonding orbital of the aromatic ring with the metal d-orbitals. This configuration was predicted for the monophosphine complexes **(3)** and **(4)**[6], and was found by the X-ray structural characterisation to be similar for the diphosphine complex **(5)**. The two *o*-tolyl ligands of the complex *trans*-[Ni(PPhMe$_2$)$_2$(*o*-tol)$_2$] are known from X-ray crystallography to have the plane of the aryl group perpendicular to the plane of the complex.[14]

Complex **(5)** is slighty distorted from a perfect square-planar complex, the C-Ni-P$_1$ and P$_2$-Ni-Cl bond angles being 170.04(6)° and 173.31(2)° respectively for **(5a)** and 172.23(6)° and 175.82(2)° for **(5b)**. The bite angle {P-Ni-P 86.50(2)° **(5a)**, 86.42(2)° **(5b)**}of the diphosphine in complex **(5)** compares closely with other nickel complexes containing dppe in a five-membered chelate ring, for example, [Ni(dppe)Cl$_2$] {P-Ni-P 87.3(2) (Form A), 86.93(6) (Form B)}.[15]

Table 1 Selected bond angles [°] for the complex [Ni(dppe)(*o*-tolyl)Cl] (**5**)



(**5**)

[Ni(dppe)(*o*-tolyl)Cl] (**5a**)		[Ni(dppe)(*o*-tolyl)Cl] (**5b**)	
Bond angles [°]		Bond angles [°]	
C (41)-Ni (1)-P (2)	83.84(6)	C (91)-Ni (2)-P (4)	85.93(6)
C (41)-Ni (1)-Cl (1)	91.30(6)	C (91)-Ni (2)-Cl (2)	91.43(6)
P (2)-Ni (1)-Cl (1)	173.31(2)	P (4)-Ni (2)-Cl (2)	175.82(2)
C (41)-Ni (1)-P (1)	170.04(6)	C (91)-Ni (2)-P (3)	172.23(6)
P (2)-Ni (1)-P (1)	86.50(2)	P (4)-Ni (2)-P (3)	86.42(2)
Cl (1)-Ni (1)-P (1)	98.52(2)	Cl (2)-Ni (2)-P (3)	96.29(2)

Table 2 Selected bond lengths [Å] for the complex [Ni(dppe)(*o*-tolyl)Cl] (**5**)

[Ni(dppe)(*o*-tolyl)Cl] (**5a**)		[Ni(dppe)(*o*-tolyl)Cl] (**5b**)	
Bond lengths [Å]		Bond lengths [Å]	
Ni (1) -C (41)	1.931 (2)	Ni (2) -C (91)	1.932 (2)
Ni (1) -Cl (1)	2.1927 (5)	Ni (2) -Cl (2)	2.1883 (6)
Ni (1) -P (2)	2.1164 (6)	Ni (2) -P (4)	2.1240 (6)
Ni (1) -P (1)	2.2442 (6)	Ni (2) -P (3)	2.2230 (6)
C (01) -C (02)	1.524 (3)	C (03) -C (04)	1.535 (6)
P (2) -C (02)	1.840 (2)	P (4) - C (04)	1.845 (2)
P (1) -C (01)	1.838 (2)	P (3) - C (03)	1.836 (2)
C (42) -C (47)	1.498 (4)	C (92) -C (97)	1.511 (3)

Although comparisons of complex (**5**) with chelating diphosphine complexes are not possible, comparisons can be made with the monophosphine complexes of the type [Ni(PR_3)$_2$RX] (**2**), although all of the complexes of type (**2**) that have been characterised by X-ray crystallography have *trans*-monophosphine ligands. The steric requirements of the two monophosphine ligands in type (**2**) complexes means that they prefer a *trans*-configuration. Chelating diphosphines are restricted here to co-ordinate only in a *cis*-configuration where one phosphorus atom is *trans*- to R and the other is *trans*- to X. Unfortunately, these differences preclude a detailed comparison but nevertheless, a qualitative assessment is found to be useful.

The Ni-C bond lengths in complexes (**5a**) and (**5b**), 1.931(2) and 1.932(2) Å respectively compare closely with known nickel (II) square-planar complexes (Ni-Ph, from 1.81 to 1.98 Å).[13,14,16-19] However, those complexes containing Ni-C aryl bonds, characterised by X-ray crystallography are *trans*-monophosphine complexes. The exception is the complex [Ni(dcpe)(3-$(CH_2)_2$-2-C_6H_4)][2] (in which both the aryl group and a -CH_2- group are co-ordinated), where the Ni-C bond lengths of 1.951(12) (Ni-C_6H_4) and 1.988(12) Å[1] (Ni-CH_2) respectively are still within the limits of other nickel (II) aryl complexes [13, 15-19] (Table 3).

Table 3 Comparison of Ni-C bond lengths between complex (**5**) and Ni-Ph

Complex	Ni-C (Å)	Ni-Cl (Å)
[Ni(dppe)(*o*-tolyl)Cl] (**5a**)	1.931(2)	2.1927(5)
[Ni(dppe)(*o*-tolyl)Cl] (**5b**)	1.932(2)	2.1883(6)
	Ni-C (Å)	Ni-C (Å)
[Ni$(PPhMe_2)_2$(*o*-tolyl)$_2$][13]	1.942(3)	
[Ni(dcpe)(3-$(CH_2)_2$-2-C_6H_4)][2]	1.951(12) (aryl)	1.988(12) (-CH_2-)

The Ni-Cl bond lengths in complexes (**5a**) and (**5b**), 2.1927(5) and 2.1883(6) Å respectively, which are *trans*- to a phosphine ligand, are slightly shorter than in the known complex [Ni(dppe)Cl_2] [15] where both the chlorine atoms are *trans*- to a phosphine (Table 4).

Table 4 Comparison of Ni-Cl bond lengths between complex (**5**) and [Ni(dppe)Cl_2][15]

Complex	Ni-C (Å)	Ni-Cl (Å)
[Ni(dppe)(*o*-tolyl)Cl] (**5a**)	1.931(2)	2.1927
[Ni(dppe)(*o*-tolyl)Cl] (**5b**)	1.932(2)	2.1883
	Ni-Cl (Å)	Ni-Cl (Å)
[Ni(dppe)Cl_2] (A)[1]	2.196(4)	2.203(4)
[Ni(dppe)Cl_2].CH_2Cl_2 (B)[1]	2.195(2)	2.205(2)

The Ni-P bond lengths of complexes (**5a**) and (**5b**) of 2.2442(6) and 2.2230(6) Å respectively where P is *trans* to the *o*-tolyl group compare with known Ni (II) complexes which range from 2.20-2.25 Å (Table 5).[13-23] For P *trans* to the Cl group, Ni-P bond lengths of 2.1164(6) and 2.1240(6) Å for (**5a**) and (**5b**) respectively, are slightly shorter than those of the monophosphine complexes, due to the *trans*-influence of the chloride ligand. The *trans*-influence of the chelating diphosphine ligands appear to be very similar to the mutual *trans*-influence of the aryl and halide group *trans* to one another, in monophosphine complexes and only minor differences in bond lengths are observed.

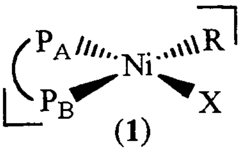
Table 5 Comparison of Ni-P bond lengths between complex (**5**) and type (**2**) complexes

Complex	Ni-P (Å)	Ni-P (Å)
[Ni(dppe)(2-$CH_3C_6H_4$)Cl] (**5**)	2.2442 *trans* to R	2.1164 *trans* to Cl
[Ni(dcpe)(3-$(CH_2)_2$-2-C_6H_4)][2]	2.170(4) *trans* to aryl	2.203(4) *trans* to (-CH_2-)
trans-[Ni$(PR_3)_2$RX] (**2**)		
[Ni$(PEt_3)_2$(2-$PPh_2C_6Cl_4$)Cl][17]	2.238(2)	2.231(2)
[Ni$(OPO)_2$(Ph)Cl][20]	2.2142(2)	2.2073(1)
[Ni$(PPhMe_2)_2$(*o*-tolyl$)_2$][13]	2.173(1)	
[Ni$(PEt_3)_2$(2,6-MePhNCH$_2$-C_6H_4)Br][21]	2.234	2.226
[Ni$(PMePh_2)_2$(C_6F_5)Br][22]	2.2164(13)	2.2148(13)

3.2.4 $^{31}P\{^1H\}$ NMR spectroscopic studies of complexes of the type [Ni(P-P)RX](1) at r.t.

The structures of complexes of type (**1**) can be assigned on the basis of $^{31}P\{^1H\}$ NMR spectroscopy. There are two phosphorus environments, P_A and P_B which gives rise to an AB spectrum with coupling constants of between 15-25 Hz. Such a spectrum is indicative of mutually *cis*, inequivalent phosphorus atoms (**ii**).

(**ii**)

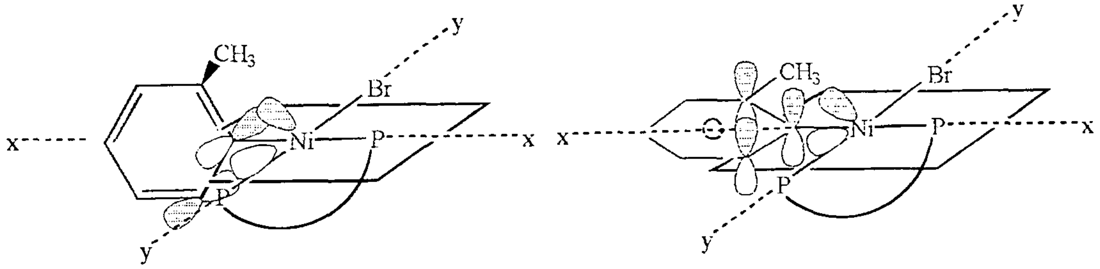


(1)

In the solid state the most stable isomer of complex (**5**) occurred when the plane of the *o*-tolyl ring was perpendicular to that of the complex. In solution, the molecules are fluxional and the $^{31}P\{^1H\}$ NMR spectrum that was observed was a time averaged spectrum.

A difference was observed in the $^{31}P\{^{1}H\}$ NMR spectra at r.t. of complexes (**5**) and (**6**), which both contained the same diphosphine ligand (dppe) and R group (*o*-tolyl), but different halide ligands. When X = Cl, complex (**5**), only one AB pattern was observed, which indicated a very rapid interchange between the isomers within the NMR timescale. However, for X = Br, complex (**6**), two AB patterns (i.e. two isomers) were observed, in a ratio of 7:1. The major isomer, M, is likely to be the most stable and of a similar structure to complex (**5**). The minor isomer, N, was only observed because the rotation of the Ni-C bond is restricted due to steric interactions of the *o*-tolyl group with the halide ligands and the phenyl group of the chelating diphosphine ligand. In the minor isomer, N, the plane of the aryl group is probably parallel to the plane of the complex, and the methyl group in a position which minimises steric interactions as shown in (**iii**).

(iii)



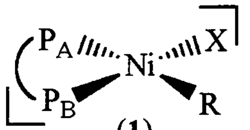
Isomer M

Isomer N

When X = Cl (**5**), the chloride ligand is small enough to allow rotation of the Ni-C bond of the aryl group, without significant steric interactions between the *o*-tolyl ligand and the chloride ligand. In contrast, when X = Br, the larger bromide ligand restricts the rotation around the Ni-C bond and steric interactions between the bromide ligand and the *o*-tolyl ligand are possible. Similarly, when comparing the effect of the diphosphine ligand in the bromide complexes, where R = *o*-tolyl, two isomers are observed for each of complexes (**8**) and (**9**). Similar observations are observed for the related complexes. The bromide complexes, [Ni(dppe)(3,5-Cl$_2$C$_6$H$_3$)Br] [23] and [Ni(dppe)(CPh=C(Ph)(3,5-Cl$_2$C$_6$H$_3$)Br], [23] which contain no *ortho*-substituent exhibit only one isomer in solution (Table 6).

The $^{31}P\{^1H\}$ NMR spectrosopic data of type (**1**) complexes are given in Table 6. It is interesting to note that [Ni(dcpe)(*o*-tolyl)I][2] is reported in the literature to give only one AB $^{31}P\{^1H\}$ NMR pattern. For [Ni(dcpe)(*o*-tolyl)I], only restricted rotation of the aryl group about the Ni-C bond occurs because of the presence of the bulky iodide ligand, and only one isomer is favoured.

Table 6 $^{31}P\{^1H\}$ NMR[1] data of complexes of the type [Ni(P-P)RX]



(**1**)

[Ni(P-P)RX] (**1**)	solvent	δP_A (ppm)	δP_B (ppm)	$J_{(P-P)}$ Hz
[Ni(dppe)(2-$CH_3C_6H_4$)Cl] (**5**)	THF	32.9	53.2	15
[Ni(dppe)(2-$CH_3C_6H_4$)Br] (**6**)	d^8-THF	35.8 M 32.9 N	55.6 M 53.2 N	16 18
[Ni(dppe)(3,5-$Cl_2C_6H_3$)Br] [23]	toluene	40.1	59.4	27
[Ni(dppe)(CPh=C(Ph)(3,5-$Cl_2C_6H_3$)Br] [23]	toluene	35.8	54.1	24
[Ni(dcpe)(2-$CH_3C_6H_4$)Br] (**7**)	THF	61.0 M 61.3 N	65.4 M 63.4 N	18 20
[Ni(dcpe)(2-$CH_3C_6H_4$)I] [2]	CD_2Cl_2	61.3	65.4	17.1
[Ni(dcpe)(2-IC_6H_4)I] [2]	CD_2Cl_2	61.6	64.2	24.1
[Ni(dcpe)(C_6H_5)I] [2]	CD_2Cl_2	64.7	69.2	19.5
[Ni(dBpe)(2-$CH_3C_6H_4$)Br] (**8**)	d^8-THF	64.5 M 65.3 N	71.6 M 70.9 N	6 7

[1] All resonances are doublets because of phosphorus-phosphorus coupling

[2] The ligand *o*-tolyl is written as 2-$CH_3C_6H_4$ to aid comparison with the different substitution of the phenyl rings of the literature complexes.

In an attempt to determine the temperature at which free rotation occurs about the nickel-carbon bond in complexes (**6**), (**7**) and (**8**), the temperature of the samples was slowly increased from r.t. to 70°C and followed by $^{31}P\ \{^1H\}$ NMR spectroscopy. Unfortunately, the complexes had decomposed by 50°C, before the required temperature at which free rotation occurs was reached. This observation infers that the lack of stabilty of complexes of type (**1**) is due to their kinetic lability at elevated temperatures which has been found previously for nickel monophosphine complexes of the type [Ni(PR_3)$_2$RX].[1]

When phosphine ligands contain two P atoms which are chemically non-equivalent, in type (**1**) complexes, it gives rise to ^{31}P spectra in which the magnitude of the phosphorus-phosphorus coupling constant, J_{P-P}, strongly affects the spectral appearance.[24] In complexes containing a chelating diphosphine ligand the coupling constant J_{P-P} depends on the sum of two separate couplings, the through metal coupling, $^{M}J_{P-P}$ and the through backbone coupling, $^{B}J_{P-P}$ (Equation 2).[25]

$$J_{P-P} = {}^{B}J_{P-P} + {}^{M}J_{P-P}$$

where $^{B}J_{P-P}$ of the co-ordinated ligand = $^{B}J_{P-P}$ of the free ligand

Equation 2

In five-membered rings, for example in complexes of type (**1**), the through backbone and through metal contributions are nearly equal but of opposite signs which leads to small values of J_{P-P} [24,25] as observed for complexes (**5**), (**6**), (**7**) and (**8**).

A correlation has previously been found between the size of the coupling constant J_{P-P} and the substituents incorporated into the chelate-ring.[24] For example, as the bulk of the alkyl substituent increases, J_{P-P} becomes more negative.[24] Furthermore, phenyl substituents are shown to have an additional positive effect.[24] The coupling constants for the complexes (**6**), (**7**), and (**8**) followed this previously observed pattern (Table 7). The coupling constant of complex (**8**) containing the bulky ^{t}Bu group was small at only 6Hz, whereas the coupling constants of complexes (**6**), and (**7**) were comparable at 16/18, and 18/20 Hz respectively, even though complex (**7**) contained the Cy groups which are bulkier than Ph groups. However, the additional positive effect of Ph groups on J_{P-P}[24] is clearly illustrated.

Table 7 $^{31}P\{^1H\}$ NMR data of complexes of the type [Ni(P-P)(*o*-tolyl)Br]

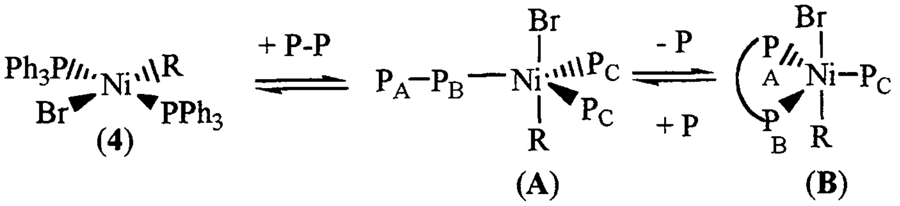
[Ni(P-P)RX] (**1**)	solvent	δP$_A$ (ppm)	δP$_B$ (ppm)	Ratio M:N	J$_{(P-P)}$ Hz
[Ni(dppe)(2-$CH_3C_6H_4$)Br] (**6**)	d^8-THF	35.8	55.6	7	16
		32.9	53.2	1	18
[Ni(dcpe)(2-$CH_3C_6H_4$)Br] (**7**)	THF	61.0	65.4	6	18
		61.3	63.4	1	20
[Ni(dBpe)(2-$CH_3C_6H_4$)Br] (**8**)	d^8-THF	64.5	71.6	3	6
		65.3	70.9	1	7

The ratio of the isomers M:N (**iii**) was found to decrease as the steric bulk of the phosphine increased. There are two possibilities, firstly the rotation of the aryl group about the Ni-C bond was more restricted in the complexes containing the bulkier diphosphine ligands, and the interchange between isomers on an NMR timescale was slower; secondly, there is a compromise of stability between the increased overlap of the π*-orbitals of the ring with metal π-type orbitals, which increases the stability, and the greater steric interactions, between the the R group of the diphosphine ligand and the methyl group of the aryl ring, which decreases the stability. Therefore, stabilisation, and consequently the observed isomer ratio in solution, depends on both the increased orbital overlap and the minimum steric interactions. Isomer, N, was observed when the steric bulk of the R group on the diphosphine ligand is large enough to interact with the *o*-tolyl ring when the ring is perpendicular to the metal-ligand plane. Thus, the lowest ratio of the isomers M:N is observed for the bulkiest *t*-butyl group.

3.2.5 $^{31}P\{^1H\}$ NMR Spectroscopic Studies at r.t. of the reaction of complex (4) with diphosphine ligands where n>2 (dppp, dcpn, and Boxylyl)

Reaction with 1,3-bis(diphenylphosphino)propane (dppp)

The $^{31}P\{^1H\}$ NMR spectrum obtained after the reaction of complex (**4**) with dppp was complex with unresolved broad resonances. In contrast to the dppe reaction, the presence of several peaks indicates that quantitative substitution by the chelating phosphine to form a single species has not occurred. Furthermore, the broadness observed in the spectrum indicates that dynamic ligand exchange equilibria are present in solution, the presence of free PPh_3 in solution indicating a ligand displacement (Scheme 3).



Scheme 3

Hence, the broad resonances are tentatively assigned as the intermediate five co-ordinate complex (**A**) and the five co-ordinate complex (**B**). The first equilibrium exists between complex (**4**), free dppp and the intermediate complex (**A**), a five co-ordinate complex which contains a monodentate dppp ligand. The second equilibrium exists between complex (**A**) and the chelating complex (**B**). The ^{31}P resonance at $\delta = -17.6$ ppm was broad and assigned to P_A and free dppp; the ^{31}P resonance at δ -5 ppm is very broad and was assigned to free PPh_3 in dynamic equilibrium with the co-ordinated PPh_3 ligands; the remaining resonances at δ 26, 27, 21.1, and 15 are assigned to co-ordinated phosphine species in complexes (**A**) and (**B**). These observations suggests that chelation of the diphosphine ligand, dppp, is not as favoured as that observed for the two carbon atom backbone phosphines. This may be attributed to the greater stabilisation obtained on forming a five membered chelate ring complex compared to a six membered chelate ring complex. Indeed, the co-ordinating ability of the diphosphine ligand decreases in the order dppe > dppp, for the ligand exchange reaction of $[Ni(bipy)Me_2]$ with a diphosphine ligand.[12]

Reaction with 1,8-bis(dicyclohexylphosphino)naphthalene (dcpn)

As found for the previous study using dppp, the reaction of complex (**4**) with dcpn did not give the desired type (**1**) complex, though the presence of free PPh_3 in solution indicated that a ligand displacement reaction had occurred. A purple solid progressively precipitated during the stirring of the reaction mixture for three days, and was attributed to the formation of $[Ni(dcpn)_2Br_2]$, isochronous with $[Ni(dcpn)_2Cl_2]$.[5] $^{31}P\{^1H\}$NMR spectroscopy indicated that the reaction was very slow, and that during the reaction, a short lived intermediate type (1) complex formed, which quickly decomposed to give $[Ni(dcpn)_2Br_2]$ and a soluble phosphorus species with a ^{31}P resonance at δ 44.4 ppm, tentively assigned to the novel $[Ni(dcpn)_2(o\text{-tolyl})_2]$ complex. Diaryl nickel (II) complexes are also stabilised by the presence of *o*-substituents on the aryl ring.[1,14.] Throughout the reaction the relative concentrations of complex (**4**) and dcpn remained constant and there was always a 4:1 molar ratio of PPh_3:dcpn species present in solution (the remaining molar quantity of "dcpn" is precipitated as the solid $[Ni(dcpn)Br_2]$ which was sufficiently insoluble in the reaction solvent such that it was not observed by ^{31}P NMR spectroscopy. Hence, the observed PPh_3:dcpn molar ratio in solution is 4:1. However, the expected stoichiometric PPh_3:dcpn molar ratio is 2:1) (Equation 3).

$$\underset{(4)}{2[Ni(PPh_3)_2(o\text{-tolyl})Br]} + 2\ dcpn \longrightarrow 2\big[[Ni(dcpn)(o\text{-tolyl})Br]\big] \longrightarrow [Ni(dcpn)(o\text{-tolyl})_2] + [Ni(dcpn)Br_2] + 4PPh_3$$

Equation 3

By integration the amount of displaced PPh_3 and the effective amount of dcpn product, allowing for the precipitated complex $[Ni(dcpn)Br_2]$ (the molar ratio is assumed), were consistant with the displacement of two PPh_3 ligands by one dcpn ligand.

1,4-bis(di-tert-butylphosphino)ortho-xylene (Boxylyl)

There was no reaction observed between the diphosphine ligand Boxylyl with complex (**4**). The large steric size of the Boxylyl ligand probably prevents attack at the metal centre and initiation of the displacement reaction.

3.2.6 Attempted alternative preparation of a type (1) complex containing the diphosphine ligand dppp *via* the oxidative addition reaction of $[Ni(dppp)(PPh_3)_2]$ with 2-chlorotoluene.

The nickel (0) complex $[Ni(dppp)_2]$ (**9**) can be prepared by the reaction of $[Ni(dppp)Cl_2]$ and one mole of dppp with sodium methoxide in methanol as the reducing agent.[26] Complex (**10**) is a very stable Ni(0) complex and is relatively unreactive toward oxidative addition and was not considered suitable as the starting material.[27] However, the complex [Ni(dppp)(PPh$_3$)$_2$] **(10)** was prepared by the reaction of [Ni(dppp)Cl$_2$] and three moles of PPh$_3$ and sodium methoxide in methanol.

The preparation of the novel complex **(10)** was based upon the literature method for the preparation of complex **(9)**.[26] However, three moles of PPh$_3$ were used in the reaction instead, in order to avoid the formation of the very stable complex **(9)**. Unfortunately, complex **(9)** was still observed by ^{31}P NMR after the reaction. Complex **(10)** was purified by solvent extraction from complex **(9)**, which was only slightly soluble in methanol. A single crystal of complex **(9)** was isolated from the reaction of complex **(10)** with 2-chlorotoluene and the structure determined by X-ray analysis (by A. S. Batsanov).

The behaviour of complexes **(9)** and **(10)**, towards oxidative addition, was similar to that expected. Complex **(9)** was too stable to oxidatively add 2-chlorotoluene. The triphenylphosphine groups in [Ni(dppp)(PPh$_3$)$_2$] **(10)**, are expected to be more labile than the chelating diphosphine and indeed complex **(10)** reacted with 2-chlorotoluene to generate new nickel-phosphorus species in solution. Attempts to isolate the desired product were unsuccessful. The oxidative addition of aryl halides is believed to proceed *via* a radical mechanism and the intermediate Ni(I) species formed are stable enough to be identified.[28] The ^{31}P{^{1}H}NMR spectrum obtained after the oxidative addition of 2-chlorotoluene with complex [Ni(dppp)(PPh$_3$)$_2$] **(10)**, contained a very broad resonance at δ -8 to 4 ppm consistant with the presence of a paramagnetic impurity and is probably due to the Ni(I) species [Ni(dppp)(PPh$_3$)Cl]. Milstein observed that the oxidative addition of aryl halides to Ni(0) complexes of the diphosphine ligand dippp, gave products with unassignable ^{31}P{^{1}H}NMR spectra which were attributed to the presence of Ni(I) paramagnetic impurities.[29] In a similar manner it was impossible to assign any of the resonances with certainty. This problem was compounded by the absence of measurable coupling constants which is a feature of six membered chelate rings.

3.2.7 Structural comparisons between complex (9) and [Ni$^{(0)}$(P-P)$_2$]

The crystal structure of [Ni(dppp)$_2$] (9) indicates a slightly distorted tetrahedral geometry (*Figure 3*). The relevant bond lengths and angles of complex (9) are reported in Tables 8 and 9.

Table 8 Bond lengths [Å] for [Ni(dppp)$_2$] (9)

Bond lengths [Å]		Bond lengths [Å]	
Ni-P(2)	2.177(1)	Ni-P(1)	2.181(1)
P(1)-C(11)	1.851(3)	P(1)-C(1)	1.856(3)
P(1)-C(21)	1.863(3)	P(2)-C(31)	1.845(3)
P(2)-C(41)	1.849(3)	P(2)-C(3)	1.852(3)
C(1)-C(2)	1.536(4)	C(1)-H(1A)	1.00(3)
C(1)-H(1B)	1.04(3)	C(2)-C(3)	1.536(4)
C(2)-H(2A)	0.99(3)	C(2)-H(2B)	0.95(3)
C(3)-H(3A)	0.94(3)	C(3)-H(3B)	1.05(3)

Table 9 Bond angles [°] for [Ni(dppp)$_2$] (9)

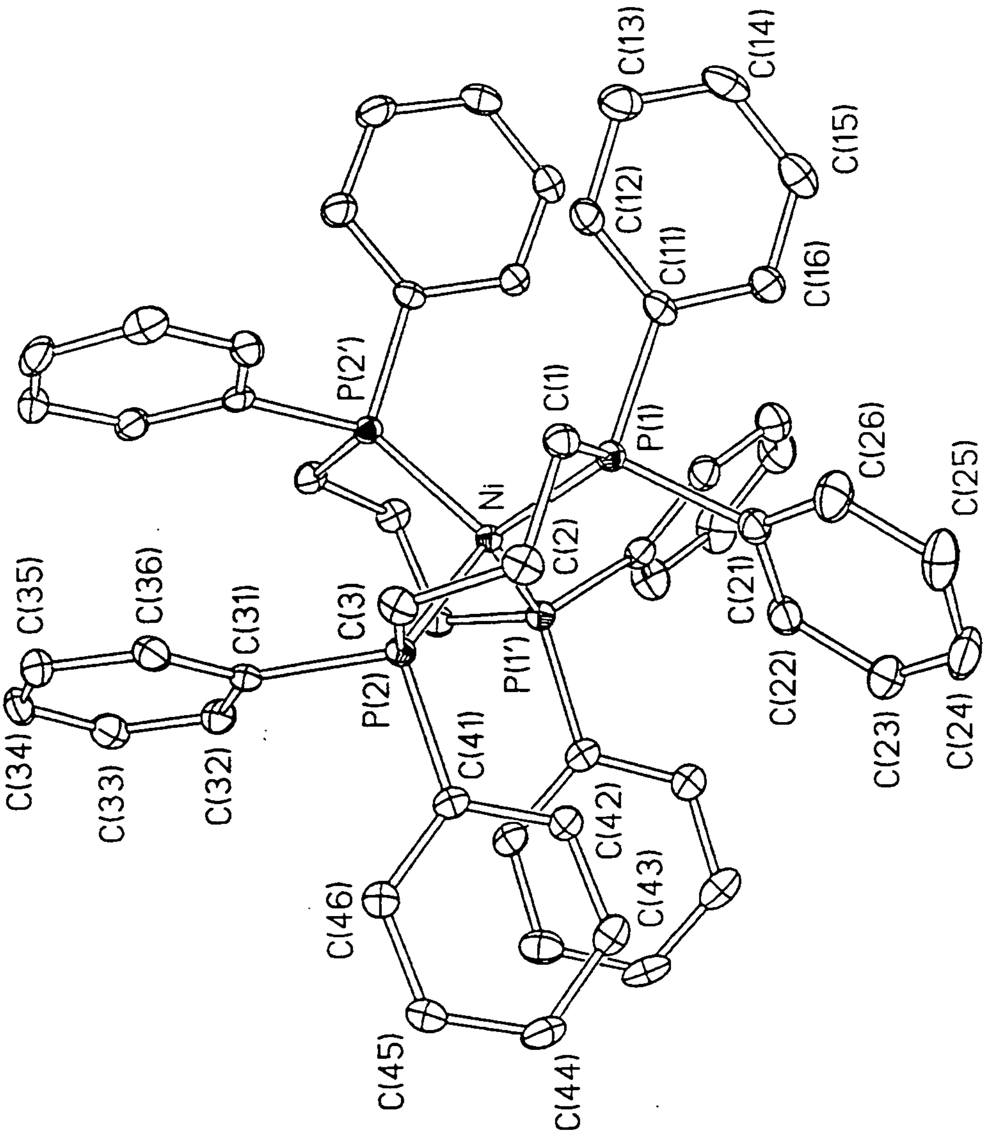
Bond Angles [°]	
P(2)-Ni-P(2')	106.34(4)
P(2)-Ni-P(1)	99.81(3)
P(2)-Ni-P(1')	115.09(3)
P(1')-Ni-P(1)	120.55(4)

The Ni-P bond lengths of complex (9) of 2.177(1) and 2.181(1) Å respectively compare with known Ni (0) complexes which range from 2.15-2.22 Å (Table 10). [30-31] The Ni-P bond lengths, in complex (9) which contains a three carbon atom backbone are slightly longer than the analogous two carbon atom backbone complex [Ni(dppe)$_2$].[30]

Table 10 Comparison of Ni-P bond lengths between complex (9) and [Ni(P-P)$_2$] complexes

[Ni(P-P)$_2$]	Bond lengths [Å]			
	Ni-P	Ni-P	Ni-P	Ni-P
[Ni(dppp)$_2$] **(11)**	2.177(1)	2.181(1)		
[Ni(dppe)$_2$][30]	2.152(3)	2.168(3)	2.161(3)	2.177(3)
[Ni(dcpm)$_2$][31]	2.214(2)	2.215(2)	2.193(2)	2.218(2)

Figure 3. **The Crystal Structure of [Ni(dppp)$_2$] (9)**



The bite angle of the dppp ligand, P1-Ni-P2, of 99.81° compares closely with the corresponding angles of other complexes containing the diphosphine, dppp, in a six membered chelate ring. The remaining P-Ni-P bond angles, which are far from the ideal tetrahedral bond angle of 109.5°, describe the distorted tetrahedral structure (Table 11). The averaged values of the P-Ni-P bond angles of complex (**9**) compares closely with the averaged value of the P-Ni-P "tetrahedral" angle of the $[Ni(dppe)_2]$ complex of 114°. This averaged value is still greater than the ideal tetrahedral angle of 109.5° and is probably due to steric factors.

Table 11 Comparison of Ni-P bond angles between complex (**9**) and $[Ni(P\text{-}P)_2]$ complexes

$[Ni(P\text{-}P)_2]$	Bond Angles [°]			
	P1-Ni-P2	P2-Ni-P2'	P1-Ni-P1'	P1'-Ni-P2
$[Ni(dppp)_2]$	99.81(3)	106.34(4)	120.55(4)	115.09(3)
$[Ni(dppe)_2]$	90.8(1)	129.3(1)	113.8(1)	114.4(1)

3.3 Summary

A series of nickel (II) diphosphine aryl halide complexes of the type [Ni(P-P)(*o*-tolyl)X] (**1**) {P-P = dppe; X = Cl, P-P = dppe, dcpe, dBpe; X = Br} have been isolated for diphosphine ligands that contain a two carbon atom backbone. The compound [Ni(dppe)(*o*-tolyl)Cl] has been characterised by X-ray crystallography. Complexes of the type (**1**) are stabilised by the increased overlap of the d-orbitals of the metal with the *o*-tolyl ring, when the ring plane is perpendicular to the plane of the complex, to give a stable isomer, M. In solution, the evidence, obtained by $^{31}P\{^1H\}$ NMR spectroscopy, indicates a compromise between the stabilisation of the increased orbital overlap, and destabilisation by steric interactions. Increasing the steric bulk of the diphosphine ligand results in a decrease in the ratio of isomers M:N, where the isomer N is the isomer with the minimum steric interactions.

Complexes of the type [Ni(P-P)(*o*-tolyl)X] (**1**) {P-P = dppp, dcpn, Boxylyl; X = Br, Cl} were not isolated for diphosphine ligands that contain a three or four carbon atom backbone. For the reaction of the ligand dppp with [Ni(PPh$_3$)$_2$(*o*-tolyl)Br], the initial co-ordination of the ligand *via* one phosphorus atom is indicated by ^{31}P{^{1}H} NMR spectroscopy where broad signals for both free PPh$_3$ and co-ordinated dppp are evident. However, the dynamic nature of the product mixture prevented characterisation of the reaction products.

For the reaction of the ligand dcpn with [Ni(PPh$_3$)$_2$(*o*-tolyl)Br], the displacement reaction was very slow, and once a type (**1**) complex is formed it quickly disproportionates to the dihalide and diaryl complexes [Ni(dcpn)Br$_2$] and [Ni(dcpn)(*o*-tolyl)$_2$].

For the ligand, Boxylyl, the large steric bulk of this diphosphine prevents attack at the metal centre and initiation of the displacement reaction.

Type (**1**) complexes disproportionate in solution to the nickel (II) dihalide and nickel (II) diaryl complexes, and the disproportionation is accelerated by an increase in temperature.

3.4 Experimental

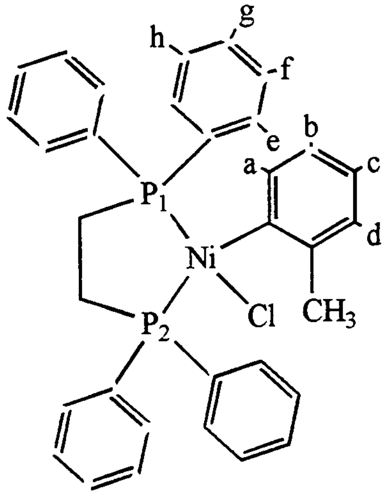
3.4.1 Synthesis of [Ni(PPh$_3$)$_2$(*o*-tolyl)Cl] (3)

[Ni(PPh$_3$)$_2$Cl$_2$] (4.82g, 7.4mmol) was placed in a thin walled Schlenk under nitrogen, together with zinc powder (3.3g, 50mmol); which had been activated by washing with saturated ammonium chloride solution and then dried in an oven at 100°C for 30 min. AIBN (0.11g, mols), 2-chlorotoluene (1.7ml, 14.5mmol) and dry THF (25ml) were quickly injected through a septum into the Schlenk, the mixture stirred mechanically, and treated with ultrasound (20,000MHz) for 20 min at 35°C. The resulting olive brown slurry was treated with dichloromethane (15ml) and the mixture filtered through celite. MeOH (40ml) was added to the filtrate which was then cooled to -20°C overnight. A small amount of yellow /brown solid crystallised (**5**) together with a yellow/ brown precipitate (a) and a fine black solid (nickel metal). The solid was removed by filtration using a coarse filter which allowed the fine black particles of metal to pass into the filtrate. The solid product was extracted with toluene (2 x 20ml) to give an orange solution which was taken to dryness under reduced pressure. Yield 0.45g (9%). ^{31}P{^{1}H}NMR (THF) δ -5 (s, PPh$_3$); δ 21.1 (s, [Ni(*P*Ph$_3$)$_2$(*o*-tolyl)Cl] (**3**)) ppm, in the ratio1:16.

3.4.2 Synthesis of [Ni(dppe)(*o*-tolyl)Cl] (5)

Dppe (0.27g, 0.68mmol) was dissolved in toluene (20ml) and was added *via* cannula to a yellow/brown solution of [Ni(PPh$_3$)$_2$(*o*-tolyl)Cl] (**1**) (0.39g, 0.55mmol) in toluene (20ml). On addition of the diphosphine the solution changed in colour to bright yellow. THF (10ml) was added and the solution was heated under reduced pressure to 60°C during which time the solution darkened to an orange solution and a grey solid precipitated. The solution was removed by cannular filtration and was left to stand at r.t. Crystals of [Ni(dppe)(*o*-tolyl)Cl] (**5**) suitable for X-ray crystallography were obtained and a structure determination was performed by D. Y. Naumov. The yellow crystals, isolated by manual separation, were dried *in vacuo*. Yield 0.1g, (31%). Found: C, 69.65; H, 5.26. $C_{73}H_{70}Cl_2Ni_2P_4$ requires C, 69.61; H, 5.60%. (unit cell contains two molecules of (**2**) and one molecule of toluene. ^{1}H NMR (d^8-THF) δ 2.3 (**3H**, s, C*H*$_3$C$_6$H$_4$Ni-); δ 2.5-2.7 (**4H**, m, C*H*$_2$P); δ 6.4-6.6 (**2H**, m, b; c); δ 6.9 (**1H**, m, d) δ

7.2 (**1H**, td, a) δ 7.2-7.4 (**4H**, m, c); δ 7.5 (**2.5H**, m,$C_6\underline{H}_5CH_3$); δ 7.6 (**8H**, m, e); δ 8.2-8.5 (**8H**, m, f) Hz. (See diagram below for key assignments) $^{31}P\{^1H\}$NMR (THF): δ 31.8 (d, P_2, $^2J_{P-P}$ 15.3Hz); δ 52.8 (d, P_1, $^2J_{P-P}$ 15.3Hz). ^{13}C (d^8-THF) NMR: δ 29.2 (m, $\underline{C}H_2$); δ 30.2 (m, $\underline{C}H_2$); δ 128.2 (d, $Ni\underline{C}_6H_4CH_3$); δ 128.9 (d, $Ni\underline{C}_6H_4CH_3$); δ 129.2 (s, $Ni\underline{C}_6H_4CH_3$); δ 129.5 (m, $Ni\underline{C}_6H_4CH_3$); δ 130.4, 130.7, 131.3, 132.0 (m, toluene); δ 132.9 (d, P$\underline{C}$, $^4J_{P-C}$ 8.4Hz); δ 133.5 (d, PCC$\underline{C}$, $^3J_{P-C}$ 10.3Hz); δ 134.7 (d, PC$\underline{C}$, $^2J_{P-C}$ 11.0Hz); δ 135.6 (d, P$\underline{C}$, $^1J_{P-C}$ 11.0Hz); δ 136.8 (m, Ni-$\underline{C}$) ppm.



3.4.3 Synthesis of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] (4)

This was synthesised by a similar method to 3.4.1. using $Ni(PPh_3)_2Br_2$ (4.50g, 6.1mmol) and 2-bromotoluene (1.6ml, 13.6mmol). Yield 2.2g (48%). Found: C, 65.71; H, 4.94. $C_{43}H_{37}BrNiP_2$ requires C, 68.97; H, 4.94%. The solid was found to be of sufficient purity to use in subsequent reactions. $^{31}P\{^1H\}$NMR (THF): δ -5 (s, PPh_3); δ 21.7 (s, [Ni($\underline{P}Ph_3$)$_2$(*o*-tolyl)Br] **(4)**); δ 22.8 (s, [Ni($\underline{P}Ph_3$)$_2$(*o*-tolyl)Br] **(4)**) ppm, in the ratio 1:2:10.

3.4.4 Synthesis of [Ni(dppe)(*o*-tolyl)Br] (6)

Dppe (0.40g, 1mmol) in toluene (20ml) was added *via* cannula to an orange solution of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br]**(4)** (0.58g, 0.78mmol) in toluene (40ml); and the mixture heated gently to 40°C to dissolve **(4)** in toluene. The orange colour lightened on addition of the phosphine. The mixture was stirred overnight resulting in the formation of a bright yellow precipitate. The filtrate was removed by cannula filtration and the solid was washed with toluene (2 x 5ml). The yellow product was dried *in vacuo*. Found: 0.32g (65%). The product was recrystallised from toluene-THF. Found: C, 64.44; H, 5.33. $C_{33}H_{38}BrNiP_2$ requires C, 63.10; H, 4.97. Calc. for $C_{37}H_{46}BrNiOP_2$ C, 63.83; H, 5.07%. ^{1}H NMR (d^8-THF): δ 2.3 (**3H**, s, $CH_3C_6H_4Ni$-); δ 2.5-2.7 (**4H**, m, CH_2P); δ 6.4-6.6 (**2H**, m, b and c); δ 6.9 (**1H**, m, d) δ 7.2 (**1H**, td, a) δ 7.2-7.4 (**4H**, m, c); δ 7.5 (**2.5H**, m,$C_6H_5CH_3$); δ 7.6 (**8H**, m, e); δ 8.2-8.5 (**8H**, m, f) Hz. $^{31}P\{^1H\}$NMR (d^8-THF): δ 32.9 (d, N, $^2J_{P-P}$ 17.9Hz); δ 35.8 (d, M, $^2J_{P-P}$ 16.8Hz); δ 53.2 (d, N, $^2J_{P-P}$ 18.9Hz); δ 55.6 (d, M, $^2J_{P-P}$ 16.0Hz) ppm, in the ratio 1:7:1:7.

3.4.5 Synthesis of [Ni(dcpe)(*o*-tolyl)Br] (7)

Dcpe (0.38g, 0.80mmol) in THF (20ml) was added slowly *via* cannula to $[Ni(PPh_3)_2(o$-tolyl)Br] (0.5g, 0.66mmol) in THF (40ml) at -78°C (acetone/Cardice). The solution was than allowed to warm to r.t. and stirred overnight. On standing nickel metal was deposited and the solution was filtered. The solvent was reduced under reduced pressure to ~10ml which resulted in further precipitation of nickel metal which was also removed by filtration. Precipitation of an orange solid occurred after refrigeration overnight at -20°C. The solid was washed with cold hexane (2 x 20ml at 0°C) and dried *in vacuo*. Yield 0.26g (60%). ^{1}H NMR (d^8-THF): δ 0.95-2.8 (**48H**, m, CH_2P and C_6H_{11}); δ 3.0 (**3H**, s, $CH_3C_6H_4Ni$-); δ 7.5 (**2.5H**, m, $C_6H_4CH_3$); δ 7.6 (**8H**, m,); δ 8.2-8.5 (**8H**, m,); $^{31}P\{^1H\}$NMR: (d^8-THF): δ 61.0 (d, M, $^2J_{P-P}$ 17Hz); δ 61.2 (d, N, $^2J_{P-P}$ 20Hz); δ 63.3 (d, N, $^2J_{P-P}$ 20Hz); δ 65.4 (d, M, $^2J_{P-P}$ 18Hz) ppm, in the ratio 6:1:1:6.

3.4.6 Synthesis of [Ni(dBpe)(*o*-tolyl)Br] (8)

DBpe (0.11g, 0.33mmol) in THF (10ml) was cooled to -78°C (acetone/cardice) and was added slowly via cannula to $[Ni(PPh_3)_2(o$-tolyl)Br] (0.25g, 0.33mmol) in THF (30ml) at -78°C (acetone/Cardice). The reaction mixture was allowed to warm to -20°C and was stirred at this temperature for 1.5h. A $^{31}P\{^1H\}$NMR spectrum was obtained which indicated that the reaction had not gone to completion so it was stirred overnight at R.T. Heating was eventually required to complete the reaction. The solvent was taken to a minimum under reduced pressure and toluene (5ml) was added which resulted in the precipitation of an orange solid after refrigeration overnight at -20°C. The solid was washed with hexane (3 x 20ml) and dried *in vacuo*. Yield 34mg, (19%) ^{1}H NMR (d^8-THF): δ 3.1 (**3H**, s, $C\underline{H}_3C_6H_4Ni$-); δ 1.2-2.2 (**40H**, m, $C\underline{H}_2P$ and $\{C(C\underline{H}_3)_3\}$); δ 6.6-6.9 (**3H**, m, $C_6\underline{H}_3HCH_3$ abc); δ 7.5-7.7 (**1H**, m, $C_6H_3CH_3$ - *o*-$\underline{H}$). $^{31}P\{^1H\}$NMR (d^8-THF): δ 64.5 (d, M, $^2J_{P-P}$ 6Hz); δ 65.3 (d, N, $^2J_{P-P}$ 7Hz); δ 70.7 (d, M, $^2J_{P-P}$ 7Hz); δ 71.6 (d, N, $^2J_{P-P}$ 6 Hz) ppm, in the ratio 3:1:1:3.

3.4.7 Reaction of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] with dppp

Dppp (0.09g, 0.22mmol) was dissolved in toluene (10ml) and was added via cannular to an orange solution of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br](**4**) (0.15g, 0.78mmol) in toluene (20ml); gentle heating was required to dissolve (**4**) in toluene. The mixture was stirred overnight. A $^{31}P\{^1H\}$NMR (toluene) spectrum indicated several products were present in equilibrium and attempts to isolate the desired product were unsuccessful. $^{31}P\{^1H\}$NMR (toluene) δ -17.6 (br, (a), dppp/Ni-dppp (exchange)); (δ -5 (v.br (b), PPh$_3$/Ni-PPh$_3$ (exchange)); δ = 15.6-15.3 (br (b), PPh$_3$/Ni-PPh$_3$); δ 21.7 (br, (a), dppp/Ni-dppp (exchange)) ppm, in the ratio 4:30:10:4.

3.4.8 Reaction of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] with dcpn

Dcpn (0.20g, 0.39mmol) in toluene (10ml) was added at r.t. to [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] **(3)** (0.25g, 0.31mmol) in toluene (20ml) with stirring. After 3 days a purple solid had precipitated leaving a yellow/brown solution. A $^{31}P\{^1H\}$NMR spectrum was obtained on the yellow/brown solution $^{31}P\{^1H\}$NMR (toluene): δ -15 (s, dcpn); δ -5 (s, PPh$_3$); δ 21.7 (s, [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] **(3)**); δ 22.8 (s, [Ni($\underline{P}$Ph$_3$)$_2$(*o*-tolyl)Br] **(3)**); δ 44.4 (s, [Ni($\underline{dcpn}$)$_2$(*o*-tolyl)$_2$]) ppm, in the ratio 12:10:2:10:10. The purple solid was attributed to the complex [Ni(dcpn)Br$_2$].

3.4.9 Reaction of [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] with Boxylyl

Boxylyl (0.05g, 0.13mmol) in THF (10ml) was added to [Ni(PPh$_3$)$_2$(*o*-tolyl)Br] **(3)** (15mg, 0.02mmol) in THF (5ml), at -20°C and allowed to warm to r.t. No colour change was observed during the mixing and $^{31}P\{^1H\}$NMR indicated that a reaction had not occurred. $^{31}P\{^1H\}$NMR (THF) δ -5 (s, PPh_3, 1); δ 24.2 (s, Boxylyl); δ 21.7 (s, [Ni(*P*Ph$_3$)$_2$(*o*-tolyl)Br] **(3)**, 2); δ 22.8 (s, [Ni(*P*Ph$_3$)$_2$(*o*-tolyl)Br] **(3)**, 10) ppm, in the ratio 1:2:10.

3.4.10 Reaction of [Ni(dppp)Cl$_2$] with 2PPh$_3$ and 2-chlorotoluene and NaOMe in MeOH

Ni(dppp)Cl$_2$ (0.50g, 0.92mmol) was placed in a Schlenk tube together with PPh_3 (0.73g, 2.8mmol). Toluene (5ml) was added in which the Ni(dppp)Cl$_2$ and the mixture was stirred overnight. NaOMe solution in methanol (0.805mols dm^{-3}, 3cm^3) was added by syringe, and resulted in an immediate colour change of the suspension from a deep red to an orange coloured solution. The mixture was stirred for 2h by which time a large amount of orange solid precipitated. The solution was filtered to give filtrate A and an orange solid B.

Filtrate A was reduced to a solid under reduced pressure and redissolved in toluene. 2-chlorotoluene was added to the toluene solution and heated to the reflux temperature under reduced pressure (50°C) for 0.5h. During this time, a colour change from red to orange was observed. After 3 days a pale green solid was removed by filtration to give an orange/yellow solution of which a $^{31}P\{^1H\}$NMR spectrum was obtained {$^{31}P\{^1H\}$NMR (toluene) δ -8 to 4 (v. br, [Ni(dppp)(PPh$_3$)Cl], paramagnetic Ni(I)); δ 15.1 (d, tentively assigned to [Ni(dppp)(*o*-tolyl)Cl])]); δ 17.5 (m); δ 32.8 (m); δ 35.9 (m), δ 36.7 (m); δ 37.0 (d, tentively assigned to [Ni(dppp)(*o*-tolyl)Cl]) ppm, in the ratio 3:1:1:1:2:3}. Attempts to isolate the desired product were unsuccessful. A single crystal identified as [Ni(dppp)$_2$] was isolated from filtrate A and an X-ray structural analysis performed by A. S. Batsanov. Selected bond lengths and angles are shown in Table 3 and 4.

The orange solid B was redissolved in toluene and 2-chlorotoluene was added (10ml, XS). The solution was stirred and heated to 65°C under reduced pressure for 2h and was stirred at r.t.overnight. On returning the solution was orange and an oxidative addition reaction of the 2-chlorotoluene had not occurred $^{31}P\{^1H\}$NMR (toluene): δ -5 (s, br ,PPh_3); δ 10.4 (s, [$Ni(dppp)_2$]) ppm.

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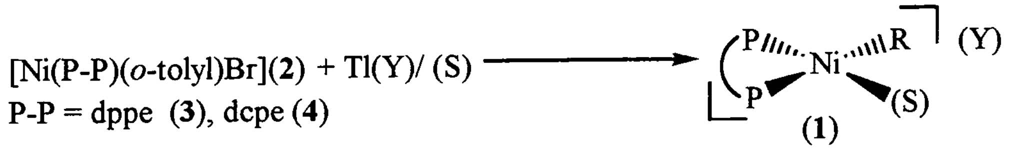
Chapter 4

Cationic Nickel Diphosphine Aryl Complexes Containing Weakly Co-ordinating Anions [Ni(P-P)(*o*-tolyl)(S)](Y)

4.1 Introduction

The synthesis of cationic complexes of the type [Ni(P-P)R(S)](Y) (**1**), which contain a free co-ordination site and a weakly co-ordinating anion, is relevant to catalysis. However, there are relatively few examples of these cationic nickel (II) complexes, which contain diphosphine ligands reported in the literature. An example is [Ni(dppe)(2,4,6-{CH_3}$_3$$C_6H_4$)(py)]($BF_4$), having an *o*-substituted aryl group.[1] Cationic nickel(II) methyl complexes containing the monophosphine ligand, PMe_3, in combination with the diphosphine ligands, dmpe and dppe, are also reported in the literature.[2] The complex [Ni(dmpe)$_2$Me](BF_4) was isolated, but the complexes [Ni(dppe)(PMe_3)$_2$Me](BF_4) and [Ni(dppe)(PMe_3)Me](BF_4) were only characterised in solution.[2] The chemistry of nickel monophosphine aryl and alkyl complexes of the type $[Ni(PR_3)_2R(S)]^+$ has been studied in greater detail than that of the complexes containing diphosphine ligands.[1,3,4] Several five co-ordinate alkyl complexes containing the tetradentate ligand, np$_3$ {tris(2-diphenylphosphinoethyl)amine}, which co-ordinates *via* three phosphorus atoms and one nitrogen atom, (e.g. [Ni(np$_3$)R]BPh_4 {R = CH_3, C_2H_5, $CH_2C_6H_5$}) have also been described and characterised previously.[5]

In the present study, the complexes of the type (**1**) have been synthesised according to Equation 1 by a metathetical displacement of a halide ion (X), from the complexes of the type [Ni(P-P)RX] (**2**) by a thallium salt containing a weakly co-ordinating counterion.

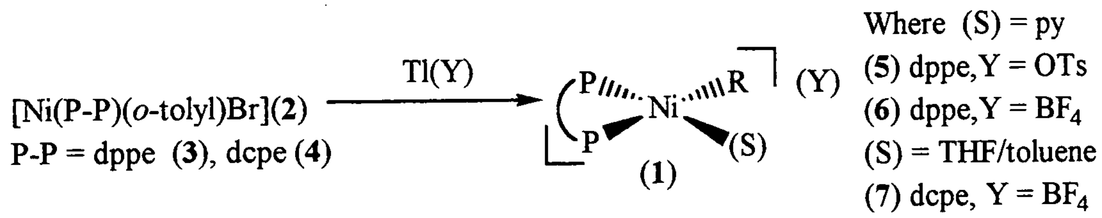


Equation 1

The co-ordination strength of the counterion influences the chemistry of these complexes and differences between the tosylate and perfluoroborate counterion have been observed by $^{31}P\{^1H\}$ NMR spectroscopy.

4.2 Results and Discussion

Cationic nickel (II) diphosphine complexes of the type [Ni(P-P)(*o*-tolyl)(S)](Y) (**2**) (Scheme 1) have been studied in solution by the reaction of complexes of the type [Ni(P-P)(*o*-tolyl)Br] (**1**) (Chapter 3), where P-P is dppe (**3**) or dcpe (**4**), with TlOTs or $TlBF_4$ in THF/toluene or THF/pyridine mixed solvents.



Scheme 1

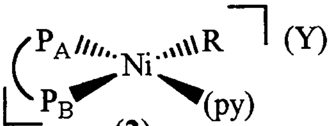
Unfortunately, the variation of the diphosphine ligand in type [Ni(P-P)(*o*-tolyl)(S)](Y) (**1**) complexes was restricted to the availability of the starting reagent i.e. [Ni(P-P)(*o*-tolyl)Br] (**2**) {P-P = dppe, dcpe, dBpe only are available). Isolation of complexes of the type [Ni(P-P)(*o*-tolyl)(S)](Y) (**1**) was difficult due to their decomposition in solution at r.t. and the limited source of the starting complexes (**2**). However, synthesis of a complex of the type [Ni(P-P)(*o*-tolyl)(S)](Y) (**2**) was achieved and the complex [Ni(dppe)(*o*-tolyl)(py)](OTs) (**5**) was isolated. Complexes (**5**), (**6**) and (**7**) were detected in solution by $^{31}P\{^1H\}$ NMR spectroscopy.

Comparison of OTs^- and BF_4^- Counterions

Complexes containing 1,2-bis(diphenylphosphino)ethane (dppe)

The comparison of the $^{31}P\{^1H\}$ NMR spectra of the complexes [Ni(dppe)(*o*-tolyl)(py)](OTs) (**5**) and [Ni(dppe)(*o*-tolyl)(py)](BF_4) (**6**) illustrates the co-ordinating ability of the anions OTs^- and BF_4^- and their influence on the structure of the nickel product. The spectrum of [Ni(dppe)(*o*-tolyl)(py)](BF_4) (**6**) (*Figure 1*) consists of sharp peaks and contains two doublets as expected for two inequivalent phosphorus atoms, whereas, the spectrum of the complex [Ni(dppe)(*o*-tolyl)(py)](OTs) (**5**) (*Figure 2*) is broad. This illustrates that in this system, the tosylate anion is a weakly co-ordinating ligand, whereas the perfluorborate anion is truly a non co-ordinating ion. A comparison of the $^{31}P\{^1H\}$ NMR spectra of dppe complexes is summarised (Table 1). [Ni(dppe)(2,4,6-$\{CH_3\}_3C_6H_3$)(py)](BF_4), which contains the perfluoroborate anion, has also been observed to exhibit sharp doublets in the $^{31}P\{^1H\}$ NMR spectrum.

Table 1 $^{31}P\{^1H\}$ NMR data of complexes of the type [Ni(dppe)R(py)](Y)



(**2**)

[Ni(dppe)R(py)](Y) (**1**)	solvent	δP_A (ppm)	δP_B (ppm)	$J_{(P-P)}$ Hz
[Ni(dppe)(2-$CH_3C_6H_4$)(py)](OTs) (**5**)	d^8-THF	40 (br)	53.7	17
[Ni(dppe)(2-$CH_3C_6H_4$)(py)](BF_4) (**6**)	d^8-THF	42.9	52.6	12
[Ni(dppe)(2,4,6-$\{CH_3\}_3C_6H_4$)(py)](BF_4)[1]	THF	36.5	49.6	9

Figure 1. **The $^{31}P\{^{1}H\}$ NMR Spectrum of $[Ni(dppe)(o\text{-tolyl})(py)](BF_4)$ (6)**

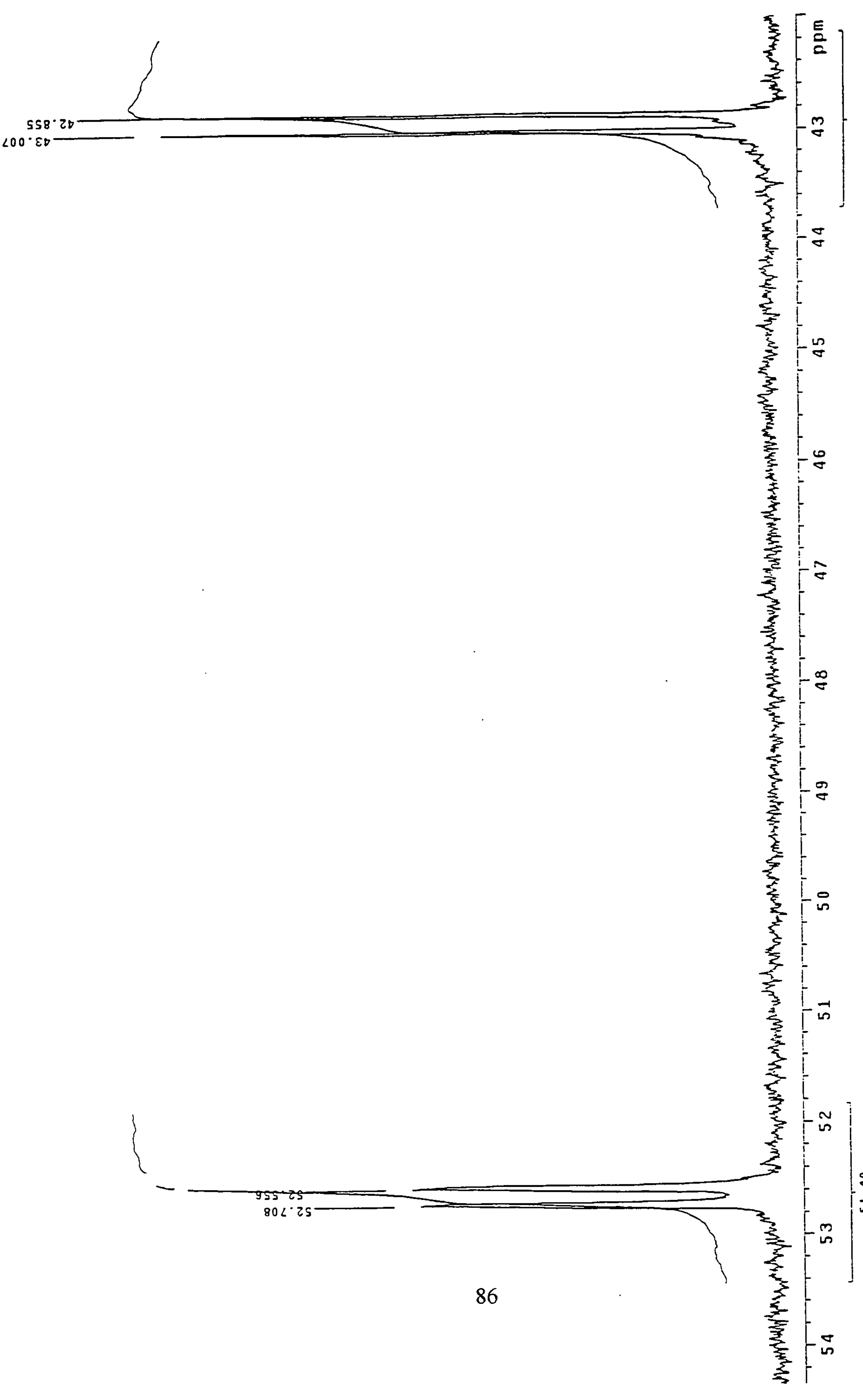
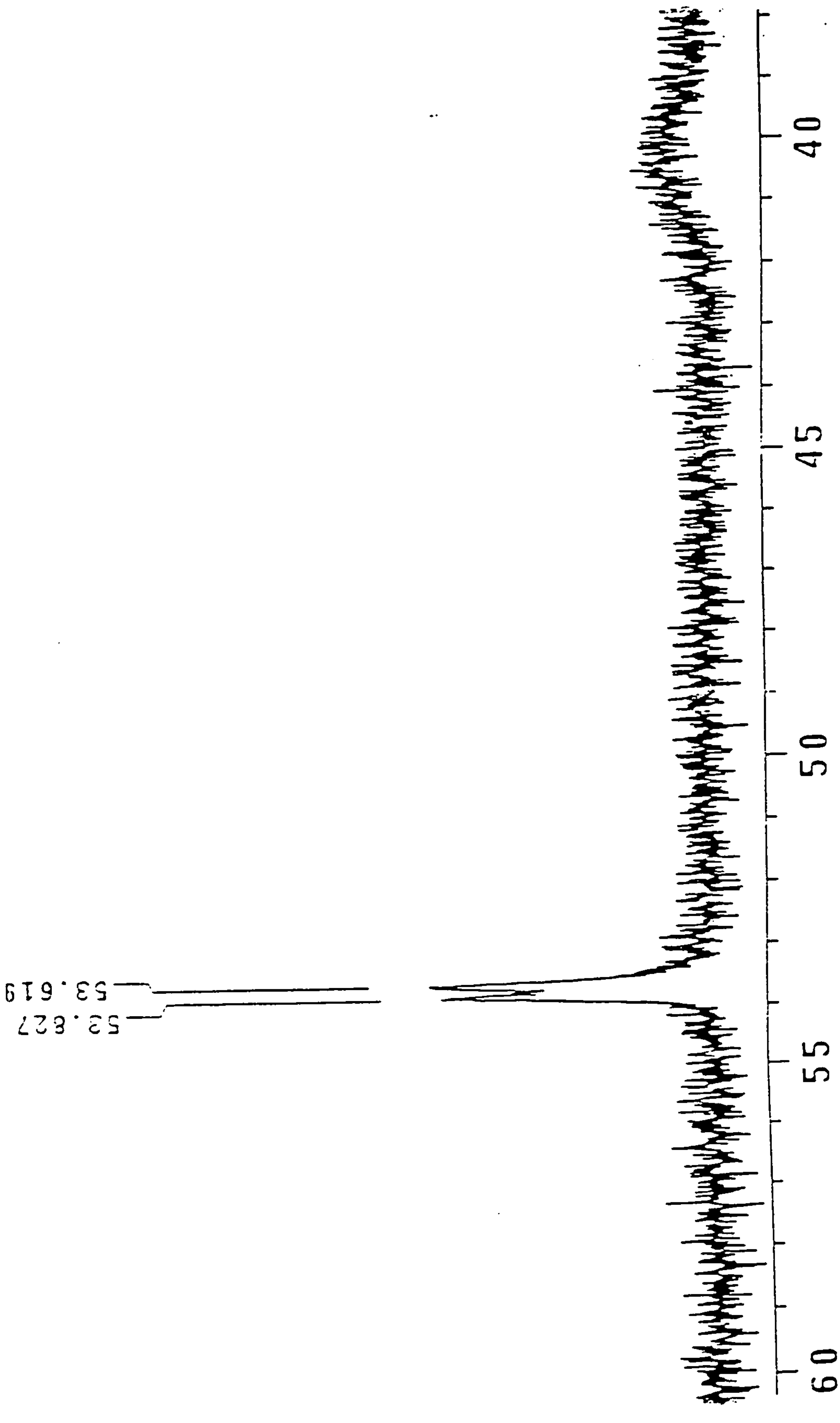


Figure 2. **The $^{31}P\{^1H\}$ NMR Spectrum of [Ni(dppe)(*o*-tolyl)(py)](OTs) (5)**



The neutral complex [Ni(dppe)(*o*-tolyl)(OTs)] (**8**), was characterised by elemental analysis, and crystallised from a pyridine solution of complex (**5**). This indicates that the tosylate group can co-ordinate as a ligand in the solid state. Elemental analysis on a sample of solid which had precipitated, rather than crystallised from the pyridine reaction solution contained both the cationic complex [Ni(dppe)(*o*-tolyl)(py)](OTs) (**5**) and the neutral complex [Ni(dppe)(*o*-tolyl)(OTs)] (**8**). When complex (**8**) is redissolved in the weakly co-ordinating solvent, pyridine, then it reverts back to the cationic complex (**5**).

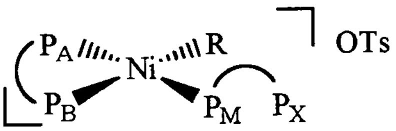
The reaction of [Ni(dppe)(*o*-tolyl)(OTs)] (**8**) with two molar equivalents of the diphosphine ligand, dppe, in pyridine resulted in a cationic complex of the type [Ni(dppe)(*o*-tolyl){dppe}](OTs) (**9**) which was identified by $^{31}P\{^{1}H\}$ NMR spectroscopy (Equation 2).

$$[\mathrm{Ni(dppe)(\mathit{o}\text{-}tolyl)(OTs)}](\mathbf{8}) + \mathrm{dppe} \xrightarrow{\mathrm{py/MeOH}} [\mathrm{Ni(dppe)(\mathit{o}\text{-}tolyl)\{dppe\}}]\mathrm{OTs} \quad (\mathbf{9})$$

Equation 2

The ABMX $^{31}P\ \{^{1}H\}$ NMR spectrum of complex (**9**) was indicative of four different phosphorus environments which correspond to one dppe ligand co-ordinated in the usual chelating fashion, and the other dppe ligand co-ordinated through only one of its phosphorus atoms (**i**).

(**i**)

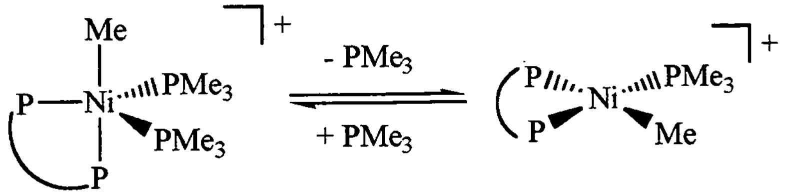


(**9**)

The observed chemical shifts, calculated coupling constants and integration support this structure: P_X appears as a broad singlet with an increase in the value of chemical shift by

0.4ppm from the chemical shift value of the free dppe ligand (the small coupling between P_M and P_X is not resolved). P_M appears as a doublet of pseudo triplets (again the small coupling between P_M and P_X is not resolved, a doublet of doublet of doublets should be observed) and a large *trans* coupling constant $^2J_{PA-PM}$ of 235Hz with P_A is observed which agrees with coupling constants of previously characterised *trans* related P atoms in square-planar complexes. P_B appears as a pseudo triplet where the *cis-* coupling constants of $^2J_{PA-PB}$ and $^2J_{PB-PM}$ are of similar magnitude. P_A appears as a doublet of doublets, the large *trans* coupling constant $^2J_{PA-PX}$ of 235Hz with P_X is confirmed and the smaller *cis-* $^2J_{PB-PM}$ of 17Hz again agrees with coupling constants for previously characterised complexes. The integration of each P atom is in the ratio $P_A : P_B : P_M : P_X$ of 1:1:1:1.

The behaviour of the 16-electron complex (**9**) in solution at r.t. followed by $^{31}P\{^1H\}$ NMR spectroscopy indicates that complex (**9**) contrasts with the five co-ordinate trigonal bypyramidal complex of the type $[Ni(dppe)(PMe_3)_2Me](BF_4)$ and the four co-ordinate square-planar complex of the type $[Ni(dppe)(PMe_3)Me](BF_4)$ containing the ligand, dppe, which had to be characterised in solution by low temperature $^{31}P\{^1H\}$ NMR spectroscopy due to their instability and fluxionality at r.t..[2] Cationic 16-electron nickel alkyl complexes are less stable than 18-electron species with which they tend to form an equilibrium. $[Ni(dppe)(PMe_3)_2Me](BF_4)$ and $[Ni(dppe)(PMe_3)Me](BF_4)$ coexist in an acetone solution of $[Ni(dppe)(PMe_3)_2Me](BF_4)$ (Equation 4).[2]



Equation 4

The absence of an equilibrium in solution for the complex [Ni(dppe)(*o*-tolyl){dppe}](OTs) (**9**) may be attributed to the enforced stereochemistry of the resultant five co-ordinate complex. The methyl group in the five co-ordinate trigonal bypyramidal complex [Ni(dppe)(PMe_3)$_2$Me](BF_4) is situated in an axial position of the trigonal bypyramid, and the chelating diphosphine ligand, dppe, co-ordinates in an axial-equatorial fashion. For d^8 electron configurations poorer σ-donors favour the equatorial sites in trigonal bypyramidal conformations and the apical sites in square-pyramidal conformations.[6] Therefore, the *o*-tolyl ligand would be expected to occupy an equatorial site of a trigonal bypyramid, and a second dppe ligand would be forced to co-ordinate in an unfavourable equatorial-equatorial fashion. Chelation of a second dppe ligand may also be achieved if a five co-ordinate square-pyramidal complex of the type [Ni(dppe)$_2$R](OTs) similar to the complex of the type [Ni(dmpe)$_2$Me](BF_4)[2] was obtained. However, this is unlikely because of the increased steric bulk of the dppe ligand compared to the dmpe ligand. The addition of a molar equivalent of the diphosphine ligand dmpe to the five co-ordinate trigonal bypyramidal complex of the type [Ni(dmpe)(PMe_3)$_2$Me](BF_4) resulted in the formation of the five co-ordinate square-pyramidal complex of the type [Ni(dmpe)$_2$Me](BF_4).[2]

Complexes containing 1,2-bis(dicyclohexylphosphino)ethane (dcpe)

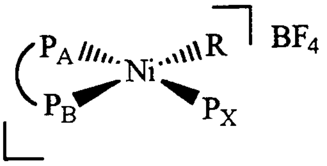
Efforts to synthesise cationic Ni(II) dcpe adducts similar to those observed for dppe, were only partially successful since the reaction of [Ni(dcpe)(*o*-tolyl)Br] (**4**) with $TlBF_4$ did not go to completion. This may be due to the low temperature (-20°) at which the reaction was carried out to avoid the decompostiton of the starting material and the potential product. The appearance of the $^{31}P\{^1H\}$ NMR spectrum at r.t. showed two new doublets corresponding to the complex [Ni(dcpe)(*o*-tolyl)(S)]BF_4 (**7**) and two sets of doublets corresponding to the presence of unreacted starting material (**4**) in the ratio of 5:2. After the NMR sample had been at r.t. for one day, the appearance of the $^{31}P\{^1H\}$ NMR spectrum was reduced to two singlets at δ -0.6 and δ 83.5 ppm, attributed to free dcpe, and [Ni(dcpe)Br_2] respectively. These were formed from the decomposition of the product [Ni(dcpe)(*o*-tolyl)(S)]BF_4 (7) and the starting material [Ni(dcpe)(*o*-tolyl)Br] (**4**). Isolation of the complex [Ni(dcpe)(*o*-tolyl)(S)]BF_4 (7) would therefore be difficult due to its thermal instability. Hence, the remaining reaction solution which contained a mixture of the complexes [Ni(dcpe)(*o*-tolyl)(S)]BF_4 (7) and [Ni(dcpe)(*o*-tolyl)Br] (**4**), which had been stored at -20°C, was reacted with the monophosphite ligand, $P(OMe)_3$ in the hope of isolating the complex [Ni(dcpe)(*o*-tolyl){$P(OMe)_3$}]BF_4 (**10**) (Equation 5).

$$[Ni(dcpe)(o\text{-tolyl})(S)]BF_4\ (7) + P(OMe)_3 \longrightarrow [Ni(dcpe)(o\text{-tolyl})\{P(OMe)_3\}]BF_4\ (\mathbf{10})$$

Equation 5

Unfortunately, complex (**10**) could not be isolated but was studied in solution by $^{31}P\{^1H\}$ NMR spectroscopy. The signals assigned to [Ni(dcpe)(*o*-tolyl)(S)]BF_4 (7) disappeared when the solution was reacted with $P(OMe)_3$ but the signals assigned to the unreacted starting complex [Ni(dcpe)(*o*-tolyl)Br] (**4**) remained unchanged. An ABX spectrum was obtained for [Ni(dcpe)(*o*-tolyl){$P(OMe)_3$}]BF_4 (**10**) (**ii**). P_A appeared as a doublet of doublets with a large *trans*- coupling constant of $^2J_{PA\text{-}PX}$ 370Hz; the smaller coupling between P_A and P_B not being resolved. The coupling between P_B and P_X was resolved and found to be 50Hz. Both coupling constants were reciprocated for P_X which confirms the assigned structure.

(ii)



(10)

Complexes containing 1,2-bis(di-tert-butylphosphino)ethane (dBpe)

The reaction of the complex [Ni(dBpe)(*o*-tolyl)Br] with TlOTs was carried out at r.t. on a very small scale. The $^{31}P\{^1H\}$ NMR spectrum obtained was very broad, and analogous to that observed for the dppe complex, [Ni(dppe)(*o*-tolyl)(py)](OTs) (**5**). However, the limited availability of starting material and the small scale of the reaction prevented further analysis.

4.3 Summary

A cationic complex of the type [Ni(dppe)(*o*-tolyl)(py)](OTs) and the cationic complexes of the type [Ni(P-P)(*o*-tolyl)(py)](BF_4) {P-P = dppe, dcpe) have been characterised in solution. In addition, the neutral complex [Ni(dppe)(*o*-tolyl)(OTs)] has been characterised by elemental analysis. In solution, the behaviour of the tosylate group as a weakly co-ordinating anion is confirmed, and compares with the truly non co-ordinating behaviour of the perfluoroborate group. In the solid state, the tosylate group can behave as a co-ordinating ligand illustrated by the characterisation of the complex [Ni(dppe)(*o*-tolyl)(OTs)] which crystallised from a pyridine solution of the complex [Ni(dppe)(*o*-tolyl)(py)](OTs).

Complexes of the type [Ni(P-P)(*o*-tolyl)(P)](Y) {P = dppe, P($OMe)_3$} have been characterised in solution. The identification of these complexes further confirms that a free co-ordination site is readily available for an incoming ligand which is neccessary for catalytic activity. The unstable nature of the complexes of the type [Ni(P-P)(*o*-tolyl)(py)](Y), indicates that the complexes must be synthesised and used immediately for testing catalytic activity.

4.4 Experimental

4.4.1 Synthesis of TlOTs

Solid Tl_2CO_3 (10g, 21.3mol) was added to a stirred solution of HOTs (9.0g, 52.3mol) dissolved in monoglyme (50ml). The resulting white solid was washed with cold water, followed by three aliquots of diethylether and dried *in vacuo*. Yield (11.55g, 72%).

4.4.2 NMR study of the reaction of [Ni(dppe)(*o*-tolyl)Br] (3) with $TlBF_4$ and pyridine

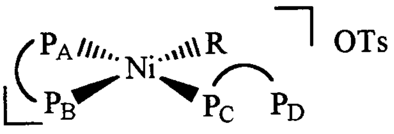
[Ni(dppe)(o-tolyl)Br] (**3**) (60mg, 0.01mmol) was dissolved in THF and stirred. Solid $TlBF_4$ (0.04g, 0.16mmol) was added in the absence of light. After 2h the precipitated TlBr was removed by filtration. Pyridine (0.01ml, 1.6mmol) in THF was added to the reaction which was then stirred overnight. The product was identified as [Ni(dppe)(*o*-tolyl)(py)]BF_4 (**6**) by $^{31}P\{^1H\}$NMR (THF): δ 52.6 (d, $^2J_{P-P}$ 12.3Hz); δ 42.9 (d, $^2J_{P-P}$ 12.3Hz);

4.4.3 Synthesis of [Ni(dppe)(*o*-tolyl)(py)]OTs

Dppe (0.40g, 1mmol) in toluene (20ml) was added via cannula to an orange solution of [Ni(PPh_3)$_2$(*o*-tolyl)Br] (0.61g, 0.81mmol) in toluene (40ml). The mixture was stirred overnight resulting in the formation of a bright yellow precipitate. The filtrate was removed by cannula filtration and the solid was washed with toluene (2 x 10ml). The yellow product was dried *in vacuo* and then dissolved in THF (30ml). Solid TlOTs (0.304g, 0.81mmol) was added to the solution in the absence of light and was stirred for 2h. The solid TlBr was removed by filtration. Pyridine (0.07ml, 0.81mmol) was added to the filtrate and the mixture stirred overnight. Further precipitation of TlBr occurred which was subsequently removed by filtration. The solvent was reduced to a minimum (10ml) and toluene (10ml) was added, resulting in the precipitation of an orange solid. Yield 0.26g (40%). $^{31}P\{^1H\}$NMR (THF): δ 53.7 (d, $^2J_{P-P}$ 16.8Hz); δ 40 (br). Over time an orange crystalline solid precipitated which was found to be [Ni(dppe)(*o*-tolyl)OTs]. Found: C, 66.89; H, 5.44. $C_{40}H_{38}NiO_3P_2S$ requires C, 66.78; H, 5.32%.

4.4.4 NMR study of the reaction of [Ni(dppe)(*o*-tolyl)(OTs)] with dppe in toluene/MeOH

[Ni(dppe)(*o*-tolyl)(OTs)] (0.1g, 0.13mmol) was placed in a flask together with dppe (0.1g, 0.25mmol) and dissolved in methanol (8ml) and toluene (5ml). A colour change from orange to yellow occurred. $^{31}P\{^{1}H\}$NMR (MeOH/toluene): δ -13.2 (s, dppe); δ -12.8 (P_D, dd, $^{2}J_{PC\text{-}PD}$ not resolved); δ 21.5 (P_C, ddd, $^{2}J_{PC\text{-}PA}$ 235Hz); δ 44.7 (P_B, pseudo t (dd)); δ 51.5 (P_A, dd, $^{2}J_{PA\text{-}PB}$ 16.8Hz, $^{2}J_{PC\text{-}PA}$ 235Hz) ppm. The data are consistent with the preparation of the following complex.



4.4.5 Reaction of [Ni(dcpe)(*o*-tolyl)Br] with $TlBF_4$ in toluene/THF

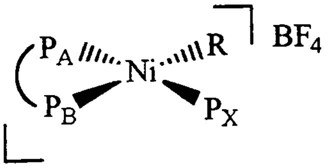
[Ni(dcpe)(*o*-tolyl)Br] (4) (50mg, 0.08mmol) was placed in a flask together with toluene (20ml) in which it was slightly soluble. THF (10ml) was added in which all complex (4) dissolved. The flask was cooled to -50°C and solid $TlBF_4$ was added. The mixture was stirred for 1h and allowed to warm to -20°C. The solid TlBr was removed by filtration and the filtrate was added directly to acetonitrile (10ml). Attempts at crystallisation from the minimum amount of solvent and cooling (-20°C) were fruitless, and resulted in the decomposition of the complex. Decomposition was identified by the change in the $^{31}P\{^{1}H\}$NMR (THF/toluene/CH_3CN) spectrum to a singlet δ 83.4ppm due to [Ni(dcpe)Br_2]. $^{31}P\{^{1}H\}$NMR (THF/toluene/CH_3CN): δ 61.1 (d, $^{2}J_{P\text{-}P}$ 17Hz, [Ni(dcpe)(*o*-tolyl)Br]); δ 64.4 (d, $^{2}J_{P\text{-}P}$ 15Hz, [Ni(dcpe)(*o*-tolyl)(S)]BF_4); δ 65.5 (d, $^{2}J_{P\text{-}P}$ 17Hz, [Ni(dcpe)(*o*-tolyl)Br]); δ 67.5 (d, $^{2}J_{P\text{-}P}$ 15Hz, [Ni(dcpe)(*o*-tolyl)(S)]BF_4) ppm, in the ratio 2:5:2:5, and where S = MeCN.

4.4.6 NMR study of the reaction of [Ni(dBpe)(*o*-tolyl)Br] with TlOTs in toluene/THF

TlOTs (0.1mmol) was added to [Ni(dBpe)(*o*-tolyl)(Br)] (6mg, 0.01mmol) in THF (5ml). TlBr was precipitated and was removed by filtration. The filtrate was added to an excess of pyridine in a methanol/toluene 2:1 solution. The $^{31}P\{^1H\}$NMR spectrum was very broad δ 50-70ppm, and the complex formed could not be identified.

4.4.7 NMR study of the reaction of [Ni(dcpe)(*o*-tol)Br] with $TlBF_4$ and $P(OMe)_3$ in toluene/THF

To an aliquot of solution from 4.4.5 at -20°C was added an excess of $P(OMe)_3$ and the mixture was shaken. An immediate colour change occurred to give a darker orange coloured solution. $^{31}P\{^1H\}$NMR (THF): δ 57.4 (P_A, dd, $^2J_{PA-PC}$ 370Hz); δ 68.3 (P_B, dd, $^2J_{PB-PX}$ 50Hz, 5); δ 111.2 (P_X, dd, $^2J_{PB-PX}$ 50, $^2J_{PA-PX}$ 372 Hz); δ 141 (s, $P(OMe)_3$) ppm corresponds to the formation of [Ni(dcpe)(*o*-tol)P(OMe)$_3$]BF$_4$.



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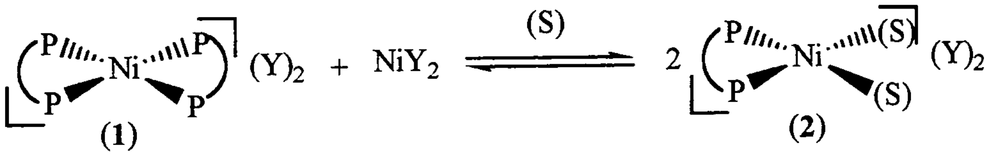
Chapter 5
Solution Studies of Nickel (II) Diphosphine and Bis-diphosphine Complexes Containing Weakly Co-ordinating Anions

5.1 Introduction

Cationic nickel (II) diphosphine complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (**1**) containing the weakly or non co-ordinating anions ($Y = NO_3, BF_4, PF_6$) have been reported in the literature.[1,2] However, no examples of type (**1**) complexes containing the weakly co-ordinating anions, Y, where Y = (OTs) and (OTf) are known. In this chapter, a series of novel cationic nickel (II) bisdiphosphine complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (**1**) and nickel (II) diphosphine complexes of the type $[Ni(P\text{-}P)(S)_2](Y)_2$ (**2**) are reported, together with details of characterisation and solution properties.

Complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (**1**) and $[Ni(P\text{-}P)(S)_2]^{2+}$ (**2**) were difficult to isolate as pure solids because of a solvent dependent equilibrium occurring in solution according to Equation 1. Consequently, the complexes were studied in solution.



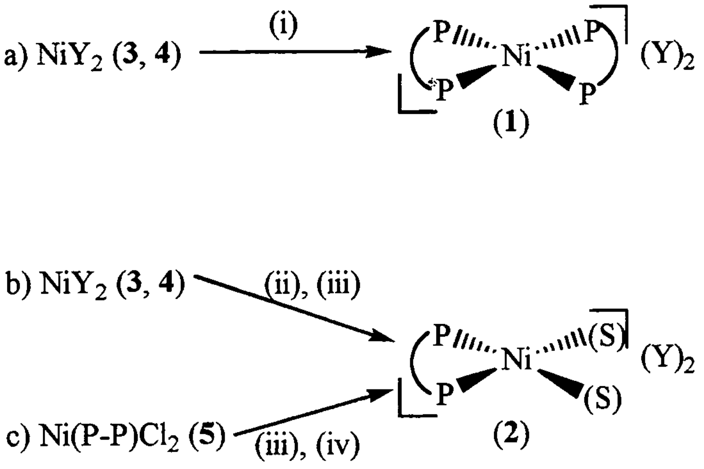
Equation 1

A complex of the type $[Ni(P\text{-}P)_2](Y)_2$ (**1**) was isolated in the case of $[Ni(dppe)_2](OTs)_2.2MeOH$ (**5a**) and was characterised by X-ray crystallography.

For type (**1**) and (**2**) complexes, when the number of carbons in the diphosphine backbone is greater than two, {P-P = dppp, dcpn or Boxylyl}, equilibria in solution, similar to that observed in the two carbon atom backbone complexes are apparent. However, for dppp, dcpn and Boxylyl, tetrahedral species occur in solution, and consequently type (1) and (2) complexes were not observed directly due to the broadening of the $^{31}P\{^1H\}$ spectrum.

5.2 Results and Discussion

A series of four co-ordinate complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ **(1)** and $[Ni(P\text{-}P)(S)_2](Y)_2$ **(2)** were observed and characterised in solution for a series of diphosphine ligands (Scheme 1). They were prepared by three different routes as shown in Scheme 1: (a) The direct reaction of nickel tosylate, $Ni(OTs)_2$, **(3)** or nickel triflate, $Ni(OTf)_2$ **(4)** with two equivalents of diphosphine; (b) The direct reaction of **(3)** or **(4)** with one equivalent of diphosphine in the presence of a weakly co-ordinating solvent; (c) A metathetical displacement of a halide ion from complexes of the type $[Ni(P\text{-}P)Cl_2]$ **(5)** using silver salts in the presence of a weakly co-ordinating solvent.



Where Y = OTs, P-P
(6) dppe, **(7)** dcpe
(8) dcpn, **(9)** dcpe,2PPh$_3$
(10) dcpe, dppe
Where Y = OTf, P-P
(11) dcpe

Where Y = OTs, P-P
(12) dcpe
Where Y = OTf, P-P
(13) dcpe

Scheme 1 (i) 2 P-P (ii) P-P (iii) CH_3CN (iv) AgOTs; AgOTf

Methods (i) and (ii) were the most effective of these routes due to difficulties in removing the silver salts produced in method (iii).

5.2.1 Synthesis of $Ni(OTs)_2$ and $Ni(OTf)_2$

Anhydrous $Ni(OTs)_2$ **(3)** was prepared, in low yield, by two different methods: firstly, the reaction of nickel acetate with *p*-toluenesulphonic acid in acetonitrile, to give an acetonitrile complex, $[Ni(CH_3CN)_6](OTs)_2$ which precipitated anhydrous $Ni(OTs)_2$ on the addition of diethylether (Equation 2); secondly, the metathetical reaction of the nickel (II) dichloride monoglyme adduct $[NiCl_2(CH_3O(CH_2)_2OCH_3)]$ with silver tosylate in methanol (Equation 3).

$$Ni(OAc)_2 + 2HOTs \xrightarrow[\text{(ii) } Et_2O]{\text{(i) } CH_3CN} Ni(OTs)_2 \text{ (3)}$$

Equation 2

$$[\,NiCl_2(CH_3O(CH_2)_2OCH_3] + 2AgOTs \xrightarrow[-2AgCl]{MeOH} Ni(OTs)_2 \text{ (3)}$$

Equation 3

The hydrated compound $Ni(OTs)_2.xH_2O$ can be prepared in much higher yields than the anhydrous $Ni(OTs)_2$. $Ni(CO_3).2Ni(OH)_2.4H_2O$ and $HOTs.H_2O$ were reacted in toluene and the water produced was removed by azeotropic distillation. The toluene was then removed under reduced pressure. The reaction was completed by heating the residue to 300°C with a bunsen flame (Equation 4).

$$Ni(CO_3).2Ni(OH).4H_2O + 2HOTs \xrightarrow[\text{Heat } 300^{\circ}C]{\text{toluene, } -H_2O} Ni(OTs)_2.xH_2O \textbf{ (3b)}$$

Equation 4

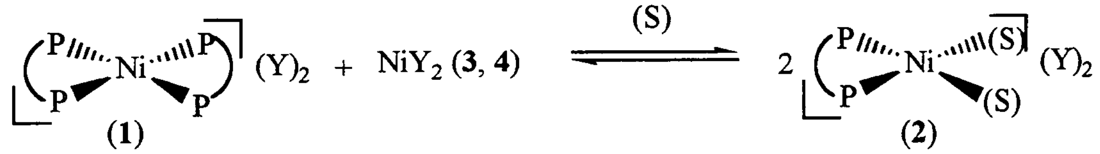
The behaviour of $Ni(OAc)_2$ contrasts with that of $Pd(OAc)_2$ when it was reacted with HOTs or HOTf in acetonitrile (Method 1). Addition of diethylether to the palladium reaction precipitates the complexes $[Pd(CH_3CN)_2(OTs)_2]$ and $[Pd(CH_3CN)_4](OTf)_2$.[3] However, in the case of nickel, the acetonitrile complexes were not isolated. Instead the nickel prefers to be six co-ordinate,[4] co-ordinating six acetonitriles in solution to give the octahedral complex $[Ni(CH_3CN)_6](OTs)_2$ **(14)**, or as a solvent free species **(3)** in the solid state.

The compound Ni(OTf)$_2$ (**4**) was prepared *via* method 2 which avoided the use of the fuming very hygrosopic acid, HOTf. The solvent employed was acetonitrile instead of methanol which resulted in the formation of a blue solution attributed to the complex [Ni(CH$_3$CN)$_6$](OTf)$_2$ (**15**). The solvent was reduced in volume to a minimum under reduced pressure which resulted in an "oily" blue liquid. Diethylether was added in an attempt to precipitate the solid Ni(OTf)$_2$ but this only resulted in the formation of two layers, therefore the diethylether was subsequently removed under reduced pressure. The oily blue liquid was heated (50°C) under reduced pressure which resulted in an oily green liquid; attributed to the complex [Ni(CH$_3$CN)$_4$](OTf)$_2$. Addition of methanol redissolved the oil to give a green solution. Both the excess acetonitrile and methanol were eventually removed by heating (90°C) under reduced pressure, which resulted in a pale green solid. Elemental analysis showed there was no co-ordination of acetonitrile in compound (**4**). However, elemental analysis suggested the presence of some co-ordinated monoglyme or methanol, indicated by the large amount of carbon present.

5.2.2 Solution Studies of [Ni(P-P)](Y)$_2$ (1) and [Ni(P-P)(S)$_2$](Y)$_2$ (2)

Extensive solution studies were carried out during the attempted synthesis of the nickel (II) complexes of the type [Ni(P-P)(S)$_2$](Y)$_2$ (**2**), which are analogous to the palladium systems that catalyse the reaction of CO and ethene in the presence of methanol to give polyketone or methyl propanoate.[3,5]

Unfortunately, attempts to isolate complexes of the type (**2**) were unsuccessful due to a solvent dependent equilibrium in solution (Equation 5). Therefore, complexes of the type (**1**) and (**2**) were studied in solution by $^{31}P\{^{1}H\}$NMR spectroscopy. The equilibrium (Equation 5) was predominantly to the left, favouring the formation of type (**1**) complexes, and the precipitation of NiY$_2$. The position of the equilibrium was dependent on the phosphine, and the solvent employed and will be discussed in detail in subsequent sections. The addition of ethereal solvents or methanol drove the equilibrium to the left and resulted in some disproportionation of the complexes to give some of complex (**1**), free diphosphine and NiY$_2$. Type (**1**) complexes were found to predominate over type (**2**) complexes even in the presence of only one mole of the diphosphine.



Equation 5

The nickel (II) diphosphine complexes [Ni(P-P)X_2] {P-P = dppe, dppv; X = Cl, Br, I, NO_3} are known to exhibit an equilibrium in solution similar to that shown in (Equation 6).[6] The order of halide affinities for Ni(P-P) was Cl>Br>I, and the tendency for bis chelation in the presence of halide or NO_3^- ions increased in the order Cl<Br<I<NO_3^-.[6] Interestingly, when nitrate ions were employed only the bis-complex [Ni(dppe)$_2$](NO_3)$_2$ was formed. This was attributed to the weakness of NO_3^- co-ordination compared to that of the halides.[6]

$$2[Ni(dppe)X_2] \rightleftharpoons [Ni(dppe)_2]X_2 + NiX_2$$

Equation 6

The bisdiphosphine complex [Ni(dppe)$_2$](OTs)$_2$.2MeOH (**6a**) was isolated in high yields and was characterised by X-ray crystallography. Bis-diphosphine complexes of the type [Ni(P-P)$_2$](BF_4)$_2$ {P-P = dppm, dppe, dppv, dppb} have been isolated previously.[2]

5.2.2.1 Reaction of Complexes of the type [Ni(P-P)Cl_2] with AgOTs/AgOTf in acetonitrile/dichloromethane

The behaviour of the tosylate, or triflate group either as a non co-ordinating anion, or effectively as a ligand, in co-ordinating or non co-ordinating solvents was investigated and was found to depend on the diphosphine ligand. The first attempted synthesis of type (**2**) complexes was *via* the metathetical reaction of nickel (II) diphosphine dihalide complexes of the type [Ni(P-P)Cl_2] (**5**) with a silver salt of a weakly co-ordinating anion in acetonitrile (Method c, Scheme 1). The reactions of (**5**) with AgOTs in dichloromethane were attempted to obtain evidence for co-ordination of the tosylate as a ligand in a non co-ordinating solvent. The reaction of [Ni(dcpe)Cl_2], [Ni(dppe)Cl_2], [Ni(dBpe)Cl$_2$], and [Ni(dppp)Cl$_2$], with AgY was different in every case. The results are summarised in Table 1 together with the $^{31}P\{^1H\}$ NMR chemical shifts.

Table 1 Summary of $^{31}P\{^1H\}$ NMR chemical shifts from the reaction of complexes of the type [Ni(P-P)Cl$_2$] (**5**) with AgY.

P-P	δ ppm (CH_3CN)	δ ppm (CH_2Cl_2)
dppe	10 br [Ni(dppe)$_2$](OTs)$_2$(**6**) + [Ni(dppe)(CH_3CN)$_2$](OTs)$_2$ + [Ni(CH_3CN)$_6$](OTs)$_2$ (**14**)	57 (s, [Ni(dppe)$_2$](OTs)$_2$, (**6**))
dcpe	94.1 (s, [Ni(dcpe)(CH_3CN)$_2$](OTs)$_2$ (**12**)	86.3 (s, br [Ni(dcpe)(OTs)$_2$] (**17**))
dBpe	96.2 (d, $^2J_{P-P}$ 39Hz) [Ni(dBpe)(CH_3CN)(OTs)](OTs) (**16**), P *trans* to OTs) 104.6 (d, $^2J_{P-P}$ 39Hz) [Ni(dBpe)(CH_3CN)(OTs)](OTs) (**16**), P *trans* to CH_3CN	-
dppp	-8 to12 v.br [Ni(CH_3CN)$_6$](OTf)$_2$ (**15**)	-

The reaction of [Ni(dppe)Cl$_2$] with AgOTs in acetonitrile led to the formation of the bisdiphosphine complex [Ni(dppe)$_2$](OTs)$_2$ (**6**). The $^{31}P\{^1H\}$NMR spectrum obtained immediately after mixing the reagents was a broad singlet, indicative of a dynamic exchange equilibrium in solution between the complex (**6**), [Ni(dppe)(CH_3CN)$_2$](OTs)$_2$ and the paramagnetic species [Ni(CH_3CN)$_6$](OTs)$_2$. Complex (**6**) was not isolated from this reaction.

The desired complex of the type [Ni(dcpe)(CH_3CN)$_2$](OTs)$_2$ (**12**) was only observed directly on reaction of the complex [Ni(dcpe)Cl$_2$] with AgOTs in acetonitrile (Equation 7).

$$[\mathrm{Ni(dcpe)Cl_2}] + 2\ \mathrm{AgOTs} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Ni(dcpe)(CH_3CN)_2}](\mathrm{OTs})_2\ (\mathbf{12}) + 2\mathrm{AgCl}$$

Equation 7

The reaction of the complex [Ni(dBpe)Cl_2] with AgOTs in acetonitrile led to the formation of the complex [Ni(dBpe)(CH_3CN)(OTs)](OTs) (**16**). Two doublets were observed by $^{31}P\{^1H\}$ NMR spectrosopy indicative of mutually *cis*, inequivalent phosphorus atoms. The magnitude of the coupling constant of 39Hz is similar to the related dppe mixed halide complexes [Ni(dppe)ClBr], [Ni(dppe)BrI], [Ni(dppe)ClI], where $J_{P\text{-}P}$ values of 64, 48, and 60Hz respectively, have been observed. Coupling in dBpe complexes is likely to be smaller than in the dppe complexes (in this case 39Hz for dBpe compared with 48-60Hz for dppe) since it has been found that as the bulk of the alkyl substituent increases then $J_{P\text{-}P}$ is reduced.[7]

The reaction of [Ni(dppp)Cl_2] with silver triflate in acetonitrile resulted in an immediate colour change from red to brown. On removal of the precipitated silver chloride, a further colour change to a blue solution was observed, attributed to the dissociation of the complex "[Ni(dppp)$(OTf)_2$]" to give [Ni$(CH_3CN)_6$]$(OTf)_2$ (**14**) and free dppp. Addition of a further half molar equivalent of dppp resulted in the formation of a deep red/brown solution and a very broad $^{31}P\{^1H\}$ NMR spectrum (δ = -8 to 12ppm). The appearance of the $^{31}P\{^1H\}$ NMR spectrum was attributed to the presence of paramagnetic species in solution. These species may be due to either a dynamic exchange equilibrium in solution between [Ni$(dppp)_2$]$(OTf)_2$, [Ni(dppp)$(CH_3CN)_2$]$(OTf)_2$, and [Ni$(CH_3CN)_6$]$(OTf)_2$ or to a square-planar - tetrahedral equilibrium in solution similar to that observed for the complex [Ni(dppp)Cl_2].

The reaction of [Ni(dppe)Cl_2] with AgOTs in dichloromethane (Equation 8) led to the formation of the bis diphosphine complex (**6**), and the precipitation of compound (**3**). The isolation of complex (**6**) from this particular reaction was not attempted.

$$2[Ni(dppe)Cl_2] + 4\ AgOTs \longrightarrow [Ni(dppe)_2](OTs)_2\ (\mathbf{6}) + Ni(OTs)_2\ (\mathbf{3}) + 4AgCl$$

Equation 8

In the reaction of [Ni(dcpe)Cl_2] with AgOTs in dichloromethane, the tosylate ligand co-ordinates, in the absence of co-ordinating solvents, to give the complex

[Ni(dcpe)(OTs)$_2$](**17**). The $^{31}P\{^1H\}$ NMR spectrum is a broad singlet. Complex (**17**) was observed in solution and could not be isolated from this reaction.

The differences, depending on the diphosphine ligand, between the metathetical reaction products of [Ni(P-P)Cl$_2$] (**5**) {P-P = dppe, dcpe, dBpe, dppp} with silver salts can be accounted for by the steric nature of the diphosphine ligand. The steric bulk of the diphosphine ligands increases in the order R = Ph<Cy<^{t}Bu. The nature of the tosylate group as a weakly co-ordinating anion favours the formation of the bis-diphosphine complexes of the type [Ni(P-P)$_2$](Y)$_2$ (**1**). It has been shown previously that the dppe ligand forms bisdiphosphine complexes as opposed to a diphosphine complex in the presence of weakly co-ordinating ligands.[3,4,6] The steric interactions between the Ph groups are minimal. However, in the case of the bulkier diphosphine ligands, dcpe and dBpe, a compromise between co-ordination of two chelating ligands to give a sterically hindered bis- complex, especially for the very bulky ^{t}Bu group, and co-ordination of the tosylate group as a ligand, is apparent. When the diphosphine ligands dcpe and dBpe are compared it was found that in the presence of acetonitrile then a difference in the co-ordinated ligands, either CH_3CN or OTs, is observed. For dcpe, both acetonitriles co-ordinate to give [Ni(dcpe)(CH_3CN)$_2$](OTs)$_2$. In contrast, for dBpe, one tosylate co-ordinates and one behaves as an anion in the presence of the co-ordinating solvent, acetonitrile to give the monocationic species [Ni(dBpe)(CH_3CN)(OTs)](OTs) (**16**).

5.2.2.2 Direct reaction of Ni(OTs)$_2$ (3) or Ni(OTf)$_2$ (4) with P-P and 2P-P (Methods a & b, Scheme 2)

A more suitable route for the preparation of the type [Ni(P-P)$_2$](Y)$_2$ (**1**) and [Ni(P-P)(S)$_2$](Y)$_2$ (**2**), was the direct reaction of (**3**) or (**4**) with two moles or one mole respectively of a diphosphine ligand (P-P), the removal of the silver biproduct being no longer necessary. Table 2 contains a brief summary of the $^{31}P\{^1H\}$ NMR data of the nickel-phosphorus species detected in solution, including complexes of the type (**1**) and (**2**). The formation of these species will be discussed in turn. Type (**2**) complexes were only observed when the diphosphine ligand, dcpe, was employed.

Table 2 Nickel-phosphorus species detected in solution by $^{31}P\{^1H\}$ NMR spectroscopy

Reaction (Solvent)	Products (δ ppm)*
$Ni(OTs)_2$ + 2dppe (CD_3COOD)	58.9 (s, $[Ni(dppe)_2](OTs)_2$ (**6**))
$Ni(OTs)_2$ + 2dcpe (CH_3CN)	67.7 (s, $[Ni(dcpe)_2](OTs)_2$ (**7**))
$Ni(OTs)_2$ + 2dcpn (CH_3CN)	-15 (s, dcpn) 45 (br, $[Ni(dcpn)_2](OTs)_2$ (**8**), broadness probably due to paramagnetic species in solution)
$Ni(OTs)_2$ + 2dppp $^{\clubsuit}$ (CD_3COOD)	Individual species unassignable due to a probable equilibrium between $[Ni(dppp)_2](OTs)_2$, $[Ni(dppp)(OTs)_2]$, and $Ni(OTs)_2$ (paramagnetic). 49 (br); 31.4 (s); 23.2 (v. br); 17.6 (s); 14.1 (v. br); 5.4 (v. br); 2.2 (s, br);
$Ni(OTs)_2$ + dcpe + $3PPh_3$ (CD_3CN)	-5 (br, $[Ni(dcpe)(PPh_3)_2](OTs)_2$ (**9**)$^{\blacklozenge}$); 67.8 (br, $[Ni(dcpe)_2](OTs)_2$); 94.8 (br, $[Ni(dcpe)(PPh_3)_2](OTs)_2$ (**9**)$^{\blacklozenge}$)
$Ni(OTs)_2$ + dcpe + 3dppe (CD_3CN)	50.2 (m, $[Ni(dcpe)(dppe)](OTs)_2$ (**10**)$^{\spadesuit}$); 55.8 (s, $[Ni(dppe)_2](OTs)_2$ (**6**)); 78.4 (m, $[Ni(dcpe)(dppe)](OTs)_2$ (**10**)$^{\spadesuit}$)
$Ni(OTf)_2$ + 3dcpe (CH_3CN)	δ -0.6 (s, dcpe); δ 65.4 (s, $[Ni(dcpe)_2](OTf)_2$ (**11**))
$Ni(OTs)_2$ + dcpe (CH_3CN)	67.7 (s, $[Ni(dcpe)_2](OTs)_2$ (**7**)) 94.3 (s, $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ (**12**))
$Ni(OTf)_2$ + dcpe (CD_3CN)	δ 65.4 (s, $[Ni(dcpe)_2](OTf)_2$ (**11**)) 99.1 (s, $[Ni(dcpe)(CD_3CN)_2](OTf)_2$ (**13**))
$Ni(OTf)_2$ + Boxylyl	Individual species unassignable due to a probable equilibrium between $[Ni(Boxylyl)_2](OTf)_2$, $[Ni(Boxylyl)(OTf)_2]$, and $Ni(OTf)_2$ (paramagnetic). 28; 38; 50 (v. br); 64.4(v. br);

	65.2 (v. br)

* All signals are singlets unless otherwise stated. ♣ The spectrum is not well resolved. ♦ Analysis immediately after reaction. ♠ The mixed ligand complex (**10**) has an AA'BB' spin system and the spectrum is second order

Attempts to prepare the dppe complex of type (**2**) led only to the formation of the complex $[Ni(dppe)_2](OTs)_2$ (**6**) irrespective of the stoichiometry of the diphosphine and Ni compound. Therefore, the reaction of (**3**) with dppe in a ratio of 1:2 resulted in the formation of the stable complex (**6**). Complex (**6**) was prepared both, by the reaction of anhydrous compound (**3a**), or the slightly hydrated compound (**3b**), with two equivalents of dppe.

Reaction of $Ni(OTs)_2$ (3) with 1,3-bis(diphenylphosphino)propane (dppp)

The appearance of the $^{31}P\{^{1}H\}$ NMR spectrum after the reaction of $Ni(OTs)_2$ (**3**) with two equivalents of dppp was broad and complex due to the presence of a paramagnetic species in solution. These paramagnetic species may arise from either the equilibrium in solution between $[Ni(dppp)_2](OTf)_2$, $[Ni(dppp)(CH_3CN)_2](OTf)_2$, and $[Ni(CH_3CN)_6](OTf)_2$ or from a square-planar - tetrahedral equilibrium similar to that observed for the complex $[Ni(dppp)Cl_2]$. On addition of dppp to a solution of $Ni(OTs)_2$ (**3**) in acetonitrile a reaction occurred which was indicated by a colour change from green to red. However, when the reaction solvent was reduced in volume under reduced pressure a mixture of brown and white solids resulted and these were attributed to the decompostition, and the disproportionation of the reaction products to a combination of $Ni(OTs)_2$, dppp, and an unidentified nickel-phosphorus species. Addition of the NMR solvent, CD_3COOD, redissolved the mixture and resulted in a deep red coloured solution. The $^{31}P\{^{1}H\}$ NMR spectrum was similar to that observed above. These observations indicate that the complex $[Ni(dppp)_2](OTs)_2$ is only stable in solution, and in the presence of an excess of the diphosphine ligand, dppp. Furthermore Miedaner observed that the bisdiphosphine complex $[Ni(dppp)_2](BF_4)_2$ could not be isolated in an analytically pure state.[2] The reaction was repeated. However, attempts to isolate the complex $[Ni(dppp)_2](OTs)_2$ only resulted in the precipitation of $Ni(OTs)_2$ (**3**), which was characterised by I.R. and elemental analysis. Hence, the reaction of (**3**) with dppp is complex, being complicated firstly by an equilibrium in solution, and secondly affecting the $^{31}P\{^1H\}$ NMR spectrum by the presence of tetrahedral parmagnetic species in solution.

Reaction of Ni(OTs)$_2$ (3) with 1,8-bis(dicyclohexylphosphino)naphthalene (dcpn)

The reaction of (**3**) with an excess of the diphosphine ligand dcpn in toluene/methanol resulted in a colour change from green to pale purple. The purple solution gave a broad signal in the $^{31}P\{^1H\}$ NMR spectrum at δ 45 ppm and was attributed to the formation of the complex [Ni(dcpn)$_2$](OTs)$_2$ (**8**), and free dcpn was present as a singlet δ -15 ppm. The large bite angle of the diphosphine ligand dcpn (P-Ni-P 96° in the complex [Ni(dcpn)Cl$_2$]^{11}) in the six-membered ring chelate complex (**8**), probably forces the resultant complex to adopt large tetrahedral distortions from an ideal square-planar complex. This is found for [Ni(dppb)$_2$](PF$_6$)$_2$ having two dppb ligands with bite angles of 85.2° and 99.0° and significant tetrahedral distortions.[2] Therefore, the broadness observed in the $^{31}P\{^1H\}$ NMR spectrum of complex (**8**) may be accounted for by paramagnetism arising from tetrahedral distortions, and also the possibility of an equilibrium in solution between [Ni(dcpn)$_2$](OTs)$_2$, [Ni(dcpn)(CH$_3$CN)$_2$](OTs)$_2$ and Ni(OTs)$_2$ can not be ruled out.

Reaction of Ni(OTf)$_2$ (4) with 1,4-bis(di-tert-butylphosphino)ortho-xylene (Boxylyl)

The reaction of two equivalents of the bulky diphosphine ligand, Boxylyl with Ni(OTf)$_2$ led to a complex $^{31}P\{^1H\}$ NMR spectrum having very broad signals. An $^{19}F\{^1H\}$ NMR spectrum was obtained and indicated only one fluorine environment was present in the complex(es) (co-ordinated and non co-ordinated triflate groups would probably give the same chemical shift value). In a similar manner to the ligand, dcpn, the bite angle of the diphosphine ligand, Boxylyl is large and tetrahedral distortions are expected to occur. Interestingly, the ligand, Boxylyl does not give a simple $^{31}P\{^1H\}$ NMR spectra when reacted with nickel dichloride.[8] Furthermore, complex spectra and broad signals are also obtained when attempting to prepare Pd(II) complexes of Boxylyl.[9] A similar equilibrium in solution between [Ni(Boxylyl)$_2$](OTs)$_2$, [Ni(Boxylyl)(CH$_3$CN)$_2$](OTs)$_2$ and Ni(OTs)$_2$ is probably occurring but the nickel-phosphorus products can not be definitely assigned.

5.2.2.3 Solvent effects on the reaction of dcpe with $Ni(OTs)_2$ (3) or $Ni(OTf)_2$ (4)

Initial studies indicated that the diphosphine ligand, dcpe, was the only diphosphine ligand in which the solvated type **(2)** complex was observed. Therefore, an extensive investigation was carried out into the solvent effect on the equilibrium position, and product outcome, of the reaction of **(3)** or **(4)** with dcpe and this has been summarised in Tables 3 and 4 (Key to reactions are labelled a-i). For this reaction the stoichiometry of the reaction does not necessarily dictate the outcome of the reaction. During the investigations the complexes $[Ni(dcpe)_2](OTs)_2)$ (7), $[Ni(dcpe)_2](OTf)_2$ **(11)** and $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ **(12)**, and $[Ni(dcpe)(CH_3CN)_2](OTf)_2$ **(13)** were observed by $^{31}P\{^1H\}$ NMR spectroscopy in solution, and the precipitated compounds **(3)** and **(4)** were characterised by infra-red spectroscopy and in one case by X-ray crystallography.

Table 3 Solvent effects on the reaction of $Ni(OTs)_2$ with x equivalents of dcpe

$$[Ni(dcpe)_2](OTs)_2\ (7) \quad + \ Ni(OTs)_2\ (\mathbf{3}) \xrightleftharpoons{(S)} [Ni(dcpe)(S)_2](OTs)_2\ (\mathbf{12})$$

(S) = CH_3CN, MeOH, THF

	Solvent (S)	x	Product(s) observed in solution by $^{31}P\{^1H\}$ NMR spectroscopy	δ = ppm
a	CH_3CN	1	**(12)**, immediately after reaction	94.3 (s)
			(7) and $Ni(OTs)_2$, over time	67.7 (s)
b	MeOH	1	(7)	67.7 (s)
			$[Ni(dcpe)(MeOH)_2](OTs)_2$ **(16)**	86 (br)
			pale green solid $Ni(OTs)_2$ precipitated	
c	CH_3CN + MeOH	1	(7)	67.7 (s)
			pale green solid $Ni(OTs)_2$ precipitated	
d	CH_3CN + THF	1	**(12)**	94.3
			(7)	67.7 (s)
			pale green solid $Ni(OTs)_2$ precipitated	
e	CH_3CN	2	(7)	67.7 (s)

In acetonitrile, the 1:1 reaction (a) of **(3)** with dcpe resulted in the formation of the complex $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ **(12)**. Attempted crystallisation of **(12)** in a conventional NMR tube, resulted in the precipitation of the complex $[Ni(H_2O)_6](OTs)_2$, which was characterised by X-ray crystallography. The remaining solution contained the bisdiphosphine complex $[Ni(dcpe)_2](OTs)_2$ (7) which was characterised by $^{31}P\{^1H\}$ NMR spectroscopy. This particular observation and complete characterisation of products further confirmed the existence of an equilibrium in solution.

Table 4 Solvent Effects on the reaction of $Ni(OTf)_2$ with x molar equivalents of dcpe

$[Ni(dcpe)_2](OTf)_2$ **(11)** + $Ni(OTf)_2$ **(4)** $\xrightleftharpoons{(S)}$ $[Ni(dcpe)(S)_2](OTf)_2$ **(13)**

(S) = CH_3CN, MeOH, THF

	Solvent (S)	x	Product(s) observed in solution by $^{31}P\{^1H\}$ NMR	δ = ppm
f	CH_3CN	1	**(14)**	99.0 (s)
			(11)	68.0 (s)
g	CH_3CN	1	**(11)** over time	67.7 (s)
			pale green solid $Ni(OTf)_2$ precipitated	
h	CH_3CN	3	**(11)**	67.7 (s)
			dcpe	-0.6 (s)
i	THF	2	**(11)**	67.7 (s)
			pale green solid $Ni(OTf)_2$ precipitated	

In acetonitrile, the 1:1 reaction (f) of **(4)** with dcpe resulted in the formation of the complex $[Ni(dcpe)(CH_3CN)_2](OTf)_2$ **(13)** and a small amount of $[Ni(dcpe)_2](OTf)_2$ **(11)**.

In acetonitrile, the 1:2 reaction (e) of (3) with dcpe resulted solely in the formation of the complex $[Ni(dcpe)_2](OTs)_2$ (7). The 1:3 reaction (h) of (4) with dcpe resulted in the formation of the complex $[Ni(dcpe)_2](OTf)_2$ **(11)** and the excess dcpe was observed as a singlet. There was no broadness observed in the NMR spectrum of either reaction (Equations 9 and 10) indicating that in acetonitrile, in the presence of at least two molar equivalents of the diphosphine ligand the reaction is simplified and the equilibrium is well over to the side of the $[Ni(P\text{-}P)_2]^{2+}$ (1) complex.

$$Ni(OTs)_2\ (\mathbf{3}) + 2dcpe \xrightarrow{CH_3CN} [Ni(dcpe)_2](OTs)_2\ (7)$$

Equation 9

$$Ni(OTf)_2\ (\mathbf{4}) + 3dcpe \xrightarrow{CH_3CN} [Ni(dcpe)_2](OTf)_2\ (\mathbf{11})$$

Equation 10

In methanol the 1:1 reaction (b) of (**3**) with dcpe resulted in the formation of the bisdiphosphine complex (**7**) and the precipitation of solid $Ni(OTs)_2$. The $^{31}P\{^1H\}$ NMR spectrum also contained a broad singlet at $\delta = 86$ppm which was assigned as the solvated complex $[Ni(dcpe)(MeOH)_2](OTs)_2$ (**16**) (the chemical shift of complex (**16**) compares with that of the complex $[Ni(dcpe)Cl_2]$ $\delta = 88$ppm[8], and the broadness was probably due to weak co-ordination of the tosylate group). The co-ordination of a triflate group as a ligand has been observed in palladium and platinum complexes of the type $[Pd(P\text{-}P)(OTf)_2]$ and $[Pt(P\text{-}P)(OTf)_2]$ {P-P = dppm, dppe, dppp}.[10] These complexes were precipitated from dichloromethane solutions on addition of diethylether. In the nickel system, addition of diethylether results in the equilibrium being driven to the left, giving the bisdiphosphine complex $[Ni(dcpe)_2](OTs)_2$ (**7**) and precipitation of $Ni(OTs)_2$ (**3**).

Addition of methanol to a solution of complex (**12**) in acetonitrile (c), resulted in the immediate formation of complex (**7**). Therefore, methanol drives the equilibrium to the left, possibly driven by solvation of the cationic complex (**7**) to form $[Ni(dcpe)_2](OTs)_2.(MeOH)_2$, or the compound $Ni(OTs)_2$ to give the solvated complex "$[Ni(CH_3OH)_6](OTs)_2$".

The addition of THF to a solution of complex (**12**) in acetonitrile (d) resulted in the equilbrium being driven to the left. Both complexes (**7**) and (**12**) were observed in solution by $^{31}P\{^1H\}$ NMR spectroscopy, and precipitation of $Ni(OTs)_2$ was observed. The reaction was much slower than was observed on the addition of MeOH and the removal of the solid $Ni(OTs)_2$ by filtration resulted in the slow precipitation of more $Ni(OTs)_2$ as the equilibrium gradually moved to the left.

5.2.2.4 Solution studies of mixed ligand complexes of the type $[Ni(P\text{-}P)(P'_2)](OTs)_2$

The reaction of $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ (**12**) with an excess of the monophosphine ligand, PPh_3, was followed by $^{31}P\{^1H\}$ NMR spectroscopy. All of the signals observed in solution were broad indicating a dynamic equilibrium between the complexes $[Ni(dcpe)_2](OTs)_2$ (**7**), $[Ni(dcpe)(PPh_3)_2](OTs)_2$ (**9**), $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ (**12**) and free PPh_3 (Equation 11).

$$[Ni(dcpe)(CH_3CN)_2](OTs)_2\ (\mathbf{12}) + 2PPh_3 \overset{CH_3CN}{\rightleftharpoons} [Ni(dcpe)_2](OTs)_2\ (\mathbf{7}) + [Ni(dcpe)(PPh_3)_2](OTs)_2\ (\mathbf{9})$$

Equation 11

However, the reaction of $Ni(OTs)_2$ (**3**) with one equivalent of dppe and two equivalents of PPh_3 led exclusively to the formation of the complex $[Ni(dppe)_2](OTs)_2$ (**6**) (Equation 12).

$$2\ Ni(OTs)_2\ (\mathbf{3}) + 2dppe + 4PPh_3 \xrightarrow{MeOH/toluene} [Ni(dppe)_2](OTs)_2\ (\mathbf{6}) + Ni(OTs)_2\ (\mathbf{3}) + 4PPh_3$$

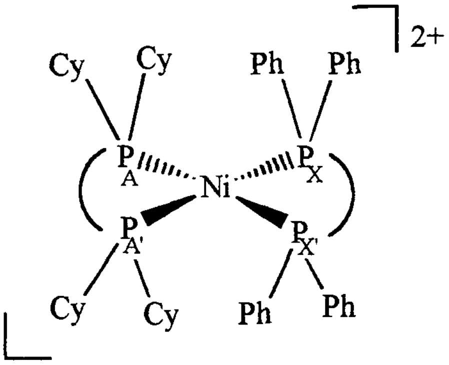
Equation 12

The reaction of three equivalents of dppe with $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ (**12**) led to the formation of $[Ni(dppe)_2](OTs)_2$ (**6**), and the mixed diphosphine ligand complex $[Ni(dcpe)(dppe)](OTs)_2$ (**10**).

$$[Ni(dcpe)(CH_3CN)_2](OTs)_2\ (\mathbf{12}) + 3dppe \xrightarrow{CH_3CN} [Ni(dcpe)(dppe)](OTs)_2\ (\mathbf{10}) + [Ni(dppe)_2](OTs)_2\ (\mathbf{6})$$

Equation 13

Complex (**10**) exhibited an AA'XX' $^{31}P\{^1H\}$ NMR spectrum which is second order (the spectrum can be found in Appendix 4). The large *trans*-coupling $^2J_{PA\text{-}PX'}$ has been determined and was found to be 185Hz which agreed closely with the assignments for previously observed mixed diphosphine ligand complexes of the type [Ni(P-P)(P-P)']$(BF_4)_2$.[2] Due to the second order nature of the spectrum the other coupling constants cannot be determined accurately without the aid of computer simulation.



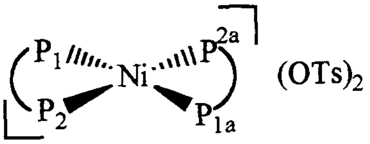
(10)

5.2.3 Structural comparisons between complex (6) and other complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (1)

Crystal Structure of $[Ni(dppe)_2](OTs)_2$ *(6)*

In the crystal structure of $[Ni(dppe)_2](OTs)_2.2MeOH$ (6) (*Figure 1*), the complex is essentially square planar. Selected bond lengths and angles of complex (6) are reported in Tables 5 and 6.

Table 5. Selected Bond Lengths [Å] for $[Ni(dppe)_2](OTs)_2.2MeOH$ (6)



Bond Length [Å]		Bond Length [Å]	
Ni(1)-P(2)#1	2.2495(12)	P(1)-C(2)	1.843(5)
Ni(1)-P(2)	2.2496(12)	P(2)-C(41)	1.823(5)
Ni(1)-P(1)#1	2.2592(11)	P(2)-C(51)	1.827(5)
Ni(1)-P(1)	2.2593(11)	P(2)-C(1)	1.828(5)
P(1)-C(21)	1.817(5)	C(1)-C(2)#1	1.544(7)
P(1)-C(31)	1.820(5)	C(2)-C(1)#1	1.543(7)

Figure 1. **The Crystal Structure of [Ni(dppe)$_2$](OTs)$_2$.2MeOH (6)**

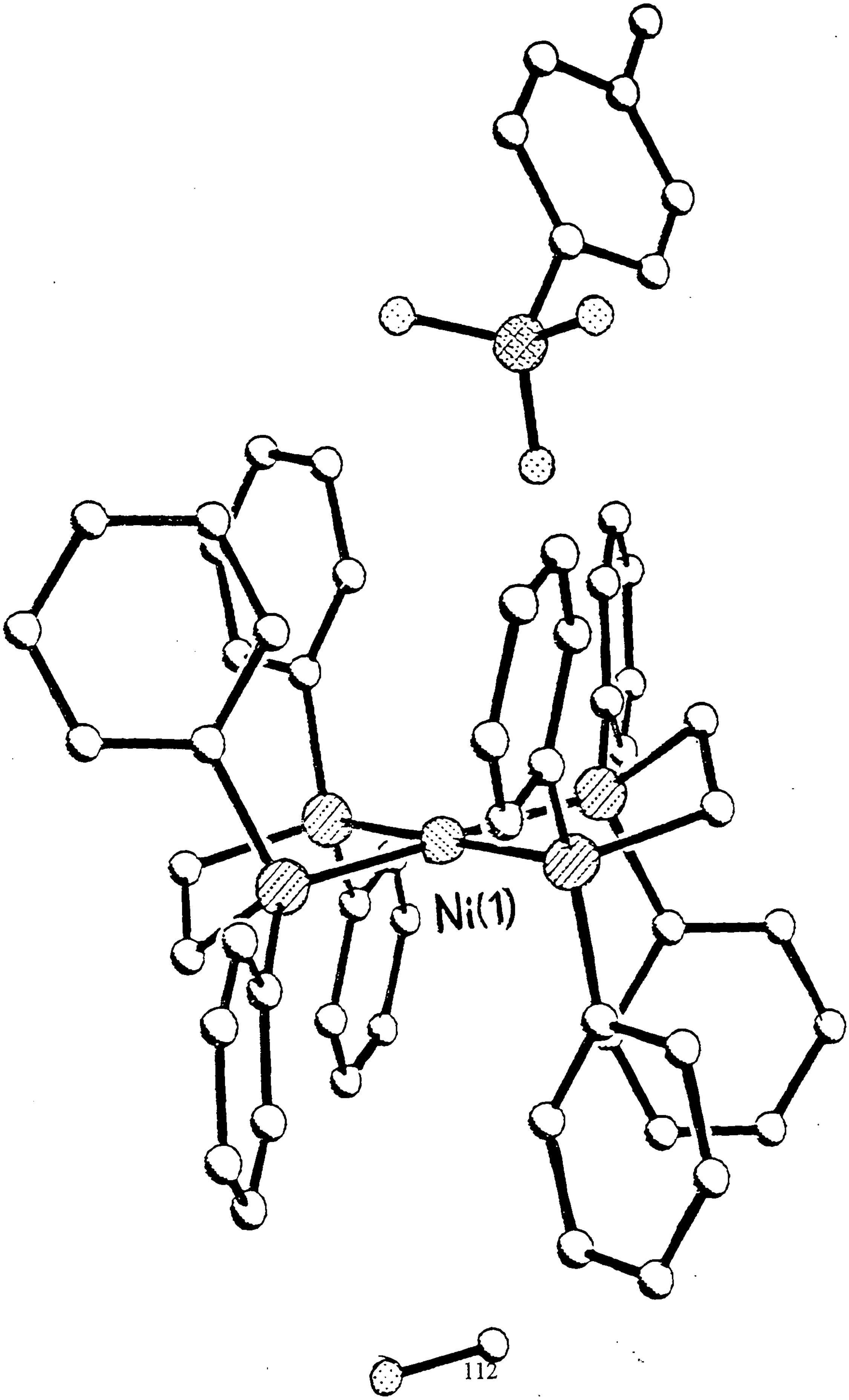
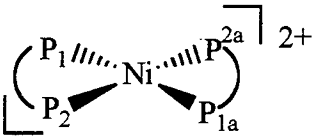


Table 6. Selected Bond Angles [°] for $[Ni(dppe)_2](OTs)_2.2MeOH$ (**6**)

Bond Angle [°]		Bond Angle [°]	
P(2)#1-Ni(1)-P(2)	180.0	C(31)-P(1)-Ni(1)	116.4(2)
P(2)#1-Ni(1)-P(1)#1	95.46(4)	C(2)-P(1)-Ni(1)	109.0(2)
P(2)-Ni(1)-P(1)#1	84.54(4)	C(41)-P(2)-C(51)	104.1(2)
P(2)#1-Ni(1)-P(1)	84.54(4)	C(41)-P(2)-C(1)	104.4(2)
P(2)-Ni(1)-P(1)	95.46(4)	C(51)-P(2)-C(1)	103.0(2)
P(1)#1-Ni(1)-P(1)	180.0	C(41)-P(2)-Ni(1)	109.2(2)
C(21)-P(1)-C(31)	106.3(2)	C(51)-P(2)-Ni(1)	128.0(2)
C(21)-P(1)-C(2)	102.9(2)	C(1)-P(2)-Ni(1)	105.7(2)
C(31)-P(1)-C(2)	103.0(2)	C(2)#1-C(1)-P(2)	106.3(3)
C(21)-P(1)-Ni(1)	117.4(2)	C(1)#1-C(2)-P(1)	110.2(3)

The Ni-P bond lengths of complex (**6**) of 2.2495(12) and 2.2592(11) Å respectively compare favourably with known Ni (II) bisdiphosphine complexes which range from 2.21-2.26 Å (Table 7).[1,2]

Table 7 Comparison of Ni-P bond lengths [Å] of complex (**6**) with other type (**1**) complexes



$[Ni(P\text{-}P)_2](Y)_2$	Bond Lengths [Å]			
	Ni-P	Ni-P	Ni-P	Ni-P
$[Ni(dppe)_2](OTs)_2$ (**6**)	2.2495(12)	2.2496(12)	2.2592(11)	2.2593(11)
$[Ni(dppe)_2](NO_3)_2$[1]	2.256(3)		2.261(3)	
$[Ni(dppv)_2](ClO_4)_2$[1]	2.258(5)		2.256(6)	
$[Ni(dppbenz)_2](PF_6)_2$[2]	2.218(6)	2.228(5)	2.216(5)	2.232(5)
$[Ni(dppm)_2](BF_4)_2$[2]	2.219(8)		2.228(9)	

Table 8 Comparison of Ni-P bond angles [°] of complex (**6**) with other type (**1**) complexes

$[Ni(P\text{-}P)_2](Y)_2$	Bond Angles [°] P_1-Ni-P_2	 P_2-Ni-P_{2a}
$[Ni(dppe)_2](OTs)_2$ (**6**)	84.54(4)	180
$[Ni(dppe)_2](NO_3)_2$[1]	83.25(12)	
$[Ni(dppv)_2](ClO_4)_2$[1]	84.2(2)	
$[Ni(dppm)_2](BF_4)_2$[2]	73.2(3)	
$[Ni(dppb)_2](PF_6)_2$[2]	85.2	164.3(3)

The bite angle, P-Ni-P 84.54(4)°, of the diphosphine in complex (**6a**) is slightly larger than in the complex $[Ni(dppe)_2](NO_3)_2$[1], P-Ni-P 83.25(12)°, which contains the nitrate counterion. This angle in turn leads to an increase in both the C-C distances in the carbon backbone by 0.18 Å (Table 9). The bite angle in complex (**6**) (84.5°) is very similar to that for the complex containing the more rigid and unsaturated backbone, dppv, which has a bite angle, P-Ni-P 84.2(2)°. The bite angle in the bisdiphosphine complex (**6**) is smaller by 2° than in the diphosphine complex, $[Ni(dppe)Cl_2]$ {P-Ni-P 87.3(2) (Form A), 86.93(6) (Form B)} which also contains dppe in a five-membered chelate ring.[14]

Table 9 Comparison of relevant bond lengths between complex (**6**) and $[Ni(dppe)_2](NO_3)_2$[1]

$[Ni(P\text{-}P)_2](Y)_2$	Bond Lengths [Å] C(1)-C(2)	 C(3)-C(4)	 P(1)-C(2)	 P(2)-C(1)
$[Ni(dppe)_2](OTs)_2$ (**6**)	1.544(7)	1.543(7)	1.843(5)	1.862(12)
$[Ni(dppe)_2](NO_3)_2$[1]	1.36(2)	1.36(2)	1.828(5)	1.841(14)

There are no apparent long range interactions with the tosylate counterions, as was observed in the nitrate complex[1].

5.3 Summary

A series of cationic bisdiphosphine complexes of the type [Ni(P-P)$_2$](Y)$_2$ (**1**) {P-P = dcpe, dppe, dppp, Boxylyl, dcpn; Y = OTs, OTf} and nickel (II) diphosphine complexes of the type [Ni(dcpe)(CH$_3$CN)$_2$](Y)$_2$ (**2**) {Y = OTs, OTf) have been characterised and observed in solution.

The bisdiphosphine complex [Ni(dppe)$_2$](OTs)$_2$ has been characterised by X-ray crystallography. [Ni(dppe)$_2$](OTs)$_2$ was observed in all syntheses which involved Ni(OTs)$_2$ and dppe; irrespective of the stoichiometry of the reaction, and is attributed to a combination of the weakly co-ordinating nature of the tosylate group and the miminal steric interactions between the Ph groups in the bis-complex.

An equilibrium in solution between the complexes of the type [Ni(P-P)$_2$](Y)$_2$ (**1**), [Ni(P-P)(S)$_2$](Y)$_2$ (**2**) and Ni(Y)$_2$ is observed for all the diphosphine ligands examined, except when P-P is dppe. The equilibrium is due to a compromise between the unfavourable steric interactions which occur in bis-complexes and the weak ligand properties of the tosylate group. In the case of the diphosphines dppp, dcpn and Boxylyl, which have more than two carbon atoms in the backbone and consequently a larger bite-angle, the increased steric interactions are overcome by a distortion towards a tetrahedral species in solution. However, the angle strain involved in a tetrahedral species of a two carbon atom backbone chelate is unfavoured. Therefore, in the bis-complexes of the type [Ni(P-P)$_2$](Y)$_2$ (**1**) that contain the ligands dcpe and dBpe, the increased steric interactions between the bulkier Cy or ^{t}Bu groups, with each other, compared to Ph, makes the formation of a bisdiphosphine complex unfavourable. Consequently, in solution complexes of the type (**1**) and (**2**) are observed for the ligands dcpe and dBpe, and in the absence of a co-ordinating solvent, weak co-ordination of the tosylate group as a ligand occurs.

The difference in the nature of the tosylate and triflate groups compared to other potentially weak co-ordinating ligands, for example BF$_4$, is illustrated by examples of co-ordination of the tosylate and triflate groups in the absence of other weakly co-ordinating ligands.

Isolation of the complexes from the reactions of $Ni(OTs)_2$ and $Ni(OTf)_2$ with the diphosphine ligands, dppp, dcpn, and Boxylyl in solution is complicated by the equilibrium similar to that observed for the two carbon atom diphosphine ligands. Unfortunately, the determination of the nature of the products in solution by $^{31}P\{^1H\}$ NMR spectroscopy is further complicated by the presence of paramagnetic species, or tetrahedral distortions which causes line broadening.

5.4 Experimental

5.4.1 Synthesis of anhydrous [Ni(OTs)$_2$] (3)

Method 1 (a)

Nickel acetate (anhydrous) (0.88g, 5.0mmol) was stirred overnight in acetonitrile (20ml). *P*-toluenesulphonic acid (2.38g, 12.5mmol) (which had been dried for four hours under reduced pressure at 100°C), in acetonitrile (10ml), was added to the nickel acetate solution. An immediate colour change was observed from green to blue. The mixture was stirred for a day at which point ether (40ml) was added which resulted in a pale yellow precipitate. The solution was filtered and the pale yellow solid was washed with ether and dried *in vacuo* (0.4g, 20%) found C, 42.03; H, 3.53. Calc. for $C_{14}H_{14}NiO_6S_2$ C,41.93; H, 3.52%. IR (solid): $\nu_{S=O}$ (sym. str.) 1183 cm^{-1}; $\nu_{S=O}$ (asym. str.) 1064 cm^{-1}(lit[12] sulphonate salts, $\nu_{S=O}$ (sym. str.) ~1175 cm^{-1}, $\nu_{S=O}$ (asym. str.) 1055 cm^{-1}.

Method 1 (b)

Nickel (II) chloride 1,2-dimethoxymethane complex [$NiCl_2(CH_3O(CH_2)_2OCH_3)$] (1.0g, 4.6mmol) was placed in a Schlenk tube and solid silver tosylate (3.17g, 11.4mmol) and monoglyme (20ml) were added. Methanol was added which resulted in a green coloured solution and the precipitation of a cream solid as the reaction occurred. The silver chloride precipitate was removed by filtration and the filtrate was taken to dryness under reduced pressure at 100°C resulting in a pale yellow coloured powder (0.314g, 17%). Found C, 41.82; H, 3.52. Calc. for $C_{14}H_{14}NiO_6S_2$ C,41.93; H, 3.52%. IR (solid): $\nu_{S=O}$ (sym. str.) 1183 cm^{-1}; $\nu_{S=O}$ (asym. str.) 1064 cm^{-1} (lit[12] sulphonate salts, $\nu_{S=O}$ (sym. str.) ~1175 cm^{-1}, $\nu_{S=O}$ (asym. str.) ~1055 cm^{-1}.

5.4.2 Synthesis of [Ni(OTs)$_2$].xH$_2$O (3)

Method 2

$Ni(CO_3).Ni(OH)_2.4H_2O$ (5.81g, 1.2mmol) was placed in a flask together with *p*-toluenesulphonic acid (4.74g, 2.5mmol) and toluene (100ml) was added. The mixture was stirred and the water was removed by azeotropic distillation using a Dean-Stark apparatus under nitrogen. The solvent was removed under reduced pressure and the solid was dried in *vacuo.* Infra-red analysis indicated that a reaction had occurred but not to completion ($Ni(CO_3).Ni(OH)_2.4H_2O$ still observed in I.R.). The mixture was stirred and the flask was heated in air with a bunsen burner (300±50°C) causing the HOTs to melt and the desired reaction to occur. After cooling to r.t. the resulting solid was placed under nitrogen and washed with toluene (2x 10ml) (degassed) followed by ether and dried in *vacuo*. At the end of this time some unreacted $Ni(CO_3).Ni(OH)_2.4H_2O$ remained (identified by I.R.) This impurity was eventually removed by dissolving the solid in methanol in which the Ni(OTs) was soluble but the $Ni(CO_3).Ni(OH)_2.4H_2O$ impurity was almost insoluble. The methanol was then removed under reduced pressure which resulted in a pale green solid, $Ni(OTs)_2.xH_2O$, 2.8g, (56%). The solid was found to be of sufficient purity to use in subsequent reactions. IR (solid): $\nu_{S=O}$ (sym. str.) 1184 cm^{-1}; $\nu_{S=O}$ (asym. str.) 1065 cm^{-1}(Lit[12] sulphonate salts, $\nu_{S=O}$ (sym. str.) ~1175 cm^{-1}, $\nu_{S=O}$ (asym. str.) 1055 cm^{-1}.

5.4.3 Synthesis of anhydrous [$Ni(OTf)_2$] (4)

$Ni(OTf)_2$ was prepared in a similar manner to 5.4.1 (method b) from {[$NiCl_2(CH_3O(CH_2)_2OCH_3$] (3.0g, 1.4mmol) and AgOTf (9.0g, 3.5mmol)}except CH_3CN was added instead of MeOH which resulted in a blue coloured solution. The silver chloride precipitate was removed by filtration. The filtrate was reduced in volume under reduced pressure which resulted in an oily blue liquid. Diethyl ether was added in an attempt to precipitate the solid $Ni(OTf)_2$ but only resulted in the formation of two layers, it was subsequently removed under reduced pressure. The oily blue liquid was heated (50°C) under reduced pressure which resulted in an oily green liquid. CH_3CN was added to redissolve the oily liquid to give a green solution. Diethylether was added which resulted in the precipitation, after storing overnight at -20°C, of a small amount of pale green solid, which was isolated by filtration. The remaining filtrate was removed under reduced pressure (90°C) and the pale green solid dried *in vacuo*. Evidence by I.R. and yield indicates co-ordination by solvent either, monoglyme or methanol. Yield 6.86g. I.R. (solid): $\nu_{S=O}$ (sym. str.) 1175 cm^{-1}; $\nu_{S=O}$ (asym. str.) 1025 cm^{-1} (Lit. AgOTf sulphonate salts, $\nu_{S=O}$ (sym. str.) ~1180 cm^{-1}, $\nu_{S=O}$ (asym. str.) 1020 cm^{-1})[12].

5.4.4 Synthesis of [Ni(dppe)$_2$](OTs)$_2$.2MeOH (6) Method 1

$[NiCl_2(CH_3OCH_2CH_2OCH_3)]$ (0.206g, 0.94mmol) in monoglyme (30ml) at reflux under reduced pressure was added to AgOTs (0.68g, 3.95mmol) in monoglyme (10ml) in the absence of light and the mixture was stirred for 4h which resulted in a green solution and a cream precipitate (AgCl). The green Ni(OTs)$_2$ solution was filtered, from the mixture containing AgCl, directly into a flask containing dppe (0.63g, 1.58mmol) which had been dissolved by heating in monogylme (30ml). An immediate colour change was observed from orange, through burgandy red, and eventually resulting in a canary yellow coloured solid and an orange solution. The solution was taken to a minimum under reduced pressure and the solid separated by filtration. The solid was washed with two aliquots of monoglyme (20ml). The yellow solid was dried *in vacuo* yield (1.2g, 63%). The yellow solid was recrystallised from a MeOH solution (-20°C). A single crystal of [Ni(dppe)$_2$](OTs)$_2$.2MeOH (**6**) was isolated and the structure determined by X-ray analysis (by J. Wen). Found C, 64.97; H, 5.22. Calc. for $C_{68}H_{70}NiO_8P_4S_2$ C, 64.72; H, 5.59%. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 59.0 (s). ^1H NMR ($CDCl_3$): δ 1.6 (**4H**, m, $C\underline{H}_2P$); δ 2.4 (**6H**, s, $C\underline{H}_3C_6H_4SO_3$); δ 3.1(**4H**, m, $C\underline{H}_2P$); δ 3.5 (**3H**, s, $C\underline{H}_3OH$) δ 7.3 (**24H**, m, *m-, p- Ph*) δ 7.5 (**8H**, m, *o- Ph*; 4H $CH_3C_6\underline{H}_4SO_3$ *o-* SO_3); δ 8.1 (**4H**, m $CH_3C_6\underline{H}_4SO_3$ *m-* SO_3).

5.4.5 Synthesis of [Ni(dppe)$_2$](OTs)$_2$ (6) Method 2

Ni(OTs)$_2$.xH$_2$O (**3b**) (2.33g, 0.46mmol) in MeOH (20mls) was added *via* cannula to dppe (4.0g, 1.0mmol) in toluene (20ml). An immediate colour change from green to yellow/brown occurred and the mixture was stirred for 1h. The solvent was taken to a minimum under reduced pressure and a canary yellow solid precipitated, which after separation by filtration was washed with toluene (20ml) and dried *in vacuo.* Yield (0.47g, 85% based on dppe) Found C, 65.88; H, 5.11. Calc. for $C_{66}H_{62}NiO_6P_4S_2$ C, 66.18; H, 5.22%. ^1H NMR (CD_3COOD): δ 2.03 ($C\underline{D}_3COOD$) δ 2.3 (**6H**, s, $C\underline{H}_3C_6H_4SO_3$); δ 2.9 (**8H**, m, $C\underline{H}_2P$) ; δ 3.4 (s, $C\underline{H}_3OH$); δ 7.14-7.18 & 7.74-7.81 (**8H**, ABq, $CH_3C_6\underline{H}_4SO_3$); δ 7.2-7.4 (**24H**, m, *m-, p- Ph*); δ 7.4-7.6 (**8H**, m, *o- Ph*); δ 11.6 ($CD_3COO\underline{D}$) Hz. $^{31}P\{^1H\}$NMR (CD_3COOD): δ 66.2 ppm. $^{13}C\{^1H\}$ NMR (CD_3COOD): δ 21.4 (s, $\underline{C}H_3C_6H_4SO_3$); δ 28.7 (m, $\underline{C}H_2P$); δ 49.7 (s, $\underline{C}H_3OH$); δ 126.0 (m, $P\underline{C}$); δ

127.0 (s, PCCC$\underline{C}$); δ 129.1 (s, $\underline{C}CH_3$); δ 129.7 (s, SCC$\underline{C}$); δ 130.8 (s, br, PC$\underline{C}$); δ 134.4 (d, P$\underline{C}$, $^3J_{P\text{-}C}$ 20.9Hz); δ 142.5 (s, $\underline{C}CS$); δ 142.7 (s, $\underline{C}S$). IR (solid): $\nu_{\text{-CH2-}}$ 1483 cm^{-1}; $\nu_{P\text{-}Ph}$ 1436 cm^{-1}; $\nu_{CH2\text{-}Ph}$ 1432 cm^{-1}; $\nu_{S=O}$ (sym. str.) 1177 cm^{-1}; $\nu_{S=O}$ (asym. str.) 1030 cm^{-1} and 1008cm^{-1} (lit[12] sulphonate salts, $\nu_{S=O}$ (sym str) ~1175 cm^{-1}, $\nu_{S=O}$ (asym str) 1055 cm^{-1}.

5.4.6 Reaction of Ni(OTs)$_2$ with 2 equivalents of dcpe

A blue coloured solution of Ni(OTs)$_2$ (**3**) (23mg, 0.06mmol) dissolved in CH_3CN (20ml) was added to a solution of dcpe (50mg, 0.12mmol) in CH_3CN (20ml). An immediate colour change from blue to orange was observed. The solvent was taken to a minimum under reduced pressure and a mixture of orange and green solids crystallised from this solution and could not be separated. $^{31}P\{^1H\}$NMR (CH_3CN): δ 67.7 (s, [Ni(dcpe)$_2$](OTs)$_2$) (**7**). IR (solid): $\nu_{\text{-CH2-}}$ 2917 cm^{-1}; $\nu_{\text{-CH2-}}$ 2849 cm^{-1}; $\nu_{\text{-CH2-}}$ 1487 cm^{-1}; $\nu_{CH2\text{-}P}$ 1446 cm^{-1}; $\nu_{S=O}$ (sym. str.) 1180cm^{-1}; $\nu_{S=O}$ (asym. str.) 1033 cm^{-1} and 1011cm^{-1} (lit[12] sulphonate salts, $\nu_{S=O}$ (sym str) ~1175 cm^{-1}, $\nu_{S=O}$ (asym str) 1055 cm^{-1} [Ni(dcpe)$_2$](OTs)$_2$ (orange) + Ni(OTs)$_2$ (green).

5.4.7 Reaction of Ni(OTs)$_2$ with 2 equivalents of dppp

Dppp (79mg, 0.12mmol) and Ni(OTs)$_2$ (50mg, 0.24mmol) were placed in a specially adapted Schlenk tube and toluene/MeOH (~1:2 mixture, 4ml) was added which caused an immediate reaction and a colour change to a dark red brown colour. The mixture was stirred for 0.5h after which time the solvents were removed under reduced pressure leaving a brown solid. The solid was redissolved in the nmr solvent CD_3COOD to form a deep red coloured solution. ^1H NMR (CD_3COOD): δ 1.0-3.2 (**12H**, m, $C\underline{H}_2P$); δ 2.3 (**6H**, s, $C\underline{H}_3C_6H_4SO_3$); δ 3.4 (s, $C\underline{H}_3OH$) δ 7.15-7.18 & 7.78-7.82 (**8H**, ABq, $CH_3C_6\underline{H}_4SO_3$); 7.2-7.8 (**40H**, P$\underline{Ph}$) Hz. $^{31}P\{^1H\}$NMR (CD_3COOD): δ 49 (br); δ 31.4 (s); δ 23.2 (v. br); δ 17.6 (s); δ 14.1 (v. br); δ 5.4 (v. br); δ 2.2 (s, br); ppm. Assigned to the presence of [Ni(dppp)$_2$](OTs)$_2$, [Ni(dppp)(OTs)$_2$] and Ni(OTs)$_2$ in equilibrium in solution. The $^{31}P\{^1H\}$NMR data can not be assigned to individual species due to the broadness of the spectrum attibuted to the presence of paramagnetic species, or tetrahedral distortions in solution.

5.4.8 Reaction of $Ni(OTs)_2$ with 2 equivalents of dcpn

Dcpn (0.46g, 0.87mmol) was dissolved in acetonitrile (8ml) and added to a solution of $Ni(OTs)_2$ (0.16g, 0.4mmol) in acetonitrile (5ml). An immediate colour change from green to orange was observed. $^{31}P\{^1H\}$NMR (CH_3CN): δ -15 (dcpn); δ 45 (v. br, $[Ni(dcpn)_2](OTs)_2$ (**8**); $[Ni(dcpn)(CH_3CN)_2](OTs)_2$) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.9 NMR study of the reaction of $Ni(OTs)_2$ with dcpe in CD_3CN

Dcpe (11mg, 0.26mmol) in CH_3CN (1ml) was added to a blue coloured solution of $[Ni(CD_3CN)_6](OTs)_2$ (0.26mmol) producing an immediate colour change from blue to yellow. ^1H NMR (CD_3CN): δ 1.5-2.8 (**54H**, m, $C\underline{H}_3C_6H_4SO_3$, $C\underline{H}_2P$, Cy); δ 7.31-7.34 & 7.70-7.73 (**8H**, ABq, $CH_3C_6\underline{H}_4SO_3$) ppm. $^{31}P\{^1H\}$NMR (CD_3CN): δ 94.3 (s, $[Ni(dcpe)(CD_3CN)_2](OTs)_2$) (**12**) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.10 Reaction of $Ni(OTs)_2$ with dcpe in MeOH

When dcpe (11mg, 0.26mmol) in MeOH (10ml) was added to a green coloured solution of $Ni(OTs)_2$ (0.26mmol) in MeOH (5ml) an immediate colour change from green to orange was observed. $^{31}P\{^1H\}$NMR (CD_3CN): δ 67.6 (s, $[Ni(dcpe)_2](OTs)_2$) (7) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.11 Reaction of $Ni(OTf)_2$ with dcpe in CH_3CN

When dcpe (11mg, 0.26mmol) in CH_3CN (10ml) was added to a blue coloured solution of $[Ni(CH_3CN)_6](OTf)_2$ (0.26mmol) an immediate colour change from blue to yellow was observed. $^{31}P\{^1H\}$NMR (CH_3CN): δ 68.0 (s, $[Ni(dcpe)_2](OTf)_2$ (**11**)) δ 99.1(s, $[Ni(dcpe)(CH_3CN)_2](OTf)_2$ (**14**) ppm. $^{19}F\{^1H\}$ NMR (CH_3CN): δ -76.7 (s) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.12 Reaction of $Ni(OTf)_2$ with Boxylyl

Boxylyl (50mg, 0.06mmol) was dissolved in a CH_3CN/toluene solution (30ml) and added to a blue coloured solution of $[Ni(CH_3CN)_6](OTf)_2\{Ni(OTf)_2$ (23mg, 0.06mmol) dissolved in CH_3CN (10ml)}. The mixture was stirred and the solvent reduced to a minimum under reduced pressure to give a pale orange coloured solution. $^{31}P\{^1H\}$NMR (CH_3CN): δ 28, 38, 50 (v. br); δ 64.4 (v. br); δ 65.2 (s, v. br) ppm. $^{19}F\{^1H\}$ NMR (CH_3CN): δ -78.0 (s) ppm. Assigned to the presence of [Ni(Boxylyl)$_2$](OTs)$_2$, [Ni(Boxylyl)(CH_3CN)$_2$](OTs)$_2$ and Ni(OTs)$_2$ in equilibrium in solution. The $^{31}P\{^1H\}$NMR data can not be assigned to individual species due to the broadness of the spectrum attributed to the presence of paramagnetic species, or tetrahedral distortions in solution. Attempts to isolate a solid product were unsuccessful.

5.4.13 Reaction of Ni(dppe)Cl_2 with AgOTs in CH_3CN

[Ni(dppe)Cl_2] (70mg, 0.13mmol) in CH_3CN (20ml) was added *via* cannular to AgOTs (74mg, 0.27mmol) in CH_3CN (5ml). The solution was stirred in the absence of light. The AgCl which was precipitated was removed by filtration. $^{31}P\{^1H\}$NMR (CH_2Cl_2): δ 5-15 (v. br) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.14 Reaction of Ni(dcpe)Cl_2 with AgOTs in CH_3CN

[Ni(dcpe)Cl_2] (40mg, 0.07mmol) in CH_3CN (20ml) was added *via* cannular to AgOTs (40mg, 0.14mmol) in CH_3CN (5ml). The solution was stirred in the absence of light. The AgCl which was precipitated was removed by filtration. $^{31}P\{^1H\}$NMR (CH_3CN): δ 94.1 (s, [Ni(dcpe)(CH_3CN)$_2$](OTs)$_2$) **(12)** ppm. Attempts to isolate a solid product were unsuccessful.

5.4.15 Reaction of Ni(dBpe)Cl_2 with AgOTs in CH_3CN

[Ni(dBpe)Cl_2] (50mg, 0.11mmol) in CH_3CN (20ml) was added *via* cannular to AgOTs (31mg, 0.22mmol) in CH_3CN (5ml). The solution was stirred in the absence of light. The AgCl which was precipitated was removed by filtration. The solution had changed colour from a burgandy red to orange. $^{31}P\{^1H\}$NMR (CH_3CN): δ 96.2 (d, $^2J_{P-P}$ 38Hz, [Ni(dBpe)(CH_3CN)(OTs)](OTs) **(13)**; δ 104.6 (d, $^2J_{P-P}$ 38Hz, [Ni(dBpe)(CH_3CN)(OTs)](OTs) **(13)** ppm. Attempts to isolate a solid product were unsuccessful.

5.4.16 Reaction of $Ni(dppe)Cl_2$ with AgOTs in CH_2Cl_2

[$Ni(dppe)Cl_2$] (54mg, 1.0mmol) was placed in a Schlenk together with (57mg, 2.1mmol) of AgOTs. Dichloromethane (20ml) was added and the solution was stirred in the absence of light. The AgCl, which precipitated, was removed by filtration. $^{31}P\{^1H\}$NMR (CH_2Cl_2): δ 2.6 (d, J_{P-P} 18Hz); δ 5.1 (d, J_{P-P} 18Hz); δ 6.5 (v. br); δ 57.0 (s, [$Ni(dppe)_2$]$(OTs)_2$ (**6b**) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.17 Reaction of $Ni(dcpe)Cl_2$ with AgOTs in CH_2Cl_2

[$Ni(dcpe)Cl_2$] (50mg, 0.09mmol) was placed in a Schlenk together with (51mg, 1.8mmol) of AgOTs. Dichloromethane (20ml) was added and the solution was stirred in the absence of light. The AgCl, which precipitated, was removed by filtration. $^{31}P\{^1H\}$NMR (CH_2Cl_2): δ 86.3 (s, br, [$Ni(dcpe)(OTs)_2$]) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.18 Reaction of $Ni(dppp)Cl_2$ with AgOTf

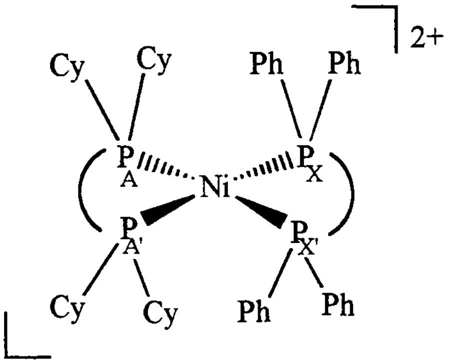
[$Ni(dppp)Cl_2$] (0.58g, 1.1mmol) was dissolved in acetonitrile (10ml) and AgOTf (0.6g, 2.3mmol) was added as a solid. An immediate colour change occurred through red to brown. After 1h stirring, a blue solution was obtained together with AgCl, which was removed by filtration. A further quantity of dppp (0.5mmol) was added which resulted in a deep red/brown solution. $^{31}P\{^1H\}$NMR (CH_3CN): δ -8 to 12 (v.br) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.19 NMR Reaction of $Ni(OTs)_2$ with dcpe + $3PPh_3$

An aliquot of solution from the reaction 5.4.6 was added to a specially adapted schlenk for NMR tubes containing approximately 3 equivalents of PPh_3. $^{31}P\{^1H\}$NMR (CH_3CN): δ -5 (s, br [$Ni(dcpe)(PPh_3)_2$]$(OTs)_2$ (**9**)); δ 67.8 (s, br [$Ni(dcpe)_2$]$(OTs)_2$) (**7**); δ 94.8 (s, br [$Ni(dcpe)(PPh_3)_2$]$(OTs)_2$ (**9**)) ppm. Attempts to isolate a solid product were unsuccessful.

5.4.20 NMR Reaction of $Ni(OTs)_2$ with dcpe + 3dppe

An aliquot of solution from the reaction 5.4.6 was added to a specially adapted schlenk for NMR tubes containing approximately 3 equivalents of dppe. $^{31}P\{^1H\}$NMR (CH_3CN): δ -13.2 (s, dppe); δ 50.2 (P_B, m, AA'XX', [Ni(dcpe)(dppe)]$(OTs)_2$ **(10)**, $^2J_{PA-PX'}$ 185Hz); δ 55.8 (s, [Ni(dppe)$_2$]$(OTs)_2$ **(6a)**); δ 78.4 (P_A, m, AA'XX', [Ni(dcpe)(dppe)]$(OTs)_2$ **(10)**, $^2J_{PA-PX'}$ 185Hz); ppm. Attempts to isolate a solid product were unsuccessful.



(10)

5.4.21 Reaction of $Ni(OTf)_2$ with 3dcpe

A blue coloured solution of $[Ni(CH_3CN)_6](OTf)_2\{Ni(OTf)_2$ (23mg, 0.06mmol) in $CH_3CN\}$was added to a solution of dcpe (50mg, 0.12mmol) in CH_3CN. An immediate colour change from blue to orange was observed. $^{31}P\{^1H\}$NMR (CH_3CN): δ -0.6 (s, dcpe); δ 65.4 (s, [Ni(dcpe)$_2$]$(OTf)_2$) **(11)** ppm. $^{19}F\{^1H\}$ NMR (CH_3CN): δ -76.7 (s) ppm. Attempts to isolate a solid product were unsuccessful.

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Chapter 6
Copolymerisation of CO and Ethene Catalysed by Cationic Nickel (II) Diphosphine Complexes

6.1 Introduction

The reaction of CO and ethene, in methanol, catalysed by palladium phosphine complexes can be tailored, depending on the steric and electronic properties of the phosphine to produce polyketone [1,2] or methyl propanoate [3] in high yields and with good selectivity (Equation 1).

$$n\ H_2C{=}CH_2 + n\ CO + MeOH \xrightarrow{[Pd]} H(CH_2CH_2CO)_nOMe$$

Equation 1

In this chapter, the catalytic copolymerisation of CO and ethene by cationic nickel (II) diphosphine complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), $[Ni(P\text{-}P)_2]^{2+}$ (**2**) and $[Ni(P\text{-}P)(o\text{-tolyl})(S)]^{+}$ (**3**), has been investigated. Nickel complexes of the type (**1**), (**2**) and (**3**) containing the weakly co-ordinating anions, OTs^- and OTf^-, are found to be catalyst precursors for the alternating copolymerisation reaction of CO and ethene to produce polyketone. Polyketone was produced in varying amounts with all of the diphosphine ligands tested.

An investigation into the potential catalyst decomposition routes and mechanisms for this reaction has been undertaken. At the end of the nickel catalysed reaction of CO and ethene to give polyketone by complexes of the type (**1**), (**2**) and (**3**), complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**) were observed

Furthermore, NMR carbonylation studies of a series of nickel diphosphine complexes of the type (**1**), (**2**) and (**3**) and complexes of the type $[Ni(P\text{-}P)(o\text{-tolyl})Br]$ (**5**) gave the dicarbonyl complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**), and found to be the thermodynamic sink for the catalyst in the nickel catalysed reaction of CO and ethene to give polyketone.[4]

6.2 Results and Discussion

The complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), $[Ni(P\text{-}P)_2]^{2+}$ (**2**) and $[Ni(P\text{-}P)(o\text{-}tolyl)(S)]^{+}$ (**3**), were tested as catalysts for the CO/ethene reaction in methanol to determine formation of polyketone and/or methyl propanoate. The results are summarised in Table 1 and briefly outlined, by run number (runs i - xx), in the immediately following paragraphs.

Polyketone was produced when catalysed by complexes of the type $[Ni(P\text{-}P)_2](OTs)_2$ (**2**) (runs iv-vii and xii-xvii) {P-P = dcpe, dppe, dppp, Boxylyl}. Only a trace amount of polyketone was obtained when P-P = dcpn (run viii). The order of catalytic activity by turnover number was dcpe>dppe>>Boxylyl and dppe>dppp under the same reaction conditions.

A type (**1**) complex, $[Ni(P\text{-}P)(S)_2]^{2+}$, analogous to the active palladium based polyketone catalysts,[1,2] was found to catalyse the reaction of CO and ethene in methanol to give polyketone only when P-P = dcpe (run i). The diphosphine ligands, dppp and Boxylyl in the complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), did not give any catalysis (runs ii and iii).

The turnover number of polyketone produced from a catalyst system containing a type (**2**) complex (a two molar equivalent of the diphosphine ligand dcpe) (run iv) was 50 times that of a catalyst system containing a type (**1**) complex (a one molar equivalent of dcpe). In the copolymerisations catalysed by type (**2**) complexes, the system containing dcpe was found to be the most active catalyst. The catalytic activity of the type (**1**) complex containing the diphosphine ligand, dcpe, may be attributed to its overall higher reactivity. However, the $^{31}P\{^1H\}$ NMR spectrum obtained before its use as a catalyst indicated that $[Ni(dcpe)(CH_3CN)_2](OTs)_2$ (**5**) and

$[Ni(dcpe)_2](OTs)_2$ (**6**), were both present in solution and an equilibrium in solution (as Chapter 5) between the complexes of the type (**1**) and (**2**) respectively was apparent.

Polyketone was produced when catalysed by complexes of the type [Ni(P-P)(*o*-tolyl)(S)]OTs (**3**) (runs ix-xi) {P-P = dppe, dBpe}. A comparison of turnover number could not be obtained because the catalyst concentration of the complex [Ni(dBpe)(*o*-tol)(py)](OTs) (**13**) was very small. Polyketone obtained in a negligible amount, (Run xi) was identified by infra-red spectroscopy, indicating that the dBpe system was an active catalyst. Unfortunately, there was no more of the ligand, dBpe, to carry out a directly comparitive reaction. The formation of polyketone with such low catalyst concentrations, indicates that the dBpe system is possibly at least as active as the dppe system.

In certain cases, the palladium catalysed CO/ethene reaction in methanol produces methyl propanoate in high yields and high selectivity, notably in the systems $(Pd(OAc)_2$/excess $PPh_3/HOTs)$[1,2] and (Pd(0)/Boxylyl/HOTs)[3]. It was found that the high selectivity to methyl propanoate formation, exhibited using a palladium catalyst containing the diphosphine ligand, Boxylyl, with a rigid backbone, was not displayed using any of the nickel(II) diphosphine complexes. The nickel complex containing the diphosphine ligand, Boxylyl, was found, however to be catalytically active but giving the alternative product, polyketone (run vii). However, methyl methanoate was detected by G.C. mass spectroscopy, (run ix) particularly when the diphosphine ligand, Boxylyl, was employed (runs iii and vii). The selectivity towards methyl propanoate formation exhibited using a palladium catalyst containing the monophosphine ligand, PPh_3, was not observed using a nickel complex. In fact no catalysis was observed when $Ni(OTs)_2$ was combined with an excess of PPh_3[1,2] in a methanol/toluene solution (run xx). Negligible catalysis was observed when employing the rigid diphosphine ligand with a large bite-angle, dcpn (run xiii).

Table 1 Nickel Catalysed Reaction of CO and Ethene

Run	Catalyst[a]	mmol	mmol Added Ligand	Added acid	mmol	time/h	Solvent[d]	Mass Polyketone	TON mol/ mol catalyst
i[b]	$[Ni(dcpe)_2](OTf)_2$ $[Ni(dcpe)(CH_3CN)_2](OTf)_2$	0.6	-	HOTf	0.6[c]	5	*a, m*	0.1	-
ii[b]	"$[Ni(dppp)(CH_3CN)_2](OTf)_2$"	1.1	0.55 dppp	HOTf	2.0[c]	12	*a*	-	-
iii[b]	"[Ni(Boxylyl)-$(CH_3CN)_2](OTf)_2$"	1.0	-	HOTf	2.0[c]	10	*a, t*	-	-
iv	$[Ni(dcpe)_2](OTs)_2$	0.45	-	HOTs	0.6	10	*m*	1.1	50
v	$[Ni(dppe)_2](OTs)_2$	0.5	-	HOTs	0.6	2	*m*	0.27	10
vi	$[Ni(dppe)_2](OTs)_2$	0.16	-	HOTs	0.6	5	*m, t*	0.27	23
vii	"$[Ni(Boxylyl)_2](OTf)_2$"	0.5	-	HOTf	0.6	2	*t, a*	0.07	2
viii	$[Ni(dcpn)_2](OTs)_2$	0.4	0.2	HOTs	0.6	2	*t, a*	tr	-
ix	[Ni(dppe)(*o*-tolyl)(S)](OTs)	0.12	0.25 dppe	Nil	-	2	*m, t*	0.04	6
x	[Ni(dppe)(*o*-tolyl)(py)](OTs)	0.4	0.8 PPh_3	Nil	-	5	*m, t, p*	0.03	1
xi	[Ni(dBpe)(*o*-tolyl)(py)](OTs)	0.01	-	Nil	-	5	*thf, m, t, p*	tr	-
xii	$[Ni(dppe)_2](OTs)_2$	0.18	-	HOTs	2.0	3[e]	*m, t*	0.04	4
xiii	$[Ni(dppe)_2](OTs)_2$	0.15	-	HOTs	5.0	2	*ac*	0.61	73
xiv	$[Ni(dppe)_2](OTs)_2$	0.1	1.0 dppe	HOTs	3.0	1	*ac*	0.66	100
xv	$[Ni(dppe)_2](OTs)_2$	0.4	0.8 PPh_3	HOTs	3.0	3	*m, t*	0.02	1
xvi	$[Ni(dppe)_2](OTs)_2$	1.0	2.0 PPh_3	HOTs	3.0	5	*m, t*	0.12	2
xvii	"$[Ni(dppp)_2](OTs)_2]$"	0.1	1.0 dppp	HOTs	0.6	5	*ac*	0.14	25
xviii	$[Ni(dppe)_2](OAc)_2$	0.9	-	HOTs	5.0	5	*m, t*	Nil	-
xix	$[Ni(dppe)_2](NO_3)_2$	1.7	-	HOTs	5.0	5	*m, t*	Nil	-
xx	"$Ni(OTs)_2 + 2PPh_3$"	1.0	12.0 PPh_3	HOTs	10.0	2	*m, t*	Nil	-

[a] Reaction carried out in 10-30 ml of solvent [d] at a temperature of 110°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental) unless stated ([b]). [b] Reaction carried out in 13ml solvent [d] at a temperature of 85°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental). [c] moles are approximate due to fuming acid. [d] Solvent Key: *m* = methanol; *t* = toluene; *a* = acetonitrile; *p* = pyridine; *thf* = tetrahydrofuran; *ac* = acetic acid. [e] 40atm ethene at 110°C for 1.5h then added 40atm of CO at 110°C for 1.5h.

Catalysis did not occur when complexes of the type $[Ni(P\text{-}P)_2]^{2+}$ (**2**) contained the anions OAc^- (Run xviii) and NO_3^- (Run xix). This lack of activity in the $Ni(OAc)_2$ system, contrasted with that of the palladium system, where similar catalytic activity was observed from the direct preparation of the catalytically active species, $[Pd(CH_3CN)_2(OTs)_2]$ combined with the ligand dppp. Without addition of acid, this complex gave catalyst systems of similar activity to those formed *in situ* by the combination of palladium (II) acetate, the ligand dppp, and the appropriate acid.[1,2]

Catalyst Systems

Two autoclaves were used for catalyst testing. Initially, an autoclave which could be isolated and transported whilst sealed was used (Autoclave A - see experimental). This transportable sealed system was used because of the potential formation of the highly toxic and volatile compound $Ni(CO)_4$. After it had been established that $Ni(CO)_4$ was not being produced, an autoclave with better stirring efficiency was used to ensure optimum mixing of the reactants and thermal control at high polyketone conversions (Autoclave B). The head of Autoclave B was fixed in the high pressure reaction rig. The stirring efficiency has previously been noted to influence the product obtained from catalysis using the palladium based systems.[5] To investigate whether any $Ni(CO)_4$ was formed under the proposed reaction conditions, after the first catalytic reaction (Run i), the autoclave was cooled in solid CO_2 before venting. There was no $Ni(CO)_4$ present by infra-red analysis after this first reaction. Subsequent reactions were all treated with caution on the first attempt of testing a new catalyst system. There was no detection of $Ni(CO)_4$ after any of the catalytic reactions. Therefore, in some cases catalyst systems that had been previously tested in Autoclave A, were tested again in autoclave B (runs vi, xiii, xiv and xvii).

The catalysts and reagents were added to the autoclave under air-free conditions. As discussed previously (see Chapter 5) the isolation of complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**) and $[Ni(P\text{-}P)_2]^{2+}$ (**2**) as solids was not possible due to an equilibrium in solution. The exception was the complex $[Ni(dppe)_2](OTs)_2$ (**7**). Therefore, the complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**) and $[Ni(P\text{-}P)_2]^{2+}$ (**2**) were prepared directly in solution and injected *via* syringe, into the autoclave (Autoclave A), containing an inert atmosphere. The acid, HOTs, was added as a solid, and the acid, HOTf, was added *via* syringe, directly into the autoclave whilst purging with nitrogen.

The solid complex $[Ni(dppe)_2](OTs)_2$ (7) isolated previously (see Chapter 5) was found to be relatively stable to air and moisture. Consequently all the reactions carried out in Autoclave B, were catalyst sytems containing the complex $[Ni(dppe)_2](OTs)_2$ (7). The complexes $[Ni(dppe)_2](OAc)_2$ (**8**) and $[Ni(dppe)_2](OAc)_2$ (**9**), which were inactive as catalysts, were prepared as solids by a similar route to the preparation of the catalytically active complex $[Ni(dppe)_2](OTs)_2$ (7) (see experimental section).

The complexes of the type $[Ni(P\text{-}P)(o\text{-tolyl})(S)]^+$ (**3**), were tested, where P-P = dppe and dBpe. Two different catalyst systems were tested for the diphosphine ligand dppe. In one case (run xi) the solid [Ni(dppe)(*o*-tolyl)(OTs)] (**10**), isolated previously (see Chapter 4), was dissolved in a solution of methanol and toluene, together with a two molar equivalents of the free diphosphine, dppe. The $^{31}P\{^1H\}$ NMR spectrum of this solution was previously shown to be complex but indicated the dissociation of the tosylate ligand in solution to give the four co-ordinate complex [Ni(dppe)(*o*-tolyl){dppe}]OTs (**11**). The free diphosphine was added in the catalyst test as a precautionary measure against the formation of $Ni(CO)_4$, (if $Ni(CO)_4$ was formed it would react with dppe to give the diphosphine dicarbonyl complex $[Ni(dppe)(CO)_2]$ instead.[6] In the other case (run x) the complex [Ni(dppe)(*o*-tolyl)(py)]OTs (**12**) was prepared by the reaction of $[Ni(PPh_3)_2(o\text{-tolyl})Br]$ with one mole of dppe, followed by the removal of the bromide ion by TlOTs, and addition of pyridine (Equation 2).

$$[Ni(PPh_3)_2(o\text{-tolyl})Br] + \text{dppe} \xrightarrow[\substack{\text{ii) TlOTs (-TlBr)} \\ \text{iii) pyridine}}]{\text{i) toluene/THF}} [Ni(dppe)(o\text{-tolyl})(py)]OTs\ \ (9) + 2PPh_3$$

Equation 2

The catalyst solution effectively consisted of [Ni(dppe)(*o*-tolyl)(py)]OTs and a two molar equivalent of PPh_3. The complex [Ni(dBpe)(*o*-tol)(py)](OTs) (**13**) was prepared directly from [Ni(dBpe)(*o*-tol)Br] and TlOTs in pyridine and the filtrate was injected directly into the autoclave.

Characterisation of Polyketone

Pure polyketone is a white solid that is insoluble in methanol and other common organic solvents.[1,2,7,8] During catalysis, polyketone which precipitated from the nickel catalysed reaction solution was recovered by filtration then washed with methanol and dichloromethane to remove any residual decomposed catalyst. The polyketone was also washed with water to remove any residual acid. Even after washing most of the samples still contained residual catalyst impurities but were not purified further. The purest samples by colour and melting point (Table 2) were obtained when the catalysts employed were [Ni(dcpe)$_2$](OTs)$_2$ (7) (run iv) and [Ni(dppe)(*o*-tolyl)(S)](OTs) (**11**) (run ix).

Table 2 Characterisation of polyketone by colour and melting point

Run	Catalyst[b]	Colour	m.p °C [a]/ decomposition [b]
i	[Ni(dcpe)$_2$](OTf)$_2$	brown	[c]
	[Ni(dcpe)(CH$_3$CN)$_2$](OTf)$_2$		
iv	[Ni(dcpe)$_2$](OTs)$_2$	cream	ca. 250
v	[Ni(dppe)$_2$](OTs)$_2$	cream	ca. 250
vi	[Ni(dppe)$_2$](OTs)$_2$	brown-grey	ca. 250
vii	[Ni(Boxylyl)$_2$](OTf)$_2$	brown-grey	ca. 250
ix	[Ni(dppe)(*o*-tolyl)(S)](OTs)	white	ca. 255
x	[Ni(dppe)(*o*-tolyl)(py)](OTs)	off white	ca. 250
xi	[Ni(dBpe)(*o*-tolyl)(py)](OTs)	brown	[d]
xii	[Ni(dppe)$_2$](OTs)$_2$	brown-grey	ca. 250
xiii	[Ni(dppe)$_2$](OTs)$_2$	brown	ca. 250
xiv	[Ni(dppe)$_2$](OTs)$_2$	off white	ca. 250
xv	[Ni(dppe)$_2$](OTs)$_2$	brown	ca. 250
xvi	[Ni(dppe)$_2$](OTs)$_2$	brown	ca. 250
xvii	"[Ni(dppp)$_2$](OTs)$_2$]"	brown	[b]

[a] Melting point of pure polyketone 257°C[2] [b] Melting points of all polyketone samples were generally from 250°C upwards at which temperature the polyketone and residual nickel salt decomposed. [c] Melting point was not obtained. [d] Not enough sample was obtained to determine the melting point.

The impurities were the nickel salts Ni(OTs)$_2$ and Ni(OTf)$_2$ and these were identified by infra-red spectroscopy (see Appendix 5). Characterisation of the polyketone was achieved by infra-red analysis and melting points. Characterisation, by $^{13}C\{^1H\}$ NMR spectroscopy and MALDI-TOF mass spectroscopy, was only obtained on the samples of polyketone from the reactions catalysed by the complexes [Ni(dcpe)$_2$](OTs)$_2$ (**7**) (run iv) and [Ni(dppe)(*o*-tolyl)(S)]OTs (**11**) (run ix).

Infra-red spectroscopy

The polyketone samples obtained in this work were characterised by infra-red spectroscopy, $\nu_{C=O}$ (~ 1690 cm^{-1} {solid}) data comparing favourably with a previously characterised sample[7] and the literature.[8] The low $\nu_{C=O}$ (~ 1695 cm^{-1} {KBr}) stretching frequency is distinctive for perfectly alternating polyketone.[8] Comparisons between an infra-red spectrum of a commercial sample, and a previously characterised sample of polyketone show that the other infra-red bands present also coincide.[7] The infra-red data of each sample of polyketone are listed in appendix 5.

$^{13}C\{^1H\}$ NMR spectroscopy

$^{13}C\{^1H\}$ NMR spectra were obtained on both the samples of polyketone derived from the reactions catalysed by the complexes [Ni(dcpe)$_2$](OTs)$_2$ (**7**) (run iv, sample A) and [Ni(dppe)(*o*-tolyl)(S)]OTs (**11**) (run ix, sample B) only. Solution $^{13}C\{^1H\}$ NMR analysis was obtained on the polyketone samples A and B in the fluorinated solvents hexafluoropropan-2-ol and trifluoroacetic acid respectively, since polyketone is not soluble in conventional nmr solvents.[1] The $^{13}C\{^1H\}$ NMR spectrum, in both cases, consisted of two resonances, at δ 35.6 and δ 213.1 ppm, with an approximate intensity ratio of 2:1 respectively, which compares favourably with the resonances of previously characterised samples of polyketone.[1,8.] The resonance at δ 35.6 ppm was ascribed to the α-methylene carbons and the resonance at δ 213.1 ppm was ascribed to the carbonyl carbons. Unfortunately, the end groups were not detected by $^{13}C\{^1H\}$ NMR spectroscopy because of their low concentrations.

MALDI-TOF Mass Spectroscopy

The molecular weights of the polyketone samples A and B were determined by MALDI-TOF Mass Spectroscopy (*Figure 1* and *2*). The average molecular weight (M_n) of both samples was ~1300, $-(CH_2CH_2CO)_n-$, where n = 23. These were much lower than the previous palladium systems reported in the literature where the average molecular weight varied from n = 45 {$Pd(OAc)_2$/dppb/HOTs/MeOH}to n = 700 {$Pd(OAc)_2$/dppp/$Cu(OTs)_2$/MeOH}.[1,2]

End Group Analysis

The molecular weight of a polyketone oligomer were used to determine the end group masses. Subtraction of the number of repeat units {56 for the repeat unit $-(CH_2CH_2CO)_n-$} from the molecular weight of the oligomer, left a residual mass which was equivalent to the combined masses of the end groups. All ion peaks are from $[M+Na]^+$ species, which means that the molecular weight of the oligomer seen at m/z = x, has an actual molecular weight of m/z = x-23. The end groups of samples A and B were a combination of keto-ester {$CH_3CH_2-(COCH_2CH_2)_n-COOCH_3$}and diketone {$CH_3CH_2CO-(CH_2CH_2CO)_n-CH_2CH_3$}end groups. An example of an end group calculation for the samples A and B follows.

Sample	Figure	m/z	m/z -23	/56	n	Combined mass of end groups
A	1	1509	1486	26.5	25	86 ∴ diketone
A	1	1511	1488	26.6	25	88 ∴ keto-ester
B	2	1005	982	17.5	16	86 ∴ diketone

G.C. mass spectroscopy was undertaken on distilled reaction solutions. There was no evidence for the formation of methyl propanoate or lower oligomers of CO/ethene copolymer. Methyl acetate was identified by G.C. mass spectroscopy but this was probably obtained from the nickel catalysed carbonylation of methanol.

Figure 1. **The MALDI-TOF Spectrum of Polyketone {Catalysed by [Ni(dcpe)$_2$](OTs)$_2$ (7) Run iv, Sample A}**

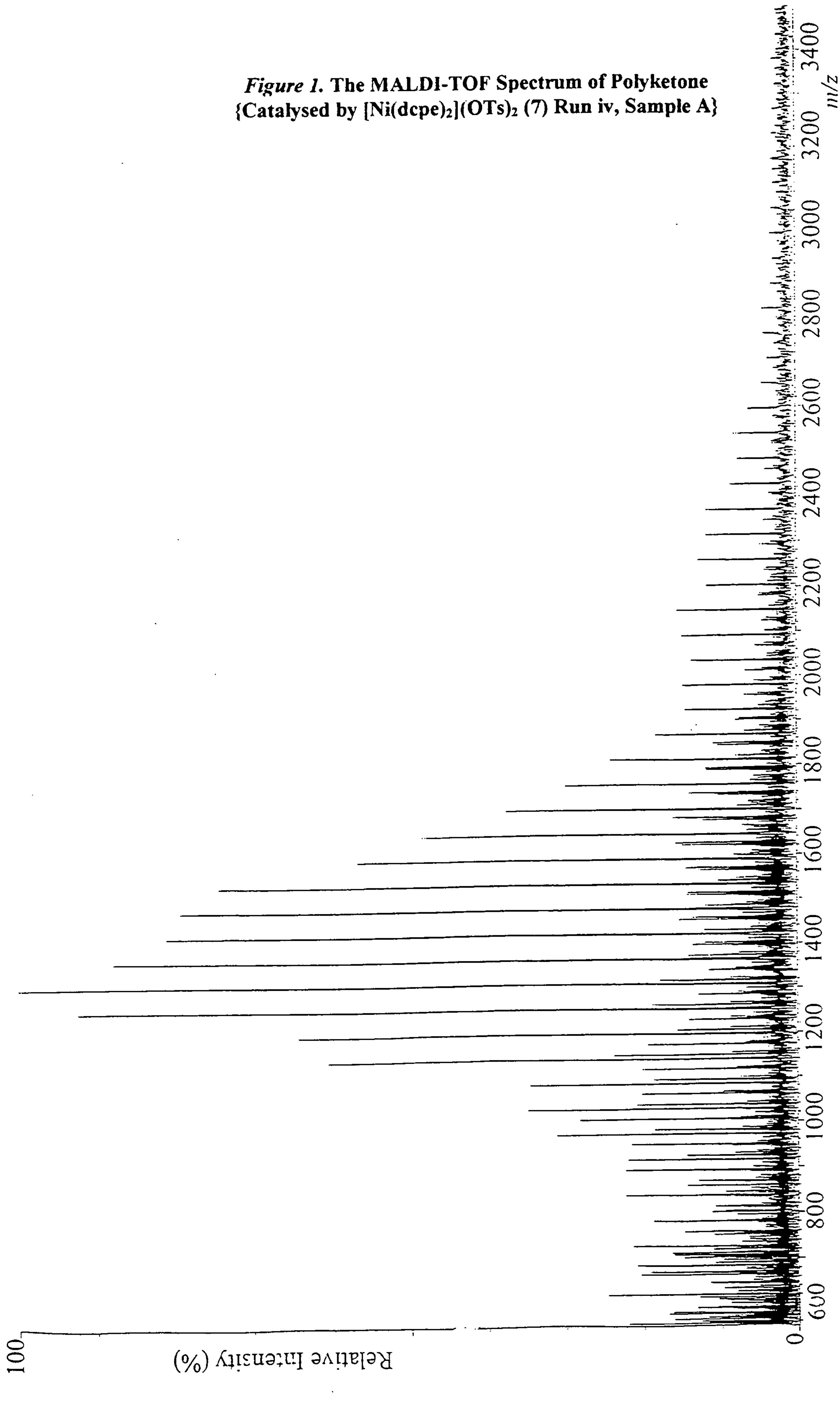
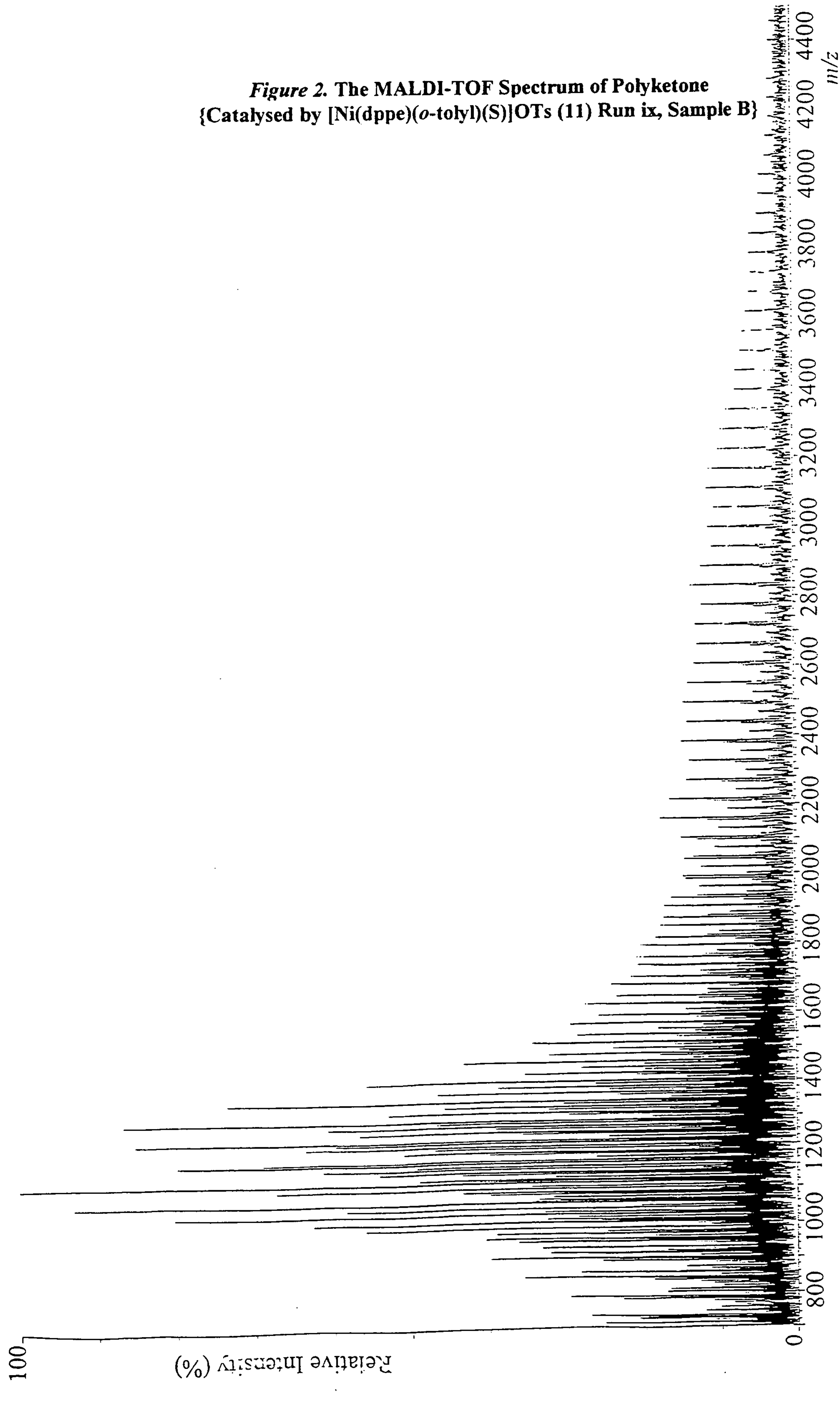


Figure 2. **The MALDI-TOF Spectrum of Polyketone {Catalysed by [Ni(dppe)(*o*-tolyl)(S)]OTs (11) Run ix, Sample B}**

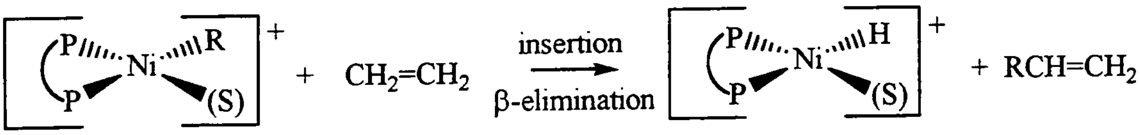


Mechanism

End group analysis of the CO/ethene polymer by MALDI-TOF mass spectroscopy indicated the presence of 100% ketone end groups (-$COCH_2CH_3$); or 50% ketone and 50% ester (-$COOCH_3$) end groups. In the case of the ketoester it has not been determined which end was formed from initiation or termination as there are different mechanisms operating which could give rise to both end groups. The mechanism of the palladium catalysed CO/ethene copolymerisation has been studied in great detail,[1,2] and this discussion is extended to the nickel based systems.

Initiation

A ketone end group can result from the initiation by a [Ni-H] species. In the catalyst systems of the type $[Ni(P\text{-}P)(o\text{-tolyl})(S)]^+$ (**3**), initiation of the catalytic cycle could easily be achieved by the generation of a nickel-hydride. The migratory insertion of ethene into the Ni-C bond of the *o*-tolyl ligand, followed by β-elimination results in the formation of a nickel hydride species of the type $[Ni(P\text{-}P)(H)(S)]^+$ (**A**) (Equation 3).



(**3**) (**A**)

Equation 3

The hydride species (**A**) was not isolated or directly detected . However, the insertion of ethene into Ni-C aryl bonds has been observed previously. Reaction of the cationic complex $[Ni(3,5\text{-}Cl_2C_6H_3)(\gamma\text{-pic})dppe)]ClO_4$ with ethene resulted in the recovery of 3,5-dichlorostyrene; no ethene dimerisation was observed.[9] The initiation continues by the reversible insertion of ethene into the nickel-hydride species (**A**) to generate a nickel-alkyl complex, $[Ni\text{-}CH_2CH_3]$ (**B**).

Insertion of CO into the Ni-C bond of the aryl group was not observed in this system. However, in contrast the rate of insertion of CO into the Ni-Ph bond, in the nickel compound, [Ni(Ph$_2$PCCH=C(Ph)O)(PEt$_3$)Ph], is quicker than the rate of ethene homopolymerisation in the presence of CO, and therefore CO is a catalyst poison.[4] If the reaction is initiated in the absence of CO, and ethene insertion has already occurred, then the nickel complex [Ni(Ph$_2$PCCH=C(Ph)O)(PEt$_3$)Ph], is a catalyst precursor for the alternating copolymerisation of CO and ethene.[4]

During catalysis hydrides may also be produced by termination *via* β-hydrogen elimination. However, vinyl ketone groups were not detected by infra-red spectroscopy in a similar manner to the palladium system where β-hydrogen elimination is not thought to be an important termination mechanism.[1]

In the catalyst systems of the type [Ni(P-P)(S)$_2$]$^{2+}$ (**1**) and [Ni(P-P)$_2$]$^{2+}$ (**2**) initiation can occur by two possible mechanisms: the hydride mechanism as described above for the catalyst systems of the type [Ni(P-P)(*o*-tolyl)(S)]$^{+}$ (**3**), or *via* a methoxycarbonyl complex of the type [Ni-COOCH$_3$] (**A'**), which are described in detail below.

Nickel-hydride species generated from [Ni(P-P)(S)$_2$]$^{2+}$ (1) and [Ni(P-P)$_2$]$^{2+}$ (2)

The generation of a nickel-hydride species (**A**) in the catalyst systems of the type [Ni(P-P)(S)$_2$]$^{2+}$ (**1**) and [Ni(P-P)$_2$]$^{2+}$ (**2**) can be achieved by (i) β-elimination from a nickel methoxide[10] (Equation 4) or (ii) *via* the watergas shift reaction[1] (Equation 5).

$$[\mathrm{(P\text{-}P)Ni}]^{2+} + \mathrm{CH_3OH} \xrightarrow{-\mathrm{H}^+} [\mathrm{(P\text{-}P)Ni\text{-}OCH_3}]^{+} \longrightarrow [\mathrm{(P\text{-}P)Ni\text{-}H}]^{+} + \mathrm{CH_2O}$$

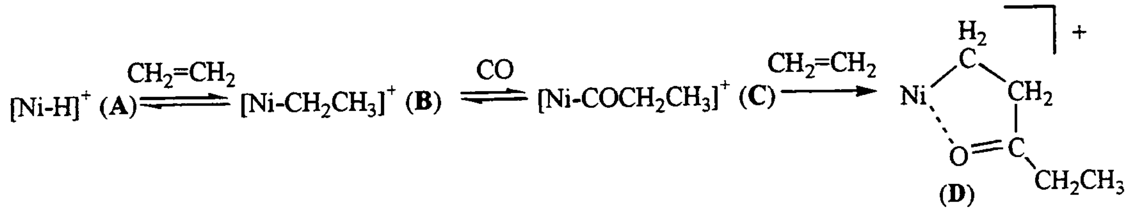
Equation 4

$$[\mathrm{(P\text{-}P)Ni}]^{2+} + \mathrm{CO} + \mathrm{H_2O} \longrightarrow [\mathrm{(P\text{-}P)Ni(CO)}]^{2+} \xrightarrow[-\mathrm{H}^+]{+\ \mathrm{MeOH}} [\mathrm{(P\text{-}P)Ni(COOMe)}]^{+} \longrightarrow [\mathrm{(P\text{-}P)Ni\text{-}Me}]^{+} + \mathrm{CO_2}$$

Equation 5

Evidence for the nickel methoxide route may be found in the literature.[10] The intermediate nickel methoxide complexes of the type [Ni(P-P)(OMe)$_2$] {P-P = dppe, dcpe, dppp} easily undergo decomposition involving β-hydride elimination from an alkoxide to form the metal-hydride, generating formaldehyde.[10] In the presence of CO, the reaction always yielded the Ni(0) complexes of the type [Ni(P-P)$(CO)_2$] (4).[10] However, for inititiation to occur the insertion of ethene into the very unstable Ni-H bond must be quicker than the formation of the dicarbonyl complexes (4).

The next step in the initiation process, after the insertion of ethene into the [Ni-H] species (**A**) to give the Ni-alkyl species, [Ni-CH_2CH_3] (**B**), is the reversible insertion of CO give the nickel-acyl species, [Ni-$COCH_2CH_3$] (**C**).[4] The second ethene insertion, into the nickel-acyl species [Ni-$COCH_2CH_3$] (**C**), is thought to be the rate limiting step because the resulting alkyl species [Ni-$CH_2CH_2COCH_2CH_3$] (**D**) could be stabilised by the formation of a five-membered chelate ring, which has been postulated for both the nickel,[4] and palladium based polyketone catalysts[1,2] (Scheme 1).

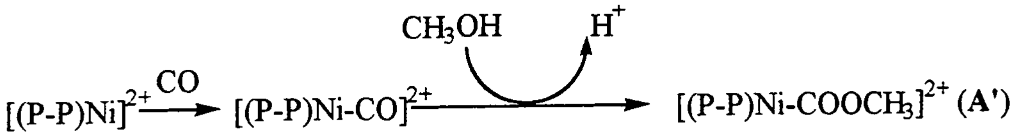


Scheme 1

Initiation *via* Methoxycarbonyl complexes of the type [Ni-$COOCH_3$] (A')

In the palladium system an alternative initiation route is *via* a methoxycarbonyl palladium species [Pd-$COOCH_3$], formed either from insertion of CO into a Pd-OMe species, or attack of MeOH on a co-ordinated CO, which leads to ester-end groups. Alkoxycarbonyl complexes of *tertiary* monophosphine complexes of Ni(II), *trans*-[Ni$(P_2)(CO_2R)$X] {P =, PMe_3, PEt_3, PEt_2Ph; R = Me, Et; X = Cl, Br} and the diphosphine complex [Ni(P-P)(CO_2R)X] {P-P = 2,6-bis-(diphenylphosphinomethyl)pyridine, X = Cl) have been studied and were prepared by treating the complex [Ni$(P_2)Cl_2$] with a stoichiometric amount of sodium alkoxide in alcohol solution under a CO atmosphere.[11,12] The nickel (II) alkoxycarbonyl complex exists [Ni$(PPh_3)_2$(COOR)Cl] but is thermally unstable, and loses CO_2 on degradation.[13] For the diphosphine complexes that contain the bidentate phosphine ligands, {P-P = dppe, dcpe, dppp), a carbonyl insertion into a Ni-OMe bond in dimethoxo- complexes of the type $[Ni(P\text{-}P)(OMe)_2]$ has never been observed (these complexes are intermediates in the alkoxide promoted reduction of complexes of the type $[Ni(P\text{-}P)Cl_2]$ in methanol).[10] In the presence of CO, the reaction always yielded the Ni(0) complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**).[10] For the diphosphine complexes, a transient carbomethoxy species may be possible but the enforced *cis*-conformation may result in decomposition to a dicarbonyl complex, before an ethene molecule can insert into the Ni-Me species that would be generated *via* loss of CO_2. CO inserts preferentially into the Ni-C bond of methyl(aryloxo) nickel (II) complexes, rather than inserting into the nickel alkoxide bond.[14]

An alternative route to the nickel carbomethoxy species, $[Ni\text{-}COOCH_3]$ (**A'**) would be by the direct attack of methanol on a co-ordinated CO molecule (Scheme 2).



$$[(P\text{-}P)Ni]^{2+} \xrightarrow{CO} [(P\text{-}P)Ni\text{-}CO]^{2+} \xrightarrow{CH_3OH \quad H^+} [(P\text{-}P)Ni\text{-}COOCH_3]^{2+}\ (\mathbf{A'})$$

Scheme 2

Examples of co-ordinated CO in nickel (II) complexes are limited due to the ease of reduction of nickel (II) to Ni(0) in the presence of CO. However, the reaction of the tetradentate phosphine ligand PP_3, with the acetonitrile complex $[Ni(CH_3CN)_6](BF_4)_2$ gives the complex $[Ni(PP_3)(CH_3CN)](BF_4)_2$.[15] The reaction of $[Ni(PP_3)(CH_3CN)](BF_4)_2$ with CO gives the complex $[Ni(PP_3)(CO)](BF_4)_2$ which is stable in the presence of CO.[15] Insertion of ethene into a carbomethoxy species must be quicker than its decarbonylation to a [Ni-Me] species. However, insertion of ethene into the [Ni-Me] species may occur to generate a nickel-hydride species and initiate catalysis. In light of these observations the alternative initiation route for palladium *via* a methoxycarbonyl route to give an ester end group, seems less important for nickel. It is probable that in the nickel system, the initiation is effectively *via* a hydride mechanism.

Propagation

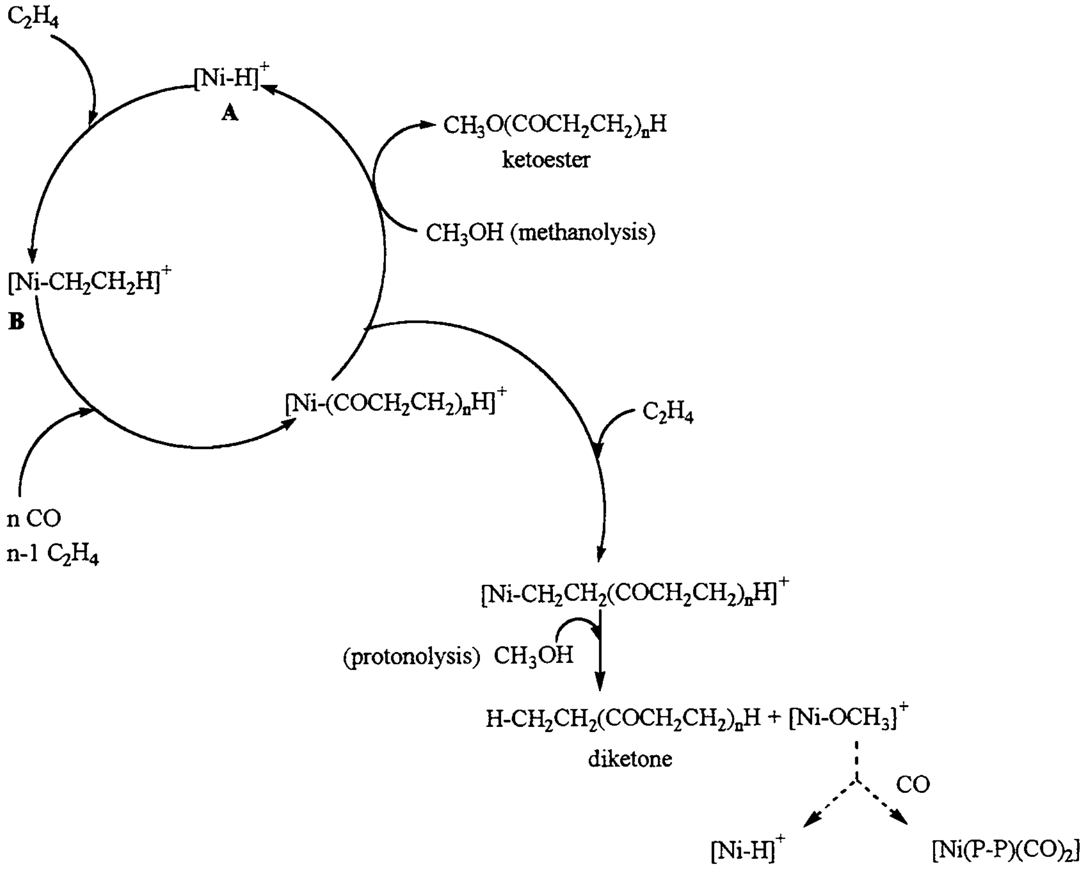
The insertion of CO into the species [Ni-$CH_2CH_2COCH_2CH_3$] (**D**) is expected to be facile and propagation continues by a series of migratory insertions of CO into the nickel-alkyl bond followed by migratory insertion of ethene into the resulting nickel-acyl bond to increase the polymer chain.[4] In a similar manner to the palladium systems, double ethene insertions are not observed. However, nickel catalysts are recognised as ethene oligomerisation and dimerisation catalysts.[16,17,18] It is interesting to note that the literature complex $[Ni(dppe)R(CH_3CN)]BF_4$[9], which is similar to the complexes of the type $[Ni(P\text{-}P)(o\text{-tolyl})(S)]^+$ (**3**), was inactive as a dimerisation catalyst whereas the analogous monophosphine complexes e.g $[Ni(PR_3)_2R(CH_3CN)]BF_4$ (for example R = Et, benzyl) were active as ethene dimerisation catalysts.[16]

The lack of double insertions of either ethene or CO may be explained by the stabilisation of the intermediate *via* a chelate ring (see previously) or thermodynamics in the case of double CO insertion.[1,2] The formation of a five membered chelate ring, thought to be the rate limiting step in the initiation of the catalysis, can continue throughout propagation. The internal co-ordination of the oxygen atom of the carbonyl group of the growing chain is thought to stabilise a chelate complex at each propagation stage.[1,2] Insertion of CO into the five membered ring complex is thought to be more facile than insertion of a ethene molecule.[1,2] The expansion from a five-membered to a six-membered chelate ring on insertion of CO reduces the stabilisation obtained, stopping the further insertion of ethene.[1,2] Hence, perfect alternation of CO and ethene in the propagating chain of the polymer is obtained.[1,2]

Termination

There are two relevant termination mechanisms for CO/ethene copolymerisation.[1,2] Methanolysis results in an ester end group and the regeneration of the active catalyst as a [Ni-H] species.[1,2] Whereas, termination by protonolysis results in the formation of a ketone end-group and the generation of a [Ni-OMe] species. In contrast to the palladium system, the actual Ni-OMe species is probably not the active catalyst for the copolymerisation of CO and ethene, but its decomposition to a [Ni-H] species may render it active. The presence of diketone end groups when catalysed by complexes of the type $[Ni(P\text{-}P)(o\text{-tolyl})(S)]^+$ (**3**), must have been initiated by a Ni-H mechanism, resulting in one ketone chain end, whilst the other ketone chain end must have been from termination *via* protonolysis. Methanolysis as a termination route is not apparent for short chains due to the lack of methyl propanoate or lower ester oligomers. Termination by β-hydrogen elimination is also not apparent due to the absence in the infra-red spectra of vinyl-ketone end groups. Therefore, the proposed mechanism is summarised in scheme 3.

Scheme 3 Proposed Reaction Mechanism of Nickel catalysed CO/ethene Copolymerisation



Changing Parameters in the Catalytic Reactions

The influence of the various parameters on the catalytic reactions of the diphosphine complexes $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), $[Ni(P\text{-}P)_2]^{2+}$ (**2**) and $[Ni(P\text{-}P)(R)(S)]^{+}$ (**3**), including the effects of added diphosphine or monophosphine, effects of solvent, excess acid, and the effect of the counterion are summarised in Tables 2-7. Generally, the order of catalytic activity by turnover number under the same conditions was dcpe>dppe>>dppp>Boxylyl and dppe>dppp.

Type (1) complexes $[Ni(P\text{-}P)(S)_2](Y)_2$

Initially, the catalyst systems tested were complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), analogous to the Pd systems employed by Drent for the copolymerisation of CO/ethene.[1,2] The results are summarised in Table 2. It was found that the complex containing the diphosphine ligand, dcpe, was the only type (**1**) catalyst that resulted in polyketone formation. However, this sample of polyketone was very impure. The diphosphine ligand, dppp, which is the most active for palladium systems, is completely inactive for type (**1**) complexes in this nickel system, and no catalysis was observed when the ligand, Boxylyl, was employed.

Table 2. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of diphosphine (P-P) in complexes of the type $[Ni(P\text{-}P)(CH_3CN)_2](Y)_2$ (**1**), (Autoclave A).

Run	P-P	Catalyst concentration/ mmol	Y	time/h	HY[a]	Mass polyketone/ g
i	dcpe	0.6	OTf	5	1 ml HOTf	0.1g
ii	dppp	1.1	OTf	12	1 ml HOTf	-
iii	Boxylyl[b]	1.0	OTf	10	1 ml HOTf	-

Reaction carried out in 13ml CH_3CN at a temperature of 85°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental). [a] Volume is approximate due to fuming acid. [b] Toluene was added to dissolve Boxylyl.

Type (2) complexes $[Ni(P\text{-}P)_2](Y)_2$

The catalytic activity of type (**2**) complexes, $[Ni(P\text{-}P)_2]^{2+}$ compared to that of type (**1**) complexes was greater for all of the diphosphine ligands employed (Table 3). A direct comparison of turnover numbers can only be applied to the ligand, dcpe, where a fifty fold increase was obtained when substituting a type (**2**) for a type (**1**) complex.

The diphosphine ligands, dppp and Boxylyl showed some catalytic activity when two molar equivalents were present, although the activity was much lower than for the ligands, dcpe and dppe. Dppe only forms a type (**2**) complex $[Ni(dppe)_2](OTs)_2$ (synthesis of a type (1) complex with dppe is not possible - see chapter 5) and therefore comparison with a type (**1**) complex was not possible, although evidence suggests that it would be less active anyway.

Table 3. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of diphosphine (P-P) in complexes of the type $[Ni(P\text{-}P)_2](Y)_2$, (Autoclave A).

Run	P-P	Catalyst concentration/ mmol	Y	time/ h	HY	Mass polyketone/g	TON mol polyketone/ mol nickel
iv	dcpe	0.45	OTs	10	0.1g HOTs	1.1	40
v[a]	dppe	0.5	OTs	2	0.1g HOTs	0.27	10
vi[b,c]	dppe	0.16	OTs	5	0.1g HOTs	0.27	23
vii	Boxylyl	0.5	OTf	2	0.3ml HOTf	0.07	2
viii	dcpn	0.4	OTs	2	0.2g HOTs	tr	-

Reaction carried out in 10-30 ml MeOH or MeOH/toluene, at a temperature of 110°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental). [a] Catalyst was not very soluble in MeOH (solvent in run iv), crystals of catalyst obtained after catalysis. [b] Catalyst used recovered from run iv. [c] Stirring more efficient than run 2, Autoclave B (see experimental).

The unexpected catalytic activity of the bisdiphosphine complexes of the type $[Ni(P\text{-}P)_2]^{2+}$ (**2**) can be attributed to a combination of factors. For catalytic activity, free co-ordination sites must be readily accessible to allow interaction with the substrates. It was originally thought that the co-ordination of a second phosphine ligand to the metal could block all of the available co-ordination sites and therefore prevent catalysis. However, the results indicate that this is clearly not the case.

Therefore, the unexpected activity of the complexes of the type $[Ni(P\text{-}P)_2]^{2+}$ (**2**) may be accounted for in two different, but complementary, ways: 1) the catalyst is transformed into a type (**1**) complex; 2) the propensity of nickel (II) to form five co-ordinate complexes.[19]

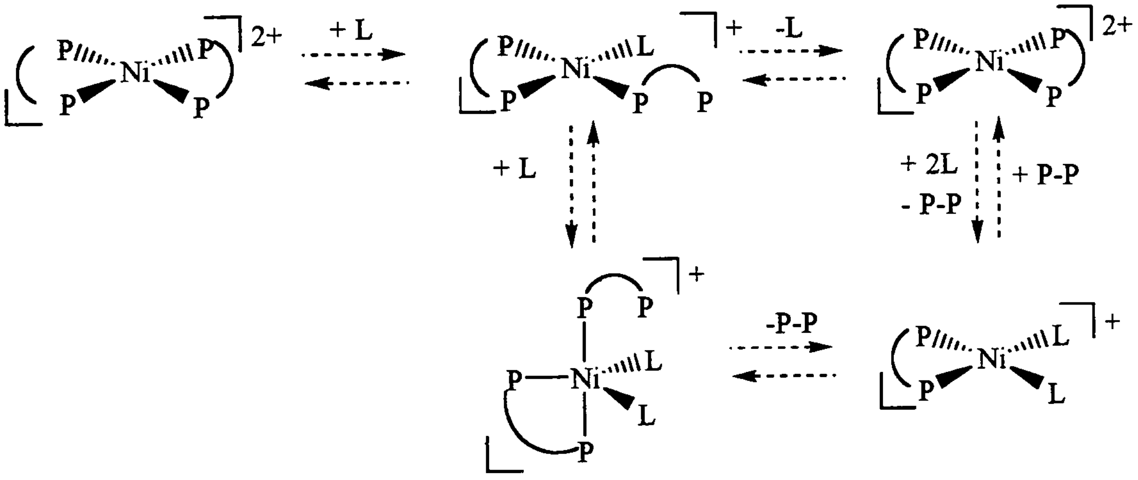
1) The actual catalytic species may be the same as the palladium systems, and therefore a type (**1**) complex is involved. For catalysis to occur only small concentrations of the actual catalyst precursor are needed to enable initiation. Solution studies of complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**) and $[Ni(P\text{-}P)_2]^{2+}$ (**2**) carried out previously (see Chapter 5) indicated an equilibrium in solution between $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**) and $[Ni(P\text{-}P)_2]^{2+}$ (**2**) (see Equation 6). In methanol, the solvent used in the catalysis, the equilbrium was predominantly to the left.

$$[Ni(P\text{-}P)_2](Y)_2 + Ni(Y)_2 \rightleftharpoons 2[Ni(P\text{-}P)(S)_2](Y)_2$$

Equation 6

An equilibrium was observed for the diphosphines, dcpe, dppp and Boxylyl (see chapter 5). However, this equilibrium was not apparent for the diphosphine ligand dppe by $^{31}P\{^1H\}$ NMR spectroscopy at r.t.. Two reactions were studied by $^{31}P\{^1H\}$ NMR spectroscopy to determine the lability of the diphosphine ligands in the complex $[Ni(dppe)_2](OTs)_2$. Firstly, a sample of the complex $[Ni(dppe)_2](OTs)_2$ was dissolved in a 1:1 mixture of toluene/MeOH and an excess of the known phosphine trap, MeI, was added. The NMR tube was heated to mimic catalytic conditions (1 min) and a $^{31}P\{^1H\}$ NMR spectrum was obtained which indicated the presence of $[Ni(dppe)_2](OTs)_2$ and the dimethylphosphonium salt, $[Ph_2P(Me)CH_2CH_2P(Me)Ph_2]I_2$, a type (**1**) complex was not detected. The presence of the dimethylphosphonium salt, $[Ph_2P(Me)CH_2CH_2P(Me)Ph_2]I_2$ was confirmed by the NMR reaction of dppe with MeI and comparison of the $^{31}P\{^1H\}$ NMR chemical shift. Secondly, the NMR reaction after heating (1 min) of $[Ni(dppe)_2](OTs)_2$ with S_8 in a toluene/methanol solution gave $[Ni(dppe)_2](OTs)_2$ and the diphosphine disulphide complex $[Ph_2P(S)CH_2CH_2P(S)Ph_2]$.

2). In the event of the two diphosphine ligands remaining co-ordinated there is still a fifth co-ordination site available for the co-ordination of a substrate ligand, L. The identification in solution by $^{31}P\{^1H\}$ NMR spectroscopy of the four co-ordinate cationic complex [Ni(dppe)(*o*-tolyl){dppe}](OTs) (see Chapter 4) in which one of the dppe ligands is co-ordinated in the usual chelating ligand fashion, and the other dppe ligand is co-ordinated through only one phosphorus atom, indicates that there is a free co-ordination site available in solution under catalytic conditions. It can be envisaged that the ability to alternate between a four co-ordinate and a five co-ordinate complex may result in additional stabilisation of the catalyst in the presence of a two molar equivalent of the diphosphine ligand (Scheme 2).



Scheme 2 L is a substrate ligand, $CH_2{=}CH_2$; CO; or growing polymer chain

The catalyst precursor complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (**2**) were recovered from solution after catalysis and were identified by $^{31}P\{^1H\}$ NMR spectroscopy (Appendix 4). However, the catalyst precursor complex $[Ni(dcpe)_2](OTs)_2$ was not recovered from run (iv) which had the longest reaction time of 10h and the greatest TON under these conditions (see Table 4). This indicates that either the rate of the reaction was very slow, or that the complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (**2**) were recovered in the presence of an effective excess of the diphosphine ligand caused by precipitation of $Ni(OTs)_2$ or $Ni(OTf)_2$. These were identified in the polyketone samples after catalysis, in line with the afore mentioned equilibrium in solution.

A series of reactions under varying conditions were carried out utilising dppe, and the summary of the reactions are shown in Table 4. The complex $[Ni(dppe)_2](OTs)_2$ was relatively easy to prepare and handle in comparison to the other diphosphine ligands, due to its isolation as a solid.

Table 4. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of; solvent, stirring efficiency, added phosphine on catalysis where P-P is dppe.

Run	Catalyst concentration/ mmol	Solvent volume/ cm^3 (Autoclave)	time /h	Added phosphine	HOTs	Mass polyketone /g	TON mol polyketone /mol nickel
v	0.5	MeOH (10ml) (A)	2	Nil	0.1g	0.27	10
vi	0.16	MeOH (10ml); toluene (20ml) (B)	2	Nil	0.1g	0.27	23
ix	0.12	MeOH (8ml); toluene (5ml) (A)	1	dppe	Nil	0.04	6
xii	0.18	MeOH (8ml); toluene (5ml) (A)	3	Nil	0.5g	0.04	4
xiii	0.15	AcOH (30ml) (B)	5	Nil	1.0 g	0.61	73
xiv	0.1	AcOH (30ml) (B)	5	10dppe	0.6g	0.66	100
xv	0.4	MeOH/ toluene 2:1 (15ml) (A)	5	$2PPh_3$	0.6g	0.12	2
xvi	1.0	MeOH/ toluene 2:1 (15ml) (A)	5	$2PPh_3$	0.6g	0.12	2

The complex $[Ni(dppe)_2](OTs)_2$ (run v) was not very soluble in a methanol solution alone and crystals of the complex $[Ni(dppe)_2](OTs)_2$ actually precipitated after the catalytic run. These crystals were subsequently recycled and tested (run vi) in a methanol/toluene solution in which the complex $[Ni(dppe)_2](OTs)_2$ was completely soluble, and a twofold increase in TON was observed. However, the increase could also be attributed to the better stirring efficiency of Autoclave B.

It was of interest to determine whether the complexes which catalysed the CO/ethene copolymerisation reaction were also catalytically active for ethene dimerisation or oligomerisation. Complexes of the type [Ni(P-O)PR] catalyse the ethene dimerisation reaction and only catalyse the CO/ethene copolymerisation reaction if the catalysis is initiated in the absence of CO, which is otherwise a catalyst poison.[4] The catalysis therefore oligomerises ethene until the CO is introduced at which point perfectly alternating copolymer is produced.[4] A similar system was therefore attempted for the complex $[Ni(dppe)_2](OTs)_2$ (run xii). Under these conditions there was a limited amount of polyketone obtained and furthermore, the infra-red analysis of the sample gave no indication of terminal alkyl groups. In previous catalysis using the diphosphine ligand dppe, ethene dimerisation was not observed.

An increase in TON was observed on the addition of a ten fold excess of the diphosphine ligand, dppe, to a solution of the complex $[Ni(dppe)_2](OTs)_2$ (run xiv). Run xiv produced the greatest overall TON for all the systems tested which combined, acetic acid as the solvent, autoclave B, and an excess of the diphosphine ligand. This turnover was the same order of magnitude as the palladium systems employed by Sen,[8] and was greater than that observed for previous nickel systems.[20]

The ligand dppp, has the highest rates and selectivities in the palladium system. Consequently, a catalytic test was carried out for dppp under the same optimum reaction conditions used for dppe, (run xvii). The choice of conditions was based on the results obtained using dppe for which a threefold increase in TON was obtained on replacing the methanol/toluene solution (run vi) with an acetic acid solution (run xiii) and an increase in TON was obtained in the presence of excess diphosphine ligand. Interestingly, for the nickel system , the dppp catalyst produced polyketone in only a quarter of the amount of the dppe ligand (Table 5).

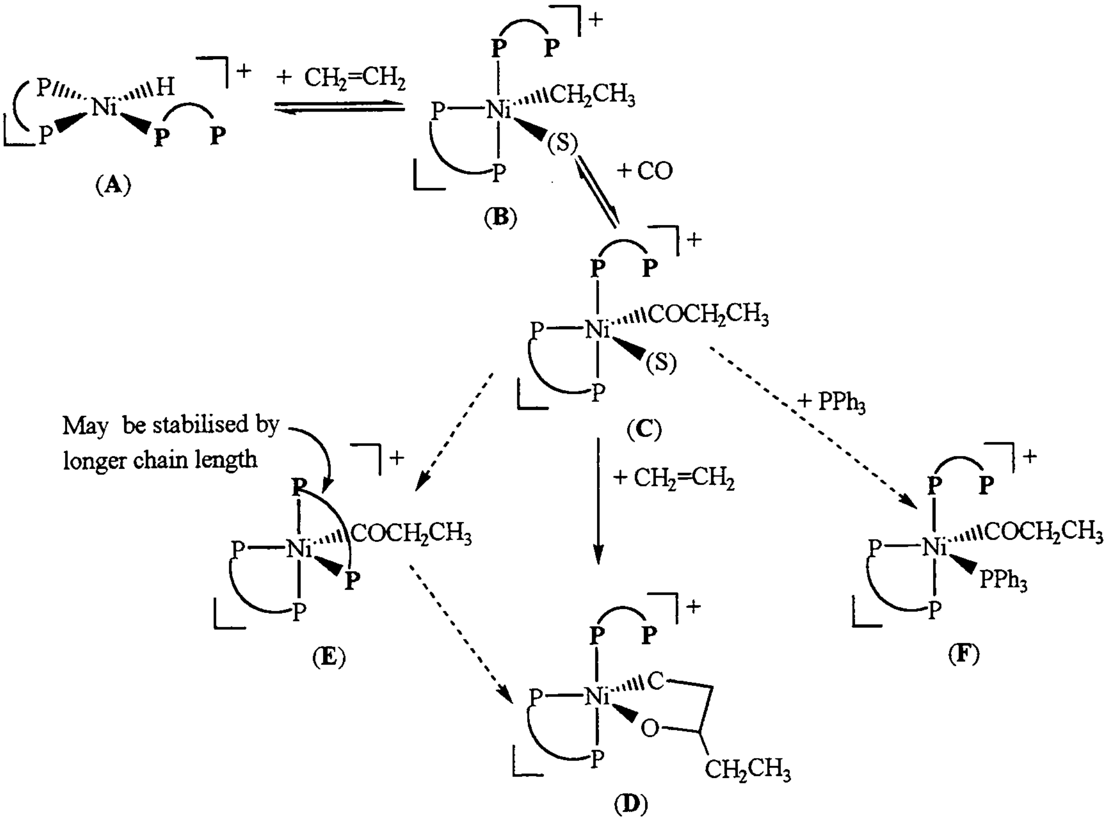
Table 5. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of diphosphine (P-P) on complexes of the type $[Ni(P\text{-}P)_2](OTs)_2$ in acetic acid, (Autoclave B).

Run	P-P	Catalyst concentration/ mmol	Added Phosphine	HOTs	Mass polyketone /g	TON mol polyketone/ mol nickel
xiii	dppe	0.15	Nil	1.0	0.61	73
xiv	dppe	0.1	10 dppe	0.6	0.66	100
xvii	dppp	0.1	10 dppp	0.6	0.14	25

Reaction carried out in 30 ml acetic acid, for a time of 5h, at a temperature of 110°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental).

The overall order of catalytic activity of the diphosphine ligands tested was dcpe ≥ dppe >> dppp >> Boxylyl >> dcpn. The two carbon atom backbone ligands are more reactive than the three, or four atom backbone ligands and this may be attributed to a difference in bite angle between the diphosphine ligands. These differences are reflected in solution studies of the bis-diphosphine complexes of the type $[Ni(P\text{-}P)_2](Y)_2$ (2) where in both cases an equilibrium exists in solution. In the case of the ligands dppp, dcpn and Boxylyl, there is evidence for a tetrahedral species in solution. These tetrahedral species may result in reduced catalytic activity due to the reduced availability of co-ordination sites which are *cis*- to each other and are required for the necessary migratory insertion reactions in the catalysis. Alternatively, the flexibility and larger chelate bite of the ligands may result in greater steric interactions with other ligands attached to the nickel centre, and results in destabilisation of an active species. Also chelation may result in blocking an active site as shown in Scheme 4. Addition of the monophosphine ligand, PPh_3, (runs xv and xvi) resulted in a fifty fold decrease in TON. This implies that the ligand PPh_3, was blocking or in competition with a substrate molecule for a free co-ordination site. These possibilities are described in scheme 4.

Scheme 4 Proposed reaction sequence for the possible blocking of co-ordination sites



It is generally accepted that the insertion of the first molecule of ethene and CO, amongst species A,B and C is reversible. As described previously, the next insertion of ethene into species C is thought to be the rate limiting step due to the stabilisation by chelation in a five membered ring of the growing polymer chain, species D. It can be envisaged that in the presence of a diphosphine ligand with a longer backbone and larger chelate bite angle, the axial to equatorial position in a five co-ordinate species is bridged more easily. Therefore, stabilisation of the growing polymer chain by co-ordination in a five membered chelate ring is inhibited by co-ordination of the second phosphorus of the diphosphine ligand (species E) which could affect the rate and the reactivity. This hypothesis is supported by the fact that the presence of the monophosphine ligand, PPh_3, greatly inhibits the catalysis of the usually catalytically active dppe ligand. PPh_3 is therefore blocking a co-ordination site, species F, in a similar fashion to the diphosphine ligands with larger bite angles.

The increase of catalytic activity on replacing the MeOH/toluene solvent with acetic acid for the active catalyst system employing [Ni(dppe)$_2$](OTs)$_2$, may also be due to inhibiting the co-ordination of a second phosphine ligand. Protonation of the unco-ordinated end of a diphosphine ligand would also prevent the blocking of the possible co-ordination site.

The effect of counterion on catalysis

The nature of the tosylate group as a weakly co-ordinating ligand is obviously important to the catalysis in this system, as was previously observed for palladium. Replacing the OTs$^-$ counterion in the complex [Ni(dppe)$_2$](OTs)$_2$ with a NO$_3^-$ or OAc$^-$ counterion, results in no catalysis (Table 6).

Table 6. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of counterion (Y) in complexes of the type [Ni(dppe)$_2$](Y)$_2$, (Autoclave A).

Run	Catalyst concentration/ mmol	Y	HY	Solvent	Mass polyketone /g	TON mol polyketone/mol nickel
vi	0.16	OTs	0.6	MeOH/toluene	0.27	23
xviii	0.9	OAc	0.8	acetic acid	Nil	-
xix	1.7	NO$_3$	0.8	MeOH/toluene	Nil	-

Reaction carried out in 10-15 ml solvent, for a time of 5h, at a temperature of 110°C, and at a pressure of 80 atm; $C_2H_4/CO = 1$ (see Experimental).

The complexes [Ni(dppe)$_2$](OAc)$_2$ and [Ni(dppe)$_2$](NO$_3$)$_2$ had completely decomposed after catalysis. A solid was recovered after the catalytic test employing the complex [Ni(dppe)$_2$](OAc)$_2$, and was found to be predominantly Ni(OAc)$_2$, which was characterised by infra-red analysis. The $^{31}P\{^1H\}$NMR spectrum of the recovered catalyst solution consisted of a a singlet at δ 16.4ppm, attributed to a diphosphonium salt [Ph$_2$P$^+$(H)CH$_2$CH$_2$P$^+$(H)Ph$_2$]$^{2+}$. Furthermore, this same phosphorus species, at a chemical shift value of δ 14-17ppm (solvent dependent), was identified after catalysis employing the complex [Ni(dppe)$_2$](OTs)$_2$ in runs (v), (ix), (xii) and (xviii) (Appendix 5).

The lack of catalytic activity of the $[Ni(dppe)_2](OAc)_2$ complex may be attributed to a co-ordination of the acetate ligand to the hard nickel(II) centre which results in the blocking of the available catalytic sites. The difficulty in replacing the acetate group on addition of the acid HOTs is a difference observed between the nickel and palladium chemistry. The synthesis of $Ni(OTs)_2$, *via* a displacement of the acetate groups from $Ni(OAc)_2$ with the acid HOTs, was low yielding and the displacement reaction is not as effective as in the palladium system. In the palladium system, addition of the acid HOTs to the $Pd(OAc)_2$ resulted in the facile replacement of the strongly co-ordinating acetate group by a weakly co-ordinating tosylate group. The catalytic activity of the palladium system was attributed in part to the weakly co-ordinating nature of the tosylate group.

The possible co-ordination of the acetate ligand is illustrated by the fact that the 1:1 reaction of $Ni(OAc)_2$ with dppe is complicated and took three days to equilibrate. However, even in the presence of the potentially co-ordinating acetate group the type (2) bis-complex $[Ni(dppe)_2](OAc)_2$ was eventually isolated.

For the complex $[Ni(dppe)_2](NO_3)_2$ the lack of catalytic activity may also be attributed to the instability of the complex under the conditions of catalysis. The NMR reaction (heat 1min) of $[Ni(dppe)_2](NO_3)_2$ with S_8, studied by NMR, resulted in the complete and immediate decomposition of the complex, and the only phosphorus species detected was the diphosphine disulphide, characterised by $^{31}P\{^1H\}$ NMR spectroscopy . In contrast, under similar conditions, after the reaction of $[Ni(dppe)_2](OTs)_2$ with S_8, the $[Ni(dppe)_2](OTs)_2$ complex still remained in solution as well as the diphosphine disulphide. It cannot be established for the acetate and nitrate system whether the catalysts are unstable, or if the acetate or nitrate are co-ordinating and completely blocking a catalytic site.

Attempted catalysis using $Ni(OTs)_2$ and PPh_3

The complete lack of activity observed for the catalyst system consisting of $Ni(OTs)_2$ with a ten fold excess of the ligand PPh_3 may be attributed to two reasons. Firstly, under the conditions a nickel complex may not have formed in a similar manner to the particular conditions necessary for the preparation of [Ni(PPh_3)$_2$Cl$_2$], and if the complex did form, it is likely that it would be tetrahedral and would therefore be unreactive.[22] Secondly, there is an increased tendency of Ni(II), to be reduced to Ni(0) in the presence of CO to give the tricarbonyl complex [Ni(PPh_3)$_n$(CO)$_{4-n}$] (n = 3,2,1).[23]

Catalysis using type (3) complexes, [Ni(P-P)(*o*-tolyl)(py)](OTs)

Catalytic systems were tested using [Ni(P-P)(*o*-tolyl)(py)](OTs) (**3**) (see Table 7). The catalysis was carried out in the absence of added acid in order to elucidate the mechanism. In run ix, the catalysis was carried out in the presence of an excess of the diphosphine ligand in case Ni(CO)$_4$ was formed, and therefore it would be quickly converted to the complex [Ni(dppe)(CO)$_2$],[6] which was identified by ^{31}P{^{1}H} NMR and infra-red spectroscopy,[10] after catalysis. The sample was obtained from the reactor, in the absence of air using a syringe. Using PPh_3, with the complex [Ni(dppe)(*o*-tolyl)(py)](OTs) (run x) resulted in reduced turnover numbers, compared with the use of dppe, in a similar fashion to that observed for the catalysts systems of the type [Ni(P-P)$_2$](OTs)$_2$ (**2**).

Table 7. Nickel-catalysed reactions of carbon monoxide with ethene: the effect of diphosphine (P-P) in complexes of the type [Ni(P-P)(*o*-tolyl)(py)](OTs), (Autoclave A).

Run	P-P	Catalyst concentration/ mmol	time/ h	Added phosphine	Mass polyketone/g	TON mol polyketone/mol nickel
ix	dppe	0.12	2	dppe	0.04	6
x	dppe	0.4	5	PPh_3	0.03	1
xi	dBpe[a]	0.01	5	nil	tr	-

Reaction carried out in 10-15 ml MeOH/toluene, at a temperature of 110°C, and at a pressure of 80 atm; C_2H_4/CO = 1 (see Experimental). [a] Limited catalyst available, reaction carried out to observe any polyketone formation.

Carbonylation of complexes of the type [Ni(P-P)(S)$_2$]$^{2+}$ (1), [Ni(P-P)$_2$]$^{2+}$ (2) and [Ni(P-P)(*o*-tolyl)Br] (5) on an NMR tube scale

The decreased reactivity in the systems that contains the diphosphine ligands dppp, dcpn and Boxylyl and in the presence of the monophosphine ligand PPh_3 may be due to the increased tendency to give complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**) and $[Ni(PPh_3)_n(CO)_{4-n}]$, (n = 1,2 ,3) in the presence of CO.[23] The complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**) are known thermodynamic sinks in the carbonylation of methanol.[4] The reaction of CO at 1atm with the complexes $[Ni(dppe)_2](OTs)_2$ and $[Ni(dcpe)_2](OTs)_2$, which were the most active catalysts, did not give the dicarbonyl complexes of the type $[Ni(P\text{-}P)(CO)_2]$ (**4**). However, the dppp and Boxylyl systems did give these dicarbonyls which were identified by infra-red spectroscopy.[10] The carbonylation of $[Ni(dcpn)_2](OTs)_2$ was not carried out because of insufficient complex being available. The reaction of [Ni(dppe)(*o*-tolyl)Br] also gave the dicarbonyl complex $[Ni(dppe)(CO)_2]$ on reaction with CO, consistent with the literature report.[23] It is also relevant that $[Ni(dppe)(CO)_2]$ was identified after catalysis (run ix) by the cationic complex [Ni(dppe)(*o*-tolyl)(S)]OTs.

6.3 Summary

The cationic nickel (II) diphosphine complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), $[Ni(P\text{-}P)_2]^{2+}$ (**2**) and $[Ni(P\text{-}P)(R)(o\text{-tolyl})]^+$ (**3**) containing the weakly co-ordinating anions, OTs^- and OTf^-, are catalyst precursors for the alternating copolymerisation reaction of CO and ethene to produce perfectly alternating polyketone. Although the catalysts are exclusively selective to polyketone formation, the activities of the catalysts and yields of polyketone are far too low for economic commercial production.

The catalytic cycle detailed by mechanistic studies for the palladium catalysed CO/ethene copolymerisation has been extended to the nickel systems, for which it is appropriate and relevant. The activity of the catalyst complexes [Ni(P-P)(R)(*o*-tolyl)](OTs) (**3**) in the absence of added acid supports a hydride initiation mechanism in this catalyst system.

The order of catalytic activity and the effects of various changing parameters such as the effects of added diphosphine or monophosphine, effects of solvent, excess acid, and the effect of the counterion have been determined and may be accounted for by the potential blocking, or impeding access to a free co-ordination site, in a number of ways which prevents, or slows the rate of, catalysis. Five co-ordinate complexes may be envisaged as intermediate species in the nickel catalyst system.

The catalytic activity of the diphosphine ligands decreases in the order: dcpe > dppe >> dppp >> Boxylyl > dcpn. For diphosphine ligands with a longer carbon atom backbone i.e. dppp, Boxylyl, and dcpn, an axial - equatorial chelation mode in a five co-ordinate intermediate species, becomes more favoured and may be the cause of low activity because available equatorial co-ordination sites may be blocked. Free co-ordination sites required for catalysis will become less available.

The complexes of the type $[Ni(P\text{-}P)_2]^{2+}$ (**2**) are more active than the complexes of the type $[Ni(P\text{-}P)(S)_2]^{2+}$ (**1**), and addition of an excess of diphosphine ligand to the former results in an increase in TON. This increase in activity in the presence of an excess of diphosphine ligand may be due to the stabilisation of the catalytic species. This is exemplified by the fact that $[Ni(P\text{-}P)(S)_2](Y)_2$ complexes containing the ligands dppp and Boxylyl were completely inactive in catalysis, but the complexes of the type $[Ni(P\text{-}P)_2](OTs)_2$ containing the same ligands were active.

An increase in TON is observed on substituting the methanol/toluene solvent with acetic acid. By increasing the acidity of the system, protonation of the diphosphine ligand would occur preventing co-ordination of a pendant phosphorus and freeing a co-ordination site.

The addition of the monophosphine ligand PPh_3, to an active diphosphine catalyst system, results in a large decrease in TON. Co-ordination of the monophosphine ligand PPh_3 may block a free co-ordination site.

Replacing the counterion in the complexes of the type $[Ni(P\text{-}P)_2](OTs)_2$ (**2**) by either OAc^- or NO_3^- results in no catalysis. The possible co-ordination of the acetate and nitrate groups may prevent catalysis by the blocking of an active site.

The dicarbonyl complexes [Ni(P-P)$(CO)_2$] are known sinks in the copolymerisation of CO and ethene. The ease of carbonylation of the complexes increases in the order dcpe < dppe < dppp ~ Boxylyl and is consistent with the order of catalytic activity; the most active catalyst systems contain the ligands dcpe and dppe which form the dicarbonyl complex less readily.

The extent of catalytic activity can therefore be attributed to a careful balance of stabilisation of a Ni (II) complex to reductive carbonylation to a nickel dicarbonyl complex [Ni(P-P)$(CO)_2$], and the extent of stabilisation which affects the rate of reaction where the free co-ordination sites are blocked to attack by the active substrates. Excess diphosphine stabilises the catalyst to decomposition but probably slows the rate of the reaction.

6.4 Experimental - Preparation of catalyst precursor complexes

All operations involving the preparation of catalyst systems and synthesis of the nickel complexes were carried out under dry nitrogen using standard schlenk techniques unless otherwise stated.

6.4.1 Run i using [Ni(dcpe)$(CH_3CN)_2$]$(OTf)_2$

AgOTf (0.38g, 1.5mmol) was added as a solid to [Ni(dcpe)Cl_2] (0.33g, 0.6mmol) in acetonitrile (10ml). The AgCl was removed by filtration. Methanol (3ml) was added to the filtrate. A $^{31}P\{^1H\}$ NMR spectrum was obtained on an aliquot of solution. HOTf (1ml) was added to the remaining solution *via* syringe. The catalyst solution consisting of [Ni(dcpe)$(CH_3CN)_2$]$(OTf)_2$ (0.6mmol), and HOTf (0.6 mmol) was transferred, to Autoclave A, *via* syringe under nitrogen. $^{31}P\{^1H\}$ NMR(CH_3CN): δ = 99.0 ppm

6.4.2 Run ii using "[Ni(dppp)$(CH_3CN)_2$]$(OTf)_2$"

AgOTf (0.6g, 2.3mmol) was added as a solid to Ni(dppp)Cl_2] (0.58g, 1.1mmol) in acetonitrile (10ml). An immediate colour change through red to brown occurred. After 1h stirring a blue solution was obtained together with AgCl which was removed by filtration. A further quantity of dppp (0.5mmol) was added which resulted in a deep red/brown solution. Methanol (3ml) was added to the filtrate and a $^{31}P\{^{1}H\}$ NMR spectrum was obtained on an aliquot of solution. HOTf (2.0mmol) was added to the flask *via* syringe. The catalyst solution consisting of $[Ni(dppp)(CH_3CN)_2](OTf)_2$ (0.6mmol) and HOTf (2.0mmol) was transferred, to Autoclave A, *via* a syringe under nitrogen.

6.4.3 Run iii using "$[Ni(Boxylyl)(CH_3CN)_2](OTf)_2$"

Boxylyl (0.5g, 1.3mmol) in toluene (5ml) was added to $Ni(OTf)_2$ (0.36g, 1.0mmol) in methanol (3ml) and acetonitrile (5ml). The solution was blue in colour. HOTf (2.0mmol) was added to the flask *via* syringe. The catalyst solution "$[Ni(Boxylyl)(CH_3CN)_2](OTf)_2$" (1.0mmol) and HOTf (2.0mmol) was transferred, to Autoclave A, *via* a syringe under nitrogen.

6.4.4 Run iv using $[Ni(dcpe)_2](OTs)_2$

Dcpe (0.43g, 0.91mmol) in methanol (10ml) was added to $Ni(OTs)_2$ (0.18g, 0.45mmol) in methanol (5ml). An immediate colour change from green to orange was observed. The catalyst solution $[Ni(dcpe)_2](OTs)_2$ (0.45mmol) was transferred *via* a syringe under nitrogen.to Autoclave A. HOTs (0.1g) was added to the autoclave as a solid whilst purging with nitrogen. $^{31}P\{^{1}H\}$ NMR (MeOH): $\delta = 67.6$ (s) ppm.

6.4.5 Run v using $[Ni(dppe)_2](OTs)_2$

Dppe (0.80g, 2.0mmol) in methanol (13ml) was added to a solution of $Ni(OTs)_2$ (0.37g, 0.92mmol) in methanol (5ml). An immediate colour change from green to canary yellow was observed. The excess dppe, not soluble in methanol, was removed by filtration. An aliquot, 10ml, of catalyst solution $[Ni(dppe)_2](OTs)_2$ (0.5mmol) was transferred *via* syringe under nitrogen, to Autoclave A. HOTs (0.1g) was added to the autoclave as a solid. $^{31}P\{^{1}H\}$ NMR (MeOH): $\delta = 54.8$ (s) ppm. The remainder of the solution was stored at -20°C and crystals of $[Ni(dppe)_2](OTs)_2.2MeOH$ were subsequently isolated.

6.4.6 Run vi using $[Ni(dppe)_2](OTs)_2$

$[Ni(dppe)_2](OTs)_2.(MeOH)_2$ (0.16mmol) (isolated from run (v)) was placed as a solid in a glass sleeve together with solid HOTs (0.1g). The glass sleeve was quickly evacuated and placed under nitrogen. Toluene (20ml) and methanol (10ml) were added under nitrogen. The glass sleeve was transferred to Autoclave B.

6.4.7 Run vii using "$[Ni(Boxylyl)_2](OTf)_2$"

Boxylyl (0.5g, 1mmol) in toluene (2ml) was added to $Ni(OTf)_2$ (0.18g, 0.5mmol) in methanol (10ml). An immediate colour change from green to pale yellow was observed. HOTf (0.6mmol) was added to the autoclave *via* syringe. The catalyst solution "$[Ni(Boxylyl)_2](OTf)_2$" (0.5mmol) was transferred, to Autoclave A, *via* a syringe under nitrogen.

6.4.8 Run viii using $[Ni(dcpn)_2](OTs)_2$

Dcpn (0.46g, 0.87mmol) in acetonitrile (8ml) was added to $Ni(OTs)_2$ (0.16g, 0.4mmol) in acetonitrile (5ml). An immediate colour change from green to orange was observed. The catalyst solution $[Ni(dcpn)_2](OTs)_2$ (0.45mmol) was transferred *via* a syringe under nitrogen, to Autoclave A. HOTs (0.2g) was added to the autoclave as a solid. $^{31}P\{^1H\}$NMR δ -15.0 (s, dcpn); δ 45 (br, $[Ni(dcpn)_2](OTs)_2$) ppm.

6.4.9 Run ix using [Ni(dppe)(*o*-tolyl)(S)](OTs) + dppe

[Ni(dppe)(*o*-tolyl)(OTs)] (0.1g, 0.13mmol), previously prepared as a solid (Chapter 3), was placed in a flask together with dppe (0.1g, 0.25mmol) and was dissolved in methanol (8ml) and toluene (5ml); a colour change from orange to yellow occurred. The catalyst solution was transferred, *via* a syringe, to Autoclave A.

6.4.10 Run x using [Ni(dppe)(*o*-tolyl)(py)](OTs) + $2PPh_3$

$[Ni(PPh_3)_2$(*o*-tolyl)(Br)] (0.3g, 0.40mmol) and dppe (0.16g, 0.4mmol) were placed in a flask, tetrahydrofuran (25ml) added and the mixture was stirred. TlOTs (0.16g, 0.4mmol) was added which resulted in the precipitation of TlBr which was removed by filtration. The filtrate was added to an excess of pyridine in tetrahydrofuran(1ml in

10ml). An aliquot of the catalyst solution "[Ni(dppe)(*o*-tol)(py)](OTs) + $2PPh_3$" (10ml) was transferred, *via* a syringe, to Autoclave A.

6.4.11 Run xi using [Ni(dBpe)(*o*-tolyl)(py)](OTs)

[Ni(dBpe)(*o*-tolyl)(Br)] (6mg, 0.01mmol), prepared previously as a solid (see Chapter 3), was dissolved in tetrahydrofuran (5ml). TlOTs (0.1g, 0.3mmol) was added which resulted in the precipitation of TlBr which was removed by filtration. The filtrate was added to an excess of pyridine (1ml) in a methanol/toluene 2:1 solution. The catalyst solution [Ni(dBpe)(*o*-tolyl)(py)](OTs) (10ml) was transferred, *via* a syringe, to Autoclave A. The solution was too dilute to obtain a phosphorus NMR.

6.4.12 Run xii using $[Ni(dppe)_2](OTs)_2$

$[Ni(dppe)_2](OTs)_2$ (0.22g, 0.18mmol), prepared previously (Chapter 4) was dissolved in a methanol/toluene 2:1 solution (15ml) and was transferred *via* a syringe into Autoclave A. HOTs (0.5g) was added to the autoclave as a solid.

6.4.13 Run xiii using $[Ni(dppe)_2](OTs)_2$

$[Ni(dppe)_2](OTs)_2$ (0.18g, 0.15mmol), prepared previously (Chapter 4), was placed as a solid in a glass sleeve together with solid HOTs (0.5g). The glass sleeve was quickly evacuated and placed under nitrogen. Acetic acid (30ml) was added under nitrogen. The glass sleeve was transferred to Autoclave B.

6.4.14 Run xiv using $[Ni(dppe)_2](OTs)_2$ + dppe

$[Ni(dppe)_2](OTs)_2$ (0.12g, 0.1mmol), prepared previously (Chapter 4), was placed as a solid in a glass sleeve together with a ten-fold excess of dppe (0.4g, 1.0mmol), and solid HOTs (0.5g). The glass sleeve was quickly evacuated and placed under nitrogen. Acetic acid (30ml) was added under nitrogen. The glass sleeve was transferred to Autoclave B.

6.4.15 Run xv using "$[Ni(dppe)_2](OTs)_2$ + PPh_3"

$[Ni(dppe)_2]Cl_2$ (0.2g, 0.38mmol) was placed in a Schlenk tube together with PPh_3 (0.2g, 0.76mmol), tetrahydrofuran (10ml) and toluene (10ml) were added and the mixture stirred, to give an orange/red solution. TlOTs (0.2g, 0.05mmol) was added as a solid and the precipitated TlCl was removed by filtration (methanol was added to dissolve the nickel complex before filtration). The catalyst solution was transferred *via* a syringe into Autoclave A. HOTs (0.6g) was added to the autoclave as a solid.

6.4.16 Run xvi using "$[Ni(dppe)_2](OTs)_2 + PPh_3$"

$Ni(OTs)_2$ (0.4g, 1.0mmol), dppe (0.40g, 1.0mmol) and PPh_3 (0.50g, 1.0mmol) were reacted in a methanol/toluene 2:1 solution (15ml). The product of the reaction was found to be $[Ni(dppe)_2](OTs)_2 + 2PPh_3$ by phosphorus nmr. The catalyst solution was transferred *via* syringe into Autoclave A. HOTs (0.5g) was added to the autoclave as a solid.

6.4.17 Run xvii using $[Ni(dppp)_2](OTs)_2$ + dppp

$Ni(OTs)_2$ (0.04g, 0.1mmol), dppp (0.50g, 1.2mmol) and HOTs (0.1g) were placed as solids in a glass sleeve The glass sleeve was quickly evacuated and placed under nitrogen. Acetic acid (30ml) was added under nitrogen to give a bright red solution. The glass sleeve was transferred to Autoclave B.

6.4.18 Run xviii using $[Ni(dppe)_2](OAc)_2$ + dppe

$[Ni(dppe)_2](OAc)_2$ (0.15g, 0.86mmol), dppe (0.34g, 1.7mmol) and HOTs (0.1g) were placed as solids in a glass sleeve. The glass sleeve was quickly evacuated and placed under nitrogen. Acetic acid (30ml) was added under nitrogen to give a bright red solution. The glass sleeve was transferred to Autoclave B.

6.4.19 Run xix using $[Ni(dppe)_2](NO_3)_2$ + dppe

Solid $[Ni(dppe)(NO_3)_2]$ (0.04g, 0.86mmol), {prepared by the reaction of $Ni(NO_3)_2.6H_2O$ (0.5g, 1.7 mmol) in hot ethanol (30ml,) with dppe (1.37g, 3.4mmol) in hot ethanol (20ml), which gave a yellow solid on cooling)[21] was dissolved in a methanol/toluene 2:1 solution (15ml). The catalyst solution was transferred *via* a syringe into Autoclave A. HOTs (0.1g) was added to the autoclave as a solid.

6.4.20 Run xx using $Ni(OTs)_2 + 28PPh_3$

$Ni(OTs)_2$ (0.2g, 0.5mmol) and PPh_3 (3.7g, 14.0mmol) were reacted in a methanol/toluene 2:1 solution (15ml). The resultant solution was pale green in colour. The catalyst solution was transferred *via* syringe into Autoclave A. HOTs (2.0g) was added to the autoclave as a solid.

6.5 Experimental - Copolymerisation of carbon monoxide with ethene

Autoclave A

Polymerisations were carried out in a 150ml Hasteloy^{TM} autoclave equipped with a glass liner. Stirring was by way of a magnetic follower. The air in the autoclave was removed by three cycles of vacuum followed by refilling with nitrogen. The autoclave was then purged with nitrogen and the catalyst solution injected *via* a syringe. The acid, HOTs, was added as a solid during purging. The autoclave was pressurised at r.t. with ethene (40atm) followed by CO (40atm). The autoclave was heated to the chosen temperature and then heated and stirred for the chosen time. At the end of the chosen time, heating was stopped and the autoclave was allowed to cool slowly. The reactant gases (C_2H_4 and CO) were vented. The solid product was collected by filtration (in air). The filtrate was set aside and $^{31}P\{^1H\}$ NMR data were obtained together with solution infra-red. The filtrate was distilled to remove the soluble catalyst, care being taken to retain the most volatile components, and G.C. analysis of the distillate was obtained. The solid product was washed with methanol, and water and dried in an oven at 80°C, (the solid was dried until no further weight loss was observed). Infra-red data was obtained on all the polyketone samples. ^{13}C NMR was obtained on some samples. Maldi-Tof mass spectroscopy was obtained on selected samples.

Autoclave B

Polymerisations were carried out in a 150ml stainless steel autoclave equipped with an overhead Magnedrive stirrer and a glass liner. The glass liner was loaded with, solid catalyst and solid HOTs, and the air was removed by three cycles of vacuum followed by refilling with nitrogen. The chosen solvent was added under nitrogen. The glass liner was quickly transferred to the steel autoclave and the reaction vessel purged. The autoclave was pressurised at r.t. with ethene (40atm) followed by CO (40atm). The autoclave was heated to the chosen temperature and then heated and stirred for the chosen time. At the end of the chosen time, heating was stopped and the autoclave was allowed to cool slowly. The reactant gases (C_2H_4 and CO) were vented. The solid product was collected by filtration (in air). The filtrate was set aside and $^{31}P\{^1H\}$ NMR data were obtained together with solution infra-red. The filtrate was distilled as above and G.C. analysis of the distillate was obtained. The solid product was washed with methanol, and water and dried in an oven at 80°C, (the solid was dried until no further weight loss was observed). Infra-red data were obtained on all the polyketone samples.

6.6 Experimental - Carbonylation of Nickel Diphosphine Complexes

6.6.1 Reaction of [Ni(dppe)$_2$](OTs)$_2$ (1) with CO

A sample of the nickel complex was placed under an inert atmosphere in an NMR tube adapted with a Young's tap. The solvent, acetic acid-d^4 was added *via* a syringe under nitrogen. The solution was frozen (-78°) and then the NMR tube was evacuated. CO was added at r.t. and 1atm and the tube was subsequently heated and shaken. Analysis was carried out by $^{31}P\ \{^1H\}$ NMR. A reaction had not occurred, the $^{31}P\{^1H\}$ NMR spectrum only contained unreacted starting material and [Ni(dppe)(CO)$_2$] was not observed by IR. $^{31}P\{^1H\}$ NMR (CD_3OOD) $\delta = 57.2$ (s, [Ni(dppe)$_2$](OTs)$_2$).

6.6.2 Reaction of [Ni(dcpe)$_2$](OTs)$_2$ (2) with CO

Reaction was carried out as described above. A dicarbonyl complex had not formed, and the starting material was the major species identified by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (CD_3OD) $\delta = 58.1$ (m); $\delta = 68.7$ (s, [Ni(dcpe)$_2$](OTs)$_2$ (**2**)); $\delta = 79.5$ (m); $\delta = 85.2$ (m); $\delta = 88.9$ (m, br). [Ni(dcpe)(CO)$_2$] was not observed by IR.

6.6.3 Reaction of [Ni(dppp)$_2$](OTs)$_2$ (3) with CO

Reaction was carried out as described above. The brown/red solution of [Ni(dppp)$_2$](OTs)$_2$ **(3)** changed to a bright red on addition of CO and a white solid precipitated. The dicarbonyl [Ni(dppp)(CO)$_2$] complex was identified by ^{31}P{^{1}H} NMR and I.R. spectrosopy. The remaining signals in the ^{31}P{^{1}H} NMR are attributed to unreacted starting material. ^{31}P{^{1}H} NMR (CD$_3$OOD) δ = 8 (v. br); δ = 17.6 (s); δ = 22.7 (br); δ = 25.9 (s, [Ni(dppp)(CO)$_2$] (7),); δ = 28.5 (br); δ = 40.3 (v. br); δ = 49.8 (s). [Ni(dppp)(CO)$_2$] (7) was observed by IR, IR (CD$_3$OOD) $\nu_{C=O}$ (sym. str.) 1999 cm^{-1}; $\nu_{C=O}$ (asym. str.) 1937 cm^{-1}(Lit^{10}, $\nu_{C=O}$ (sym. str.) 1997 cm^{-1}, $\nu_{S=O}$ (asym. str.) 1938 cm^{-1}.

6.6.4 Reaction of [Ni(Boxylyl)$_2$](OTs)$_2$ (4) with CO

Reaction was carried out as described above. The purple solution of [Ni(Boxylyl)$_2$](OTs)$_2$ **(4)** remained the same colour after addition of CO. A white solid precipitated over time. The dicarbonyl [Ni(Boxylyl)(CO)$_2$] complex was identified by I.R. The ^{31}P{^{1}H} NMR spectrum was very broad and the peaks could not be assigned. ^{31}P{^{1}H} NMR (CH$_3$CN): δ = 29.2 (s); δ = 30.2 (v. br); δ = 35.8 (v. br); δ = 47.8 (m); δ = 49.9 (m); δ = 62.4 (d); δ = 64.2 (s); δ = 68.5 (d). [Ni(Boxylyl)(CO)$_2$] **(8)** was observed by IR, IR (solid): $\nu_{C=O}$ (sym. str.) 1975 cm^{-1}; $\nu_{C=O}$ (asym. str.) 1909 cm^{-1}

6.6.5 Reaction of [Ni(dppe)(*o*-tolyl)Br] (8) with CO

Reaction was carried out as described above. The dicarbonyl [Ni(dppe)(CO)$_2$] complex was identified by ^{31}P{^{1}H} NMR and I.R. spectroscopy. ^{31}P{^{1}H} NMR (CH$_3$CN): δ = 47.7 (s, [Ni(dppe)(CO)$_2$] (5). IR (CH$_3$CN): $\nu_{C=O}$ (sym. str.) 2000 cm^{-1}; $\nu_{C=O}$ (asym. str.) 1945 cm^{-1} (Lit^{10} $\nu_{C=O}$ (sym. str.) 2000 cm^{-1}, $\nu_{S=O}$ (asym. str.) 1940 cm^{-1}).

6.6.6 Reaction of [Ni(dcpe)(*o*-tolyl)Br] (9) with CO

Reaction was carried out as described above. The ^{31}P{^{1}H} NMR spectrum was complex. A singlet peak attributed to [Ni(dcpe)Br$_2$]) was identified and was due to the decomposition of the starting material. However, the [Ni(dcpe)(CO)$_2$] (**6**) was not observed by $^{31}P\{^1H\}$ NMR or IR spectroscopy. $^{31}P\{^1H\}$ NMR ($CD_3OD/CDCl_3$): δ = 30.2 (s); δ = 54.7 and 59.5 (br); δ = 83.5 (s, [Ni(dcpe)Br$_2$]); δ = 84.8 (d); δ = 85.5 (d); δ = 87.1 (d); δ = 87.7 (d); δ = 89.3 (s).

6.6.7 Reaction of [Ni(dBpe)(*o*-tolyl)Br] (10) with CO

Reaction was carried out as described above. The $^{31}P\{^1H\}$ NMR spectrum was broad and attributed to the decompositon of the starting material. However, the dicarbonyl complex [Ni(dBpe)(CO)$_2$] was not observed by IR. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 90.6 (v. br); δ = 97 (v. br).

6.7 Experimental - NMR reactions relevant to catalysis

6.7.1 Reaction of complexes of the type [Ni(dppe)$_2$](Y)$_2$ with sulphur

The reactions of complexes of the type [Ni(dppe)$_2$](Y)$_2$ with sulphur were carried out on an NMR scale and the $^{31}P\{^1H\}$ NMR spectra were observed.

6.7.1.1 Reaction of dppe with sulphur.

Dppe and sulphur (excess) were placed in an NMR tube and the air was removed. Toluene was added and the tube was heated with a heat gun for 1min. $^{31}P\{^1H\}$ NMR δ = 43.0 (s, $Ph_2P\{S\}CH_2CH_2P\{S\}Ph_2$).

6.7.1.2 Reaction of [Ni(dppe)$_2$](OTs)$_2$ in toluene and methanol with sulphur in the absence of air

[Ni(dppe)$_2$](OTs)$_2$ and sulphur (excess) were placed in an NMR tube and the air was removed. A mixture of degassed toluene/MeOH 1:1 was added and the tube was heated with a heat gun for 1min. $^{31}P\{^1H\}$ NMR δ = 45.2 (s, $Ph_2P\{S\}CH_2CH_2P\{S\}Ph_2$); δ = 56.5 [Ni(dppe)$_2$](OTs)$_2$.

6.7.1.3 Reaction of $[Ni(dppe)_2](OTs)_2$ in toluene and methanol with sulphur in air

$[Ni(dppe)_2](OTs)_2$ and sulphur (excess) were placed in an NMR tube. A mixture of toluene/MeOH 1:1 was added and the tube was heated with a heat gun for 1min. $^{31}P\{^1H\}$ NMR $\delta = 35.7$ (s, $Ph_2P\{O\}CH_2CH_2P\{O\}Ph_2$, 1); $\delta = 44.1$ ($Ph_2P\{S\}CH_2CH_2P\{S\}Ph_2$, 4); $\delta = 55.5$ (s, $[Ni(dppe)_2](OTs)_2$, 5).

6.7.1.4 Reaction of $[Ni(dppe)_2](NO_3)_2$ in toluene and methanol with sulphur in air

$[Ni(dppe)_2](NO_3)_2$ and sulphur (excess) were placed in an NMR tube. A mixture of toluene/MeOH 1:1 was added and the tube was heated with a heat gun for 1min. The nickel complex visually decomposed resulting in a colourless solution. $^{31}P\{^1H\}$ NMR $\delta = 44.1$ (s, $Ph_2P\{S\}CH_2CH_2P\{S\}Ph_2$).

6.7.2 Reactions of the complex $[Ni(dppe)_2](OTs)_2$ to determine phosphine lability

The reaction of $[Ni(dppe)_2](OTs)_2$ with HOTs/ MeI / EtI were carried out on an NMR scale and the $^{31}P\{^1H\}$ NMR spectrum observed.

6.7.2.1 Reaction of $[Ni(dppe)_2](OTs)_2$ in toluene and methanol with MeI

$[Ni(dppe)_2](OTs)_2$ was placed in an NMR tube and the air was removed. MeI (excess) in toluene/MeOH 1:1 was added and the tube was heated with a heat gun for 1min. $^{31}P\{^1H\}$ NMR $\delta = 32.7$ (s, $[Ph_2P\{Me\}CH_2CH_2P\{Me\}Ph_2](I)_2$); $\delta = 58.1$ (s, $[Ni(dppe)_2](OTs)_2$)

6.7.2.3 Reaction of dppe with MeI

Dppe was placed in an NMR tube and the air was removed. MeI was added and the tube was heated with a heat gun for 1min which did not lead to an increase in solubility. Therefore, acetonitrile was added and the tube heated. $^{31}P\{^1H\}$ NMR (CH_3CN) $\delta = 27.0$ (s, $[Ph_2P\{Me\}CH_2CH_2P\{Me\}Ph_2](I)_2$)

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Chapter 7

A Comparison of Nickel with Palladium as Catalysts for CO/Ethene Conversions

This thesis is concerned with the chemistry of nickel-chelating phosphine compounds as alternative catalysts to those currently employed in the palladium catalysed conversion of CO and ethene to yield either polyketone or methyl propanoate.[1,2,3.]

The complexes were designed to be phosphine complexes that are cationic and contain a weakly co-ordinating anion. This is a common feature of all of the active palladium catalysts for the copolymerisation of CO and ethene.[1,2] When the co-ordinating anion was a tosylate or triflate group the greatest catalytic activity was observed in the palladium system, and hence the nickel complexes used in this work were designed to contain these weakly co-ordinating groups in preference to other alternatives, such as BF_4^-.

It was found that the cationic nickel (II) diphosphine complexes of the type $[Ni(P\text{-}P)_2]^{2+}$ **(1)** {P-P = dppe, dcpe, dppp, Boxylyl}, $[Ni(P\text{-}P)(S)_2]^{2+}$**(2)** {P-P = dcpe}and [Ni(P-P)(*o*-tolyl)(S)]$^+$ **(3)** {P-P = dppe, dBpe} containing the weakly co-ordinating anions, OTs$^-$ and OTf, are catalyst precursors for the alternating copolymerisation reaction of CO and ethene to produce perfectly alternating polyketone.

These nickel systems were more active than the original cyanide nickel systems for polyketone formation, which did not contain diphosphine ligands,[4] and equally active as the originally tested palladium phosphine systems which contained BF_4^- counterions.[5] It was found that the high selectivity to methyl propanoate formation, exhibited using a palladium catalyst containing a diphosphine with a rigid backbone, was not displayed using any of the nickel(II) diphosphine complexes. The nickel complex containing the diphosphine with a rigid backbone, Boxylyl, so successful with palladium was found, however to be moderately catalytically active but giving the alternative product, polyketone.

Attempted synthesis of the type (**2**) complexes analogous to the active palladium complexes, $[Pd(P\text{-}P)(S)_2]^{2+}$, was only observed for the diphosphine ligand dcpe. This was attributed to an equilibrium in solution between type (**2**) complexes, type (**1**) complexes, and $Ni(Y)_2$. The tendency of nickel to form bisdiphosphine (**1**) complexes in preference to the diphosphine complexes (**2**) in the presence of weakly co-ordinating ligands is a basic difference between the nickel and palladium chemistry. An excess of diphosphine ligand was found to increase the catalytic activity of the nickel system where a 2:1 diphosphine:[Ni] complex i.e. $[Ni(P\text{-}P)_2]^{2+}$ (**1**), was more active than a 1:1 diphosphine:[Ni] complex i.e. $[Ni(P\text{-}P)(S)_2]^{2+}$(**2**). The industrial palladium systems involve a 1:1 diphosphine:[Pd] complex.

The nickel catalyst complexes containing OTs^- or OTf^- must be preformed, in contrast to the palladium systems to achieve catalysis. The *in situ* preparation of a nickel species, in a similar manner to the palladium system, from a combination of $[Ni(dppe)_2](OAc)_2$ with HOTs, gave a completely inactive system. In contrast, the palladium system was equally active for a catalyst that was preformed or prepared *in situ*.[1] The metathesis of a tosylate for an acetate group appears to be more facile for palladium than nickel.

The nickel complexes can be preformed such that the compounds $Ni(OTs)_2$ or $Ni(OTf)_2$ can be combined with two molar equivalents of a diphosphine ligand under air free conditions, either in the reaction vessel itself, or can be previously combined and the precatalyst solution can be subsequently syringed into the reaction vessel. The catalyst precursor complex $[Ni(dppe)_2](Y)_2$ can be isolated as a solid. Extensive solution studies on the nature of the species present in the precatalyst solution have been carried out and an equilibrium observed between type (**1**) and type (**2**) complexes is found to depend on the diphosphine ligand and the solvent. A similar equilibrium was not reported for the complexes of the type $[Ni(P\text{-}P)_2](BF_4)_2$.[6]

The reduced catalytic activity of the nickel compared to the palladium catalysts is attributed to the ease of formation of the [Ni(P-P)(CO)$_2$], complexes which are readily available sinks in the presence of CO. There is no mention of these dicarbonyl species being formed in the palladium chemistry. Excess diphosphine presumably stabilises the nickel catalysts to reductive carbonylation but probably slows the rate of the reaction. The nature of the diphosphine ligand, particularly the nature of the backbone influenced the reactivity. This was partly attributed to the comparative ease of formation of the dicarbonyl complexes, where the more active catalysts were less prone to form these inactive species and the blockage of catalytic sites in five co-ordinate intermediates by ligands able to chelate an axial and equatorial site. For example the ease of carbonylation of the complexes increases in the order dcpe < dppe < dppp ~ Boxylyl and is consistent with the order of catalytic activity; the most active catalyst systems contain the ligands dcpe and dppe which form the dicarbonyl complex less readily. Therefore, increasing the ratio of CH_2=CH_2:CO may result in increased activity.

The disadvantage of a nickel system was the possible formation of the highly toxic compound [Ni(CO)$_4$]. However, [Ni(CO)$_4$] was not detected in any of the catalyst systems tested, though the presence of an excess of diphosphine ligand favours the formation of the diphosphine carbonyl complexes in preference.

The addition of an excess of the monophosphine ligand PPh$_3$, resulted in a large decrease in activity. The PPh$_3$ ligand was originally added to stabilise an intermediate complex but also it may vacate a co-ordination site more readily due to its greater lability compared to a diphosphine ligand. However, the nickel carbonyl species of the PPh$_3$ ligand [Ni(PPh$_3$)$_3$(CO)] and [Ni(PPh$_3$)$_2$(CO)$_2$] are formed readily.

The nickel catalysts investigated in this system are selective to polyketone formation but the activities are too low for commercial production. Therefore, the economic benefits which would be gained if these nickel catalyst were as active as the palladium analogues have not been realised.

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Appendix 1

Experimental Parameters

Unless otherwise stated , all reactions were carried out under a dry, oxygen free nitrogen atmosphere, using standard vacuum line and Schlenk techniques, and the solvents were dried and freshly distilled before use. The diphosphines dcpe, dBpe and Boxylyl were supplied by ICI Acrylics, the diphosphine ligand, dcpn, was synthesised in this laboratory by a co worker, the complexes [Ni(dppe)Cl_2], [Ni(dppp)Cl_2], [Ni$(PPh_3)_2Cl_2$], and [Ni$(PPh_3)_2Br_2$], were synthesised by literature procedures, all other reagents were purchased commercially.

The NMR spectra were recorded on a Varian 200MHz, spectrometer at ambient temperature at the following frequencies: phosphorus 81MHz, carbon 50MHz, proton 200MHz; or a Bruker AC 250 spectrometer at ambient temperature at the following frequencies: phosphorus 101MHz, carbon 70MHz, proton 250MHz. The proton and carbon NMR spectra are referenced to the ^{1}H and ^{13}C chemical shifts of the solvents as an internal standard, and reported with respect to $SiMe_4$. The ^{31}P spectra are referenced to an external frequency lock, and reported with respect to 85% H_3PO_4 at 0ppm. Unless otherwise stated, the infra-red spectra were recorded as solids on the Golden Gate attachment on a Perkin-Elmer 1600 series FT-IR spectrometer. The carbon, hydrogen and nitrogen elemental analyses were measured on a CE 440 elemental analyser.

Appendix 2

Supplementary Data for Chapter 2

Table 1. Crystal data and structure refinement for [Ni(dcpe)Cl$_2$] (**2**).

Empirical formula	C26 H48 Cl2 Ni P2
Formula weight	552.19
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 7.241(1) A alpha = 94.26(1) deg.
	b = 9.441(1) A beta = 107.29(1) deg.
	c = 10.761(1) A gamma = 98.71(1) deg.
Volume, Z	688.7(1) A^3, 1
Density (calculated)	1.331 Mg/m^3
Absorption coefficient	1.027 mm^-1
F(000)	296
Crystal size	0.4 x 0.2 x 0.1 mm
Theta range for data collection	2.00 to 30.00 deg.
Limiting indices	-10<=h<=10, -13<=k<=13, -10<=l<=14
Reflections collected	5553
Independent reflections	4426 [R(int) = 0.0244]
Absorption correction	Semiempirical on Laue equivalents
Max. and min. transmission	0.9714 and 0.7399
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4412 / 3 / 281
Goodness-of-fit on F^2	1.129
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0691
R indices (all data)	R1 = 0.0355, wR2 = 0.0759
Absolute structure parameter	0.60(2)
Largest diff. peak and hole	0.346 and -0.313 e.A^-3

Table 2 Selected Bond Lengths and Angles for the complex [Ni(dcpe)Cl$_2$] (**2**)

Bond Length [Å]		Bond Length [Å]	
C(11)-C(16)	1.535(5)	C(31)-C(36)	1.537(5)
C(11)-C(12)	1.542(4)	C(31)-C(32)	1.538(4)
C(12)-C(13)	1.536(5)	C(32)-C(33)	1.540(5)
C(13)-C(14)	1.530(5)	C(33)-C(34)	1.527(6)

C(14)-C(15)	1.527(5)	C(34)-C(35)	1.525(5)
C(15)-C(16)	1.546(5)	C(35)-C(36)	1.536(5)
C(21)-C(22)	1.537(5)	C(41)-C(42)	1.542(4)
C(21)-C(26)	1.540(4)	C(41)-C(46)	1.543(5)
C(22)-C(23)	1.533(5)	C(42)-C(43)	1.544(5)
C(23)-C(24)	1.532(5)	C(43)-C(44)	1.516(6)
C(24)-C(25)	1.524(5)	C(44)-C(45)	1.528(5)
C(25)-C(26)	1.537(5)	C(45)-C(46)	1.536(5)

Bond Angle [°]		Bond Angle [°]	
C(16)-C(11)-C(12)	110.7(3)	C(36)-C(31)-C(32)	110.4(3)
C(16)-C(11)-P(1)	114.3(2)	C(36)-C(31)-P(2)	114.4(2)
C(12)-C(11)-P(1)	111.9(2)	C(32)-C(31)-P(2)	113.0(2)
C(13)-C(12)-C(11)	110.0(3)	C(31)-C(32)-C(33)	110.4(3)
C(14)-C(13)-C(12)	111.3(3)	C(34)-C(33)-C(32)	111.4(3)
C(15)-C(14)-C(13)	110.6(3)	C(35)-C(34)-C(33)	111.3(3)
C(14)-C(15)-C(16)	111.7(3)	C(34)-C(35)-C(36)	110.3(3)
C(11)-C(16)-C(15)	110.0(3)	C(35)-C(36)-C(31)	110.4(3)
C(22)-C(21)-C(26)	110.7(3)	C(42)-C(41)-C(46)	110.6(3)
C(22)-C(21)-P(1)	113.4(2)	C(42)-C(41)-P(2)	115.4(2)
C(26)-C(21)-P(1)	111.0(2)	C(46)-C(41)-P(2)	110.7(2)
C(23)-C(22)-C(21)	110.5(3)	C(41)-C(42)-C(43)	110.7(3)
C(24)-C(23)-C(22)	111.7(3)	C(44)-C(43)-C(42)	110.9(3)
C(25)-C(24)-C(23)	110.1(3)	C(43)-C(44)-C(45)	111.0(3)
C(24)-C(25)-C(26)	111.9(3)	C(44)-C(45)-C(46)	111.3(3)
C(25)-C(26)-C(21)	111.2(3)	C(45)-C(46)-C(41)	111.5(3)

Table 3. Crystal data and structure refinement for [Ni(dBpe)Cl$_2$].2CHCl$_3$.

Empirical formula	C20 H42 Cl8 Ni P2
Formula weight	686.79
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.040(1) A alpha = 90 deg. b = 18.660(1) A beta = 92.84(1) deg. c = 15.445(1) A gamma = 90 deg.
Volume, Z	3177.9(4) A^3, 4
Density (calculated)	1.435 Mg/m^3
Absorption coefficient	1.393 mm^-1

F(000)	1424
Crystal size	0.3 x 0.3 x 0.2 mm
Theta range for data collection	1.71 to 30.03 deg.
Limiting indices	-14<=h<=15, -24<=k<=26, -21<=l<=15
Reflections collected	25653
Independent reflections	8744 [R(int) = 0.0856]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.7812 and 0.5820
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8666 / 0 / 444
Goodness-of-fit on F^2	1.218
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1247
R indices (all data)	R1 = 0.0966, wR2 = 0.1542
Largest diff. peak and hole	1.142 and -1.256 e.A^-3

Table 4 Selected Bond Lengths and Angles for the complex [Ni(dBpe)Cl$_2$] **(3)**

Bond Length [Å]		Bond Length [Å]	
C(1)-H(11)	0.95(5)	C(11)-C(13)	1.546(6)
C(1)-H(12)	0.92(4)	C(12)-H(121)	1.04(5)
C(2)-H(21)	0.95(4)	C(12)-H(122)	0.95(5)
C(2)-H(22)	0.96(5)	C(12)-H(123)	0.95(6)
C(3)-C(5)	1.528(6)	C(13)-H(131)	1.00(5)
C(3)-C(4)	1.540(6)	C(13)-H(132)	0.97(5)
C(3)-C(6)	1.541(6)	C(13)-H(133)	0.97(5)
C(4)-H(41)	0.95(5)	C(14)-H(141)	0.97(7)
C(4)-H(42)	1.05(5)	C(14)-H(142)	0.91(5)
C(4)-H(43)	1.00(4)	C(14)-H(143)	0.99(5)
C(5)-H(51)	0.91(6)	C(15)-C(17)	1.539(6)
C(5)-H(52)	1.04(5)	C(15)-C(18)	1.540(6)
C(5)-H(53)	0.92(5)	C(15)-C(16)	1.542(6)
C(6)-H(61)	1.00(5)	C(16)-H(161)	1.05(6)
C(6)-H(62)	1.00(6)	C(16)-H(162)	1.01(5)
C(6)-H(63)	0.98(5)	C(16)-H(163)	0.98(6)
C(7)-C(8)	1.532(6)	C(17)-H(171)	0.98(5)
C(7)-C(9)	1.544(6)	C(17)-H(172)	1.01(5)
C(7)-C(10)	1.547(6)	C(17)-H(173)	0.97(5)
C(8)-H(81)	1.05(5)	C(18)-H(181)	0.93(5)
C(8)-H(82)	0.98(5)	C(18)-H(182)	0.96(6)
C(8)-H(83)	0.99(5)	C(18)-H(183)	1.02(6)
C(9)-H(91)	0.98(5)	Cl(3)-C(19)	1.756(5)
C(9)-H(92)	0.97(5)	Cl(4)-C(19)	1.760(5)

C(9)-H(93)	0.96(5)	Cl(5)-C(19)	1.751(5)
C(10)-H(101)	1.00(5)	C(19)-H(19)	0.94(5)
C(10)-H(102)	0.97(6)	Cl(6)-C(20)	1.752(5)
C(10)-H(103)	1.02(5)	Cl(7)-C(20)	1.763(6)
C(11)-C(12)	1.536(6)	Cl(8)-C(20)	1.736(6)
C(11)-C(14)	1.542(6)	C(20)-H(20)	0.96

Bond Angle [°]		Bond Angle [°]	
C(2)-C(1)-H(11)	112(3)	C(12)-C(11)-C(13)	108.4(4)
P(1)-C(1)-H(11)	108(3)	C(14)-C(11)-C(13)	107.7(4)
C(2)-C(1)-H(12)	113(3)	C(12)-C(11)-P(2)	107.7(3)
P(1)-C(1)-H(12)	103(3)	C(14)-C(11)-P(2)	111.8(3)
H(11)-C(1)-H(12)	107(4)	C(13)-C(11)-P(2)	113.3(3)
C(1)-C(2)-P(2)	112.6(3)	C(11)-C(12)-H(121)	114(3)
C(1)-C(2)-H(21)	111(2)	C(11)-C(12)-H(122)	112(3)
P(2)-C(2)-H(21)	111(2)	H(121)-C(12)-H(122)	106(4)
C(1)-C(2)-H(22)	111(3)	C(11)-C(12)-H(123)	109(3)
P(2)-C(2)-H(22)	104(3)	H(121)-C(12)-H(123)	106(4)
H(21)-C(2)-H(22)	107(4)	H(122)-C(12)-H(123)	109(4)
C(5)-C(3)-C(4)	108.3(4)	C(11)-C(13)-H(131)	115(3)
C(5)-C(3)-C(6)	108.2(4)	C(11)-C(13)-H(132)	107(3)
C(4)-C(3)-C(6)	108.2(3)	H(131)-C(13)-H(132)	108(4)
C(5)-C(3)-P(1)	108.3(3)	C(11)-C(13)-H(133)	113(3)
C(4)-C(3)-P(1)	112.3(3)	H(131)-C(13)-H(133)	107(4)
C(6)-C(3)-P(1)	111.4(3)	H(132)-C(13)-H(133)	106(4)
C(3)-C(4)-H(41)	108(3)	C(11)-C(14)-H(141)	112(4)
C(3)-C(4)-H(42)	109(3)	C(11)-C(14)-H(142)	111(3)
H(41)-C(4)-H(42)	108(4)	H(141)-C(14)-H(142)	115(5)
C(3)-C(4)-H(43)	112(2)	C(11)-C(14)-H(143)	107(3)
H(41)-C(4)-H(43)	107(4)	H(141)-C(14)-H(143)	107(5)
H(42)-C(4)-H(43)	114(4)	H(142)-C(14)-H(143)	104(4)
C(3)-C(5)-H(51)	112(4)	C(17)-C(15)-C(18)	107.2(4)
C(3)-C(5)-H(52)	113(3)	C(17)-C(15)-C(16)	107.7(4)
H(51)-C(5)-H(52)	108(5)	C(18)-C(15)-C(16)	110.0(4)
C(3)-C(5)-H(53)	116(3)	C(17)-C(15)-P(2)	107.7(3)
H(51)-C(5)-H(53)	98(5)	C(18)-C(15)-P(2)	111.7(3)
H(52)-C(5)-H(53)	110(4)	C(16)-C(15)-P(2)	112.3(3)
C(3)-C(6)-H(61)	114(3)	C(15)-C(16)-H(161)	113(3)
C(3)-C(6)-H(62)	106(3)	C(15)-C(16)-H(162)	111(3)
H(61)-C(6)-H(62)	108(4)	H(161)-C(16)-H(162)	107(4)
C(3)-C(6)-H(63)	113(3)	C(15)-C(16)-H(163)	114(3)
H(61)-C(6)-H(63)	108(4)	H(161)-C(16)-H(163)	107(5)

H(62)-C(6)-H(63)	110(4)	H(162)-C(16)-H(163)	106(4)
C(8)-C(7)-C(9)	107.6(4)	C(15)-C(17)-H(171)	111(3)
C(8)-C(7)-C(10)	107.0(4)	C(15)-C(17)-H(172)	111(3)
C(9)-C(7)-C(10)	110.3(4)	H(171)-C(17)-H(172)	110(4)
C(8)-C(7)-P(1)	107.7(3)	C(15)-C(17)-H(173)	106(3)
C(9)-C(7)-P(1)	111.1(3)	H(171)-C(17)-H(173)	112(4)
C(10)-C(7)-P(1)	112.8(3)	H(172)-C(17)-H(173)	107(4)
C(7)-C(8)-H(81)	114(3)	C(15)-C(18)-H(181)	109(3)
C(7)-C(8)-H(82)	107(3)	C(15)-C(18)-H(182)	109(3)
H(81)-C(8)-H(82)	103(4)	H(181)-C(18)-H(182)	113(5)
C(7)-C(8)-H(83)	114(3)	C(15)-C(18)-H(183)	107(3)
H(81)-C(8)-H(83)	110(4)	H(181)-C(18)-H(183)	114(4)
H(82)-C(8)-H(83)	108(4)	H(182)-C(18)-H(183)	105(5)
C(7)-C(9)-H(91)	113(3)	Cl(5)-C(19)-Cl(3)	110.5(3)
C(7)-C(9)-H(92)	107(3)	Cl(5)-C(19)-Cl(4)	111.1(3)
H(91)-C(9)-H(92)	117(4)	Cl(3)-C(19)-Cl(4)	109.2(3)
C(7)-C(9)-H(93)	109(3)	Cl(5)-C(19)-H(19)	101(3)
H(91)-C(9)-H(93)	103(4)	Cl(3)-C(19)-H(19)	114(3)
H(92)-C(9)-H(93)	107(4)	Cl(4)-C(19)-H(19)	111(3)
C(7)-C(10)-H(101)	112(3)	Cl(8)-C(20)-Cl(6)	110.5(3)
C(7)-C(10)-H(102)	111(3)	Cl(8)-C(20)-Cl(7)	112.2(3)
H(101)-C(10)-H(102)	112(4)	Cl(6)-C(20)-Cl(7)	109.3(3)
C(7)-C(10)-H(103)	109(3)	Cl(8)-C(20)-H(20)	109.2(2)
H(101)-C(10)-H(103)	109(4)	Cl(6)-C(20)-H(20)	111.4(2)
H(102)-C(10)-H(103)	104(4)	Cl(7)-C(20)-H(20)	104.1(2)
C(12)-C(11)-C(14)	107.8(4)		

Table 5. Crystal data and structure refinement for [Ni(dcpn)Cl$_2$] **(4)**.

Empirical formula	C35 H52 Cl4 Ni P2
Formula weight	735.22
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Tetragonal
Space group	P4(3)2(1)2
Unit cell dimensions	a = 14.642(2) A alpha = 90 deg.
	b = 14.642(2) A beta = 90 deg.
	c = 17.539(2) A gamma = 90 deg.
Volume, Z	3760.3(7) A^3, 4
Density (calculated)	1.299 Mg/m^3
Absorption coefficient	0.908 mm^-1
F(000)	1552
Crystal size	0.45 x 0.30 x 0.20 mm
Theta range for data collection	1.81 to 27.49 deg.

Limiting indices	-14<=h<=19, -19<=k<=16, -22<=l<=22
Reflections collected	27165
Independent reflections	4326 [R(int) = 0.0865]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4325 / 1 / 192
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0884
R indices (all data)	R1 = 0.0630, wR2 = 0.1005
Absolute structure parameter	-0.01(2)
Largest diff. peak and hole	0.579 and -0.734 e.A^-3

Appendix 3

Supplementary Data for Chapter 3

Table 1. Crystal data and structure refinement for [Ni(dppe)(*o*-tolyl)Cl] (5).

Empirical formula	C73 H70 Cl2 Ni2 P4
Formula weight	1259.49
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic, P 1 2(1)/c 1
Space group	P1
Unit cell dimensions	a = 17.4913(1) A alpha = 90 deg. b = 23.8688(2) A beta = 115.288(1) deg. c = 16.7499(2) A gamma = 90 deg.
Volume, Z	6322.89(10) A^3
Density (calculated)	4, 1.323 Mg/m^3
Absorption coefficient	0.824 mm^-1
F(000)	2632
Crystal size	0.44 x 0.34 x 0.32 mm
Theta range for data collection	1.29 to 30.53 deg.
Limiting indices	-23<=h<=24, -29<=k<=32, -21<=l<=23
Reflections collected	44724 / 16568 [R(int) = 0.0420]
Completeness to 2theta	30.53 83.8%
Absorption correction	Empirical
Max. and min. transmission	1.000000 and 0.798142
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16568 / 0 / 734
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.0833
R indices (all data)	R1 = 0.0742, wR2 = 0.0917
Absolute structure parameter	0.00011(4)
Largest diff. peak and hole	0.512 and -0.405 e.A^-3

Table 2. Selected Bond lengths [Å] and angles [°] for complexes [Ni(dppe)(*o*-tol)Cl] (**5a**) and [Ni(dppe)(*o*-tol)Cl] (**5b**)

[Ni(dppe)(*o*-tol)Cl] (**5a**)		[Ni(dppe)(*o*-tol)Cl] (**5b**)	
Bond length [Å]		Bond length [Å]	
P(1)-C(1)	1.819(2)	P(3)-C(51)	1.816(2)
P(1)-C(11)	1.824(2)	P(3)-C(61)	1.824(2)
P(1)-C(01)	1.838(2)	P(3)-C(03)	1.836(2)

C(01)-C(02)	1.524(3)	C(03)-C(04)	1.535(3)
C(1)-C(2)	1.386(3)	C(51)-C(52)	1.387(3)
C(1)-C(6)	1.394(3)	C(51)-C(56)	1.390(3)
C(2)-C(3)	1.394(3)	C(52)-C(53)	1.387(3)
C(3)-C(4)	1.358(4)	C(53)-C(54)	1.372(4)
C(4)-C(5)	1.376(4)	C(54)-C(55)	1.369(4)
C(5)-C(6)	1.388(3)	C(55)-C(56)	1.385(3)
C(11)-C(12)	1.388(3)	C(61)-C(66)	1.379(3)
C(11)-C(16)	1.393(3)	C(61)-C(62)	1.379(3)
C(12)-C(13)	1.391(3)	C(62)-C(63)	1.385(3)
C(13)-C(14)	1.374(3)	C(63)-C(64)	1.367(4)
C(14)-C(15)	1.374(3)	C(64)-C(65)	1.362(4)
C(15)-C(16)	1.390(3)	C(65)-C(66)	1.396(3)
P(2)-C(31)	1.819(2)	P(4)-C(81)	1.813(2)
P(2)-C(21)	1.822(2)	P(4)-C(71)	1.819(2)
P(2)-C(02)	1.840(2)	P(4)-C(04)	1.845(2)
C(21)-C(22)	1.385(3)	C(71)-C(72)	1.392(3)
C(21)-C(26)	1.400(3)	C(71)-C(76)	1.401(3)
C(22)-C(23)	1.382(3)	C(72)-C(73)	1.383(3)
C(23)-C(24)	1.379(3)	C(73)-C(74)	1.381(3)
C(24)-C(25)	1.376(4)	C(74)-C(75)	1.379(3)
C(25)-C(26)	1.382(3)	C(75)-C(76)	1.380(3)
C(31)-C(32)	1.387(3)	C(81)-C(82)	1.390(3)
C(31)-C(36)	1.395(3)	C(81)-C(86)	1.394(3)
C(32)-C(33)	1.387(3)	C(82)-C(83)	1.388(3)
C(33)-C(34)	1.381(3)	C(83)-C(84)	1.384(4)
C(34)-C(35)	1.380(3)	C(84)-C(85)	1.366(4)
C(35)-C(36)	1.387(3)	C(85)-C(86)	1.383(3)
C(41)-C(46)	1.400(3)	C(91)-C(96)	1.402(3)
C(41)-C(42)	1.403(3)	C(91)-C(92)	1.407(3)
C(42)-C(43)	1.403(3)	C(92)-C(93)	1.392(3)
C(42)-C(47)	1.498(4)	C(92)-C(97)	1.511(3)
C(43)-C(44)	1.374(4)	C(93)-C(94)	1.383(4)
C(44)-C(45)	1.373(4)	C(94)-C(95)	1.376(4)
C(45)-C(46)	1.395(3)	C(95)-C(96)	1.385(3)

[Ni(dppe)(o-tol)Cl] (**5a**)		[Ni(dppe)(o-tol)Cl] (**5b**)	
Bond Angle [°]		Bond Angle [°]	
C(1)-P(1)-C(11)	103.59(9)	C(51)-P(3)-C(61)	103.51(9)
C(1)-P(1)-C(01)	104.52(10)	C(51)-P(3)-C(03)	106.91(10)
C(11)-P(1)-C(01)	103.50(10)	C(61)-P(3)-C(03)	103.30(10)
C(1)-P(1)-Ni(1)	125.64(7)	C(51)-P(3)-Ni(2)	122.60(7)

C(11)-P(1)-Ni(1)	110.16(7)	C(61)-P(3)-Ni(2)	111.45(7)
C(01)-P(1)-Ni(1)	107.31(7)	C(03)-P(3)-Ni(2)	107.41(7)
C(02)-C(01)-P(1)	106.67(14)	C(04)-C(03)-P(3)	105.35(14)
C(2)-C(1)-C(6)	118.4(2)	C(52)-C(51)-C(56)	118.6(2)
C(2)-C(1)-P(1)	122.53(18)	C(52)-C(51)-P(3)	122.69(18)
C(6)-C(1)-P(1)	119.02(18)	C(56)-C(51)-P(3)	118.63(17)
C(1)-C(2)-C(3)	120.6(3)	C(53)-C(52)-C(51)	120.4(3)
C(4)-C(3)-C(2)	120.3(3)	C(54)-C(53)-C(52)	120.0(3)
C(3)-C(4)-C(5)	120.1(2)	C(55)-C(54)-C(53)	120.6(2)
C(4)-C(5)-C(6)	120.4(3)	C(54)-C(55)-C(56)	119.8(3)
C(5)-C(6)-C(1)	120.1(3)	C(55)-C(56)-C(51)	120.7(2)
C(12)-C(11)-C(16)	119.0(2)	C(66)-C(61)-C(62)	118.4(2)
C(12)-C(11)-P(1)	121.72(17)	C(66)-C(61)-P(3)	120.05(17)
C(16)-C(11)-P(1)	119.29(16)	C(62)-C(61)-P(3)	121.55(17)
C(11)-C(12)-C(13)	120.2(2)	C(61)-C(62)-C(63)	121.1(2)
C(14)-C(13)-C(12)	120.4(2)	C(64)-C(63)-C(62)	120.0(2)
C(15)-C(14)-C(13)	120.0(2)	C(65)-C(64)-C(63)	119.7(2)
C(14)-C(15)-C(16)	120.4(2)	C(64)-C(65)-C(66)	120.6(3)
C(15)-C(16)-C(11)	120.1 (2)	C(61)-C(66)-C(65)	120.1(2)
C(31)-P(2)-C(21)	108.08(9)	C(81)-P(4)-C(71)	108.33(10)
C(31)-P(2)-C(02)	103.88(9)	C(81)-P(4)-C(04)	105.04(10)
C(21)-P(2)-C(02)	101.14(9)	C(71)-P(4)-C(04)	101.56(10)
C(31)-P(2)-Ni(1)	122.33(7)	C(81)-P(4)-Ni(2)	118.68(7)
C(21)-P(2)-Ni(1)	108.84(7)	C(71)-P(4)-Ni(2)	111.08(7)
C(02)-P(2)-Ni(1)	110.48(7)	C(04)-P(4)-Ni(2)	110.65(7)
C(01)-C(02)-P(2)	107.61(14)	C(03)-C(04)-P(4)	108.43(14)
C(22)-C(21)-C(26)	118.74(19)	C(72)-C(71)-C(76)	118.91(19)
C(22)-C(21)-P(2)	122.93(16)	C(72)-C(71)-P(4)	123.82(16)
C(26)-C(21)-P(2)	117.95(16)	C(76)-C(71)-P(4)	116.97(16)
C(23)-C(22)-C(21)	120.6(2)	C(73)-C(72)-C(71)	120.0(2)
C(24)-C(23)-C(22)	120.3(2)	C(74)-C(73)-C(72)	120.5(2)
C(25)-C(24)-C(23)	119.7(2)	C(75)-C(74)-C(73)	120.0(2)
C(24)-C(25)-C(26)	120.5(2)	C(74)-C(75)-C(76)	120.0(2)
C(25)-C(26)-C(21)	120.1(2)	C(75)-C(76)-C(71)	120.5(2)
C(32)-C(31)-C(36)	118.71(19)	C(82)-C(81)-C(86)	118.4(2)
C(32)-C(31)-P(2)	121.86(16)	C(82)-C(81)-P(4)	120.89(16)
C(36)-C(31)-P(2)	119.39(16)	C(86)-C(81)-P(4)	120.46(17)
C(33)-C(32)-C(31)	120.8(2)	C(83)-C(82)-C(81)	120.7(2)
C(34)-C(33)-C(32)	120.1(2)	C(84)-C(83)-C(82)	119.9(2)
C(35)-C(34)-C(33)	119.7(2)	C(85)-C(84)-C(83)	119.9(2)
C(34)-C(35)-C(36)	120.5(2)	C(84)-C(85)-C(86)	120.7(2)
C(35)-C(36)-C(31)	120.2(2)	C(85)-C(86)-C(81)	120.5(2)

C(46)-C(41)-C(42)	117.8(2)	C(96)-C(91)-C(92)	117.5(2)
C(46)-C(41)-Ni(1)	121.34(18)	C(96)-C(91)-Ni(2)	121.23(16)
C(42)-C(41)-Ni(1)	120.86(17)	C(92)-C(91)-Ni(2)	121.27(16)
C(41)-C(42)-C(43)	119.6(2)	C(93)-C(92)-C(91)	119.6(2)
C(41)-C(42)-C(47)	120.6(2)	C(93)-C(92)-C(97)	119.9(2)
C(43)-C(42)-C(47)	119.9(2)	C(91)-C(92)-C(97)	120.5(2)
C(44)-C(43)-C(42)	121.4(3)	C(94)-C(93)-C(92)	121.7(2)
C(45)-C(44)-C(43)	119.7(3)	C(95)-C(94)-C(93)	119.2(2)
C(44)-C(45)-C(46)	119.9(3)	C(94)-C(95)-C(96)	119.9(2)
C(45)-C(46)-C(41)	121.6(3)	C(95)-C(96)-C(91)	122.0(2)
C(91)-Ni(2)-P(4)	85.93(6)	C(6')-C(1')-C(2')	120.3(3)
C(91)-Ni(2)-Cl(2)	91.43(6)	C(3')-C(2')-C(1')	117.5(3)
P(4)-Ni(2)-Cl(2)	175.82(2)	C(3')-C(2')-C(7')	122.8(3)
C(91)-Ni(2)-P(3)	172.23 (6)	C(1')-C(2')-C(7')	119.7(3)
P(4)-Ni(2)-P(3)	86.42(2)	C(2')-C(3')-C(4')	121.5(3)
Cl(2)-Ni(2)-P(3)	96.29(2)	C(5')-C(4')-C(3')	121.2(3)
C(51)-P(3)-C(61)	103.51(9)	C(4')-C(5')-C(6')	117.9(3)
C(51)-P(3)-C(03)	106.91(10)	C(1')-C(6')-C(5')	121.7(3)

Table 3. Crystal data and structure refinement for $[Ni(dppp)_2]$.

Empirical formula	C54 H52 Ni P2	
Formula weight	821.61	
Temperature	120(2) K	
Wavelength	0.71073 A	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.160(1) A	alpha = 90 deg.
	b = 13.220(1) A	beta = 109.66(1) deg.
	c = 19.882(1) A	gamma = 90 deg.
Volume, Z	4	
Density (calculated)	1.214 g/cm^3	
Absorption coefficient	0.538 mm^-1	
F(000)	1736	
Crystal size	0.20 x 0.11 x 0.09 mm	
Theta range for data collection	1.95 to 27.50 deg.	
Limiting indices	-25<=h<=22, -18<=k<=18, -27<=l<=27	
Reflections collected	15907	
Completeness to 2theta	5171 [R(int) = 0.0666]	
Observed reflections	I>2sigma(I) 3863	
Absorption correction	Integration	
Max. and min. transmission	0.9539 and 0.9312	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5053 / 0 / 371
Goodness-of-fit on F^2	1.146
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.0819
R indices (all data)	R1 = 0.0826, wR2 = 0.1015
Largest shift/e.s.d. ratio	0.004
Largest diff. peak and hole	0.375 and -0.431 e.A^-3

Table 4 Bond lengths [Å] and angles [°] for [Ni(dppp)$_2$]

Bond length [Å]		Bond length [Å]	
Ni-P(2)	2.177(1)	Ni-P(1)	2.181(1)
P(1)-C(11)	1.851(3)	P(1)-C(1)	1.856(3)
P(1)-C(21)	1.863(3)	P(2)-C(31)	1.845(3)
P(2)-C(41)	1.849(3)	P(2)-C(3)	1.852(3)
C(1)-C(2)	1.536(4)	C(1)-H(1A)	1.00(3)
C(1)-H(1B)	1.04(3)	C(2)-C(3)	1.536(4)
C(2)-H(2A)	0.99(3)	C(2)-H(2B)	0.95(3)
C(3)-H(3A)	0.94(3)	C(3)-H(3B)	1.05(3)
C(11)-C(12)	1.397(4)	C(11)-C(16)	1.410(4)
C(12)-C(13)	1.403(4)	C(12)-H(12)	0.96(3)
C(13)-C(14)	1.382(5)	C(13)-H(13)	0.96(3)
C(14)-C(15)	1.388(5)	C(14)-H(14)	0.88(3)
C(15)-C(16)	1.393(4)	C(15)-H(15)	0.97(3)
C(16)-H(16)	0.98(3)	C (21)-C(22)	1.393(4)
C(21)-C(26)	1.398(4)	C(22)-C(23)	1.397(4)
C(22)-H(22)	0.91(3)	C(23)-C(24)	1.377(5)
C(23)-H(23)	0.98(3)	C(24)-C(25)	1.401(5)
C(24)-H(24)	0.95(4)	C(25)-C(26)	1.391(4)
C(25)-H(25)	0.94(3)	C(26)-H(26)	1.00(3)
C(31)-C(36)	1.396(4)	C(31)-C(32)	1.399(4)
C(32)-C(33)	1.389(4)	C(32)-H(32)	0.97(3)
C(33)-C(34)	1.386(4)	C(33)-H(33)	0.94(3)
C(34)-C(35)	1.382(4)	C(34)-H(34)	0.88(3)
C(35)-C(36)	1.393(4)	C(35)-H(35)	0.95(3)
C(36)-H(36)	0.98(3)	C (41)-C(42)	1.396(4)
C(41)-C(46)	1.396(4)	C(42)-C(43)	1.387(4)
C(42)-H(42)	0.94(3)	C(43)-C(44)	1.384(4)
C(43)-H(43)	0.96(3)	C(44)-C(45)	1.395(4)
C(44)-H(44)	1.00(3)	C(45)-C(46)	1.390(4)
C(45)-H(45)	0.94(3)	C(46)-H(46)	0.99(3)

Bond angles °		Bond angles °	
P(2)-Ni-P(2')	106.34(4)	P(2)-Ni-P(1')	115.09(3)
P(2)-Ni-P(1)	99.81(3)	P(1')-Ni-P(1)	120.55(4)
C(11)-P(1)-C(1)	98.85(12)	C(11)-P(1)-C(21)	99.89(12)
C(1)-P(1)-C(21)	98.44(13)	C(11)-P(1)-Ni	122.25(9)
C(1)-P(1)-Ni	112.48(10)	C(21)-P(1)-Ni	120.51(9)
C(31)-P(2)-C(41)	100.55(12)	C(31)-P(2)-C(3)	100.44(13)
C(41)-P(2)-C(3)	98.81(12)	C(31)-P(2)-Ni	118.52(9)
C(41)-P(2)-Ni	119.31(9)	C(3)-P(2)-Ni	115.68(9)
C(2)-C(1)-P(1)	112.8(2)	C(2)-C(1)-H(1A)	110(2)
P(1)-C(1)-H(1A)	110(2)	C(2)-C(1)-H(1B)	111(2)
P(1)-C(1)-H(1B)	106(2)	H(1A)-C(1)-H(1B)	107(2)
C(3)-C(2)-C(1)	113.1(2)	C(3)-C(2)-H(2A)	108(2)
C(1)-C(2)-H(2A)	110(2)	C(3)-C(2)-H(2B)	111(2)
C(1)-C(2)-H(2B)	109(2)	H(2A)-C(2)-H(2B)	106(2)
C(2)-C(3)-P(2)	113.4(2)	C(2)-C(3)-H(3A)	108(2)
P(2)-C(3)-H(3A)	109(2)	C(2)-C(3)-H(3B)	109(2)
P(2)-C(3)-H(3B)	110(2)	H(3A)-C(3)-H(3B)	107(2)
C(12)-C(11)-C(16)	117.8(3)	C(12)-C(11)-P(1)	120.1(2)
C(16)-C(11)-P(1)	122.1(2)	C(11)-C(12)-C(13)	121.3(3)
C(11)-C(12)-H(12)	121(2)	C(13)-C(12)-H(12)	118(2)
C(14)-C(13)-C(12)	119.8(3)	C(14)-C(13)-H(13)	123(2)
C(12)-C(13)-H(13)	118(2)	C(13)-C(14)-C(15)	120.0(3)
C(13)-C(14)-H(14)	120(2)	C(15)-C(14)-H(14)	120(2)
C(14)-C(15)-C(16)	120.4(3)	C(14)-C(15)-H(15)	120(2)
C(16)-C(15)-H(15)	120(2)	C (15)-C(16)-C(11)	120.8(3)
C(15)-C(16)-H(16)	122(2)	C(11)-C(16)-H(16)	117(2)
C(22)-C(21)-C(26)	118.0(3)	C(22)-C(21)-P(1)	119.0(2)
C(26)-C(21)-P(1)	122.9(2)	C(21)-C(22)-C(23)	121.2(3)
C(21)-C(22)-H(22)	121(2)	C(23)-C(22)-H(22)	118(2)
C(24)-C(23)-C(22)	120.3(3)	C(24)-C(23)-H(23)	123(2)
C(22)-C(23)-H(23)	117(2)	C(23)-C(24)-C(25)	119.5(3)
C(23)-C(24)-H(24)	121(2)	C(25)-C(24)-H(24)	120(2)
C(26)-C(25)-C(24)	119.9(3)	C(26)-C(25)-H(25)	125(2)
C(24)-C(25)-H(25)	115(2)	C(25)-C(26)-C(21)	121.1(3)
C(25)-C(26)-H(26)	117(2)	C(21)-C(26)-H(26)	122(2)
C(36)-C(31)-C(32)	117.6(3)	C(36)-C(31)-P(2)	124.8(2)
C(32)-C(31)-P(2)	117.5(2)	C(33)-C(32)-C(31)	121.6(3)
C(33)-C(32)-H(32)	117(2)	C(31)-C(32)-H(32)	121(2)
C(34)-C(33)-C(32)	119.7(3)	C(34)-C(33)-H(33)	121(2)
C(32)-C(33)-H(33)	119(2)	C(35)-C(34)-C(33)	119.8(3)
C(35)-C(34)-H(34)	122(2)	C(33)-C(34)-H(34)	118(2)

C(34)-C(35)-C(36)	120.4(3)	C(34)-C(35)-H(35)	120(2)
C(36)-C(35)-H(35)	120(2)	C(35)-C(36)-C(31)	120.9(3)
C(35)-C(36)-H(36)	119(2)	C(31)-C(36)-H(36)	120(2)
C(42)-C(41)-C(46)	118.2(3)	C(42)-C(41)-P(2)	117.7(2)
C(46)-C(41)-P(2)	124.1(2)	C(43)-C(42)-C(41)	121.1(3)
C(43)-C(42)-H(42)	118(2)	C(41)-C(42)-H(42)	121(2)
C(44)-C(43)-C(42)	120.3(3)	C(44)-C(43)-H(43)	121(2)
C(42)-C(43)-H(43)	119(2)	C(43)-C(44)-C(45)	119.5(3)
C(43)-C(44)-H(44)	121(2)	C(45)-C(44)-H(44)	119(2)
C(46)-C(45)-C(44)	119.9(3)	C(46)-C(45)-H(45)	120(2)
C(44)-C(45)-H(45)	120(2)	C(45)-C(46)-C(41)	121.0(3)
C(45)-C(46)-H(46)	120(2)	C(41)-C(46)-H(46)	120(2)

Appendix 4

Supplementary Data for Chapter 5

Table 1. Crystal data and structure refinement for [Ni(dppe)$_2$](OTs)$_2$.(MeOH)$_2$ **(6)**.

Empirical formula	C54 H52 Ni P2
Formula weight	821.61
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 18.160(1) A alpha = 90 deg.
	b = 13.220(1) A beta = 109.66(1) deg.
	c = 19.882(1) A gamma = 90 deg.
Volume, Z	4494.9(5) A^3, 4
Density (calculated)	1.214 g/cm^3
Absorption coefficient	0.538 mm^-1
F(000)	1736
Crystal size	0.20 x 0.11 x 0.09 mm
Theta range for data collection	1.95 to 27.50 deg.
Limiting indices	-25<=h<=22, -18<=k<=18, -27<=l<=27
Reflections collected	15907
Independent reflections	5171 [R(int) = 0.0666]
Observed reflections,	I>2sigma(I) 3863
Absorption correction	Integration
Max. and min. transmission	0.9539 and 0.9312
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5053 / 0 / 371
Goodness-of-fit on F^2	1.146
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.0819
R indices (all data)	R1 = 0.0826, wR2 = 0.1015
Largest shift/e.s.d. ratio	0.004
Largest diff. peak and hole	0.375 and -0.431 e.A^-3

Table 2. Selected Bond lengths [Å] and angles [°] for [Ni(dppe)$_2$](OTs)$_2$.2MeOH **(6a)**

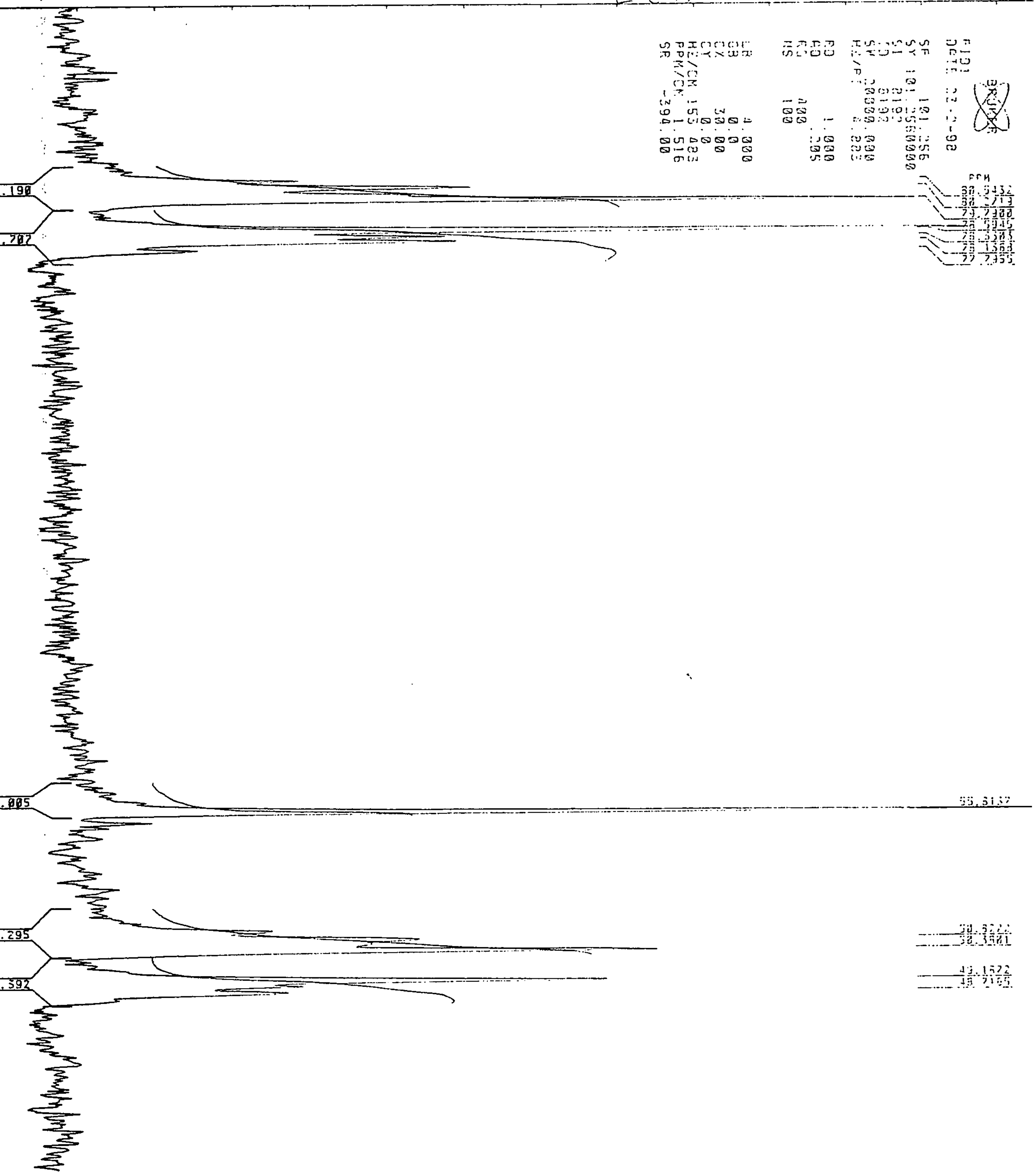
Bond Length [Å]		Bond Length [Å]	
C(1)-C(2)#1	1.544(7)	C(31)-C(36)	1.395(7)
C(2)-C(1)#1	1.543(7)	C(31)-C(32)	1.402(7)
C(11)-C(16)	1.381(8)	C(32)-C(33)	1.398(7)
C(11)-C(12)	1.386(8)	C(33)-C(34)	1.369(8)

C(11)-S(1)	1.787(5)	C(34)-C(35)	1.395(8)
C(12)-C(13)	1.396(8)	C(35)-C(36)	1.392(7)
C(13)-C(14)	1.377(9)	C(41)-C(42)	1.403(7)
C(14)-C(15)	1.391(8)	C(41)-C(46)	1.408(7)
C(14)-C(141)	1.527(8)	C(42)-C(43)	1.391(7)
C(15)-C(16)	1.405(8)	C(43)-C(44)	1.388(8)
S(1)-O(1C)	1.446(4)	C(44)-C(45)	1.380(8)
S(1)-O(1B)	1.454(4)	C(45)-C(46)	1.395(7)
S(1)-O(1A)	1.460(4)	C(51)-C(56)	1.392(7)
C(21)-C(22)	1.400(7)	C(51)-C(52)	1.396(7)
C(21)-C(26)	1.402(6)	C(52)-C(53)	1.390(7)
C(22)-C(23)	1.391(7)	C(53)-C(54)	1.382(8)
C(23)-C(24)	1.384(8)	C(54)-C(55)	1.388(8)
C(24)-C(25)	1.385(8)	C(55)-C(56)	1.389(7)
C(25)-C(26)	1.386(8)	O(1)-C(01)	1.412(8)

Bond Angle °		Bond Angle °	
C(16)-C(11)-C(12)	119.6(5)	C(26)-C(21)-P(1)	119.2(4)
C(16)-C(11)-S(1)	121.2(4)	C(23)-C(22)-C(21)	120.2(5)
C(12)-C(11)-S(1)	119.2(4)	C(24)-C(23)-C(22)	120.3(5)
C(11)-C(12)-C(13)	119.6(6)	C(23)-C(24)-C(25)	120.0(5)
C(14)-C(13)-C(12)	121.4(5)	C(24)-C(25)-C(26)	120.2(5)
C(13)-C(14)-C(15)	118.9(5)	C(25)-C(26)-C(21)	120.5(5)
C(13)-C(14)-C(141)	120.3(6)	C(36)-C(31)-C(32)	119.2(5)
C(15)-C(14)-C(141)	120.8(6)	C(36)-C(31)-P(1)	120.4(4)
C(14)-C(15)-C(16)	120.0(6)	C(32)-C(31)-P(1)	120.3(4)
C(11)-C(16)-C(15)	120.3(5)	C(33)-C(32)-C(31)	120.0(5)
O(1C)-S(1)-O(1B)	113.1(3)	C(52)-C(51)-P(2)	119.6(4)
O(1C)-S(1)-O(1A)	112.5(3)	C(53)-C(52)-C(51)	119.6(5)
O(1B)-S(1)-O(1A)	112.7(3)	C(54)-C(53)-C(52)	120.6(5)
O(1B)-S(1)-C(11)	106.2(3)	C(53)-C(54)-C(55)	119.9(5)
O(1A)-S(1)-C(11)	105.1(3)	C(54)-C(55)-C(56)	120.1(5)
C(22)-C(21)-C(26)	118.7(5)	C(55)-C(56)-C(51)	120.1(5)
C(22)-C(21)-P(1)	122.1(4)		

Figure 1. **The $^{31}P\{^1H\}$ NMR Spectrum of [Ni(dppe)(dcpe)] (10)**

[Ni(dcpe)(CH3CN)2](OTf)2 + dppe in MeOH, CH3CN + cat



Appendix 5

5.1 Supplementary ^{31}P{^{1}H}NMR Data for Chapter 6

Table 1 Comparison of ^{31}P{^{1}H}NMR spectroscopic data obtained on catalyst solutions before and after catalysis

	^{31}P{^{1}H}NMR δ ppm	
Run	Before Catalysis (under nitrogen)	After Catalysis (in air)
i	δ = 94.6 (MeOH) (s, [Ni(dcpe)(CH$_3$CN)$_2$](OTf)$_2$) δ = 67.7 (s, [Ni(dcpe)$_2$](OTf)$_2$)	δ = 99.0 (s, [Ni(dcpe)(CH$_3$CN)$_2$](OTf)$_2$)
iv	δ = 67.6 (s) [Ni(dcpe)$_2$](OTs)$_2$ (MeOH)	**δ = 25.8 (s) (MeOH, CH$_2$Cl$_2$)** δ = 38.4 (m) δ = 39.0 (m, br) δ = 56-57 (m, br) δ = 85.5 (m, br)
v	δ = 58.9 (s, [Ni(dppe)$_2$](OTs)$_2$) (MeOH)	δ = 56.8 (s, [Ni(dppe)$_2$](OTs)$_2$) (MeOH) **δ = 15.6 (s)**
vi	δ = 58.9 (s, [Ni(dppe)$_2$](OTs)$_2$) (MeOH)	δ = 57.6 (s, [Ni(dppe)$_2$](OTs)$_2$) (MeOH) δ = 56.2 (s) δ = 49.8 (s)
vii	δ = 25-70 br; δ = 27; δ =40; δ = 50; δ = 65	δ = 45 (s, br), δ = 51.2 (s, br)
viii	δ = -15 (s, dcpn) δ = 45 (br, [Ni(dcpn)$_2$](OTs)$_2$)	δ = 69-73 (v. br)
ix	δ -13.2 (s, dppe) (MeOH); [Ni(dppe)(*o*-tol){dppe}]OTs δ -12.8 (P$_D$, dd, ^{2}J$_{PC-PD}$ not resolved); δ 21.5 (P$_C$, td, ^{2}J$_{PC-PA}$ 235Hz); δ 44.7 (P$_B$, t (dd)); δ 51.5 (P$_A$, dd, ^{2}J$_{PA-PB}$ 16.8Hz, ^{2}J$_{PC-PA}$ 235Hz).	**δ = 14.5 2nd main peak*** **δ = 45.6 (s, [Ni(dppe)(CO)$_2$]) main peak**
xi	(yellow)	(orange)
xii	δ = 58.9 (s, [Ni(dppe)$_2$](OTs)$_2$)	**δ = 16.9 (s)**

	(MeOH)	$\delta = 28.5$ (s) $\delta = 58.1$ (s, $[Ni(dppe)_2](OTs)_2$) (MeOH)
xiv	$\delta = 55.4$ (s, $[Ni(dppe)_2](OTs)_2$) (AcOH)	$\delta =$ **16.1 (s)** $\delta = 29.4$ and 30.2 (m, br) $\delta = 41.4$ (s, ?) $\delta = 55.8$ (s, $[Ni(dppe)_2](OTs)_2$) (AcOH)
xv	Not obtained	$\delta = 24.5$ (s, $P(O)Ph_3$) $\delta = 26.3$ (d) $\delta = 27.6$ (d)
xvi	$\delta = 58.1$ (s, $[Ni(dppe)_2](OTs)_2$) (MeOH/toluene) $\delta = -3.0$ (s, PPh_3)	$\delta = 24.3$ (s, $P(O)Ph_3$) $\delta = 58.5$ (s, $[Ni(dppe)_2](OTs)_2$)
xvii	Not obtained	$\delta = 35.2$ (s) (AcOH) $\delta = 38.7$ (m, v. br) $\delta = 39.1$ (v. br) $\delta = 39.9$ (s, v. br) $\delta = 40.0$ (s)
xviii	$\delta = 58.3$ (s, $[Ni(dppe)_2](OAc)_2$) (AcOH)	$\delta =$ **16.4 (s)**
xix	$\delta = 55.1$ (s, $[Ni(dppe)_2](NO_3)_2$) (MeOH/toluene)	$\delta = 48\text{-}52$ (v. br)

* $^{31}P\{^1H\}$ NMR spectrum obtained in the absence of air

5.2 Supplementary Infra Red Data for Chapter 6

Tables 2-7 contain selected I.R. data obtained on solid samples recovered from catalysis. The solid samples consist of polyketone and either $Ni(OTs)_2$, $Ni(OTf)_2$, and HOTs or a combination of these impurities. G.C. and I.R. analysis was obtained on distilled solutions after catalysis. G.C. mass spectroscopy confirmed the presence of methyl acetate as the only organic component other than the reaction solvents. I.R. data on these distilled reaction solutions are reported where appropriate i.e. in the presence of methyl acetate solvents. In both cases in the I.R. spectra a distinctive carbonyl band is present, polyketone $\nu_{C=O}$ = 1690(±4)cm^{-1} and other bands (**in bold**); methyl acetate $\nu_{C=O}$ = 1742(±4)cm^{-1} (underlined). The comparative I.R. bands for $Ni(OTs)_2$, $Ni(OTf)_2$, and HOTs are given (*in italics*)

Table 2 I.R. Data from the solid sample obtained from Run (i) [Ni(dcpe)(CH_3CN)$_2$](OTf)$_2$

Polyketone (pure)	Ni(OTf)$_2$ anhydrous	Run (i)
806		**802**
	1025	*1027*
1055		
	1093	*1094*
	1175	1164
	1203	
	1225	1226
		1240
1258		
	1270	
	1284	
	1310	
1331		**1331**
1407		**1408**
		1438
		1662
1690		**1692**
		1750
		1782
2916		
		3097
		3193

Table 3 I.R. Data for distilled reaction solution from Run (ii) $[Ni(dppp)(CH_3CN)_2](OTf)_2]$ and Run (iii) $[Ni(Boxylyl)(CH_3CN)_2](OTf)_2]$

The presence of methyl acetate was confirmed by G.C. mass spec. analysis.

Methyl Acetate	Run (ii)	Run (iii)
840	847	847
1030	1002	1028
		1082
		1179
1230		1250
1282		
1370		
1429	1486	
	1655	1603
1742	1740	1744
	1831	1813
	1897	1868
		1952

Table 4 I.R. Data from the solid sample obtained from
Run (iv) $[Ni(dcpe)_2](OTs)_2$
Run (v) $[Ni(dppe)_2](OTs)_2$

Polyketone	$Ni(OTs)_2$ anhydrous	Run (iv) (crude)	Run (iv)	Run (v)
806		**810**	**811**	**809**
	1016	*1012*		*1012 w*
	1040	*1034*		
1055		**1054**	**1055**	**1055**
	1064			
	1105			
	1137	1120		
	1183	1184		
		1208		
1258		**1258**	**1258**	**1259**
1331		**1331**	**1333**	**1333**
	1380			
	1400			
1407		**1405**	**1405**	**1405**
	1602			
1690		**1688**	**1689**	**1689**
2916		**2910**	**2912**	**2911**

Table 5 I.R. Data from the solid and solution samples obtained from
Run (vi) [Ni(dppe)$_2$](OTs)$_2$
Run (vii) [Ni(Boxylyl)$_2$](OTf)$_2$

Polyketone	Ni(OTs)$_2$ anhydrous	Ni(OTf)$_2$ anhydrous	Methyl Acetate	Run (vi) (solid)	Run (vi) (solution)	Run (vii) (solid)	Run (vii) (solution)
806			840	811		809	
	1016	1025	1030			*1018*	
	1040						
1055				1055		1055	
	1064	1093	1230				
	1105	1175	1282			1166	1186
	1137	1203					
	1183	1225				1224	
						1239	1237
1258				**1258**			
1331		1270		1332		1333	
	1380	1284	1370				
	1400	1310	1429				
1407				**1405**		**1405**	
	1602				1603	1425,1552, 1556,1610, 1644,1661	1605
1690				**1689**		**1689**	
			1742		1737		1744
2916				2911		2909	

Table 6 I.R. Data from the solid and solution samples obtained from
Run (ix) [Ni(dppe)(*o*-tolyl)(py)]OTs
Run (x) [Ni(dppe)(*o*-tolyl)(py)]OTs + $2PPh_3$
Run (xi) [Ni(dBpe)(*o*-tolyl)(py)]OTs

Polyketone	$Ni(OTs)_2$ anhydrous	Run (ix) (solid)	Run (ix) (solution)	Run (x) (solid)	Run (xi) (solid)
806		**811**		**811**	**811**
	1016			*1017*	1008, 1031
	1040				
1055		**1055**		**1055**	**1055**
	1064			1092	1094
	1105				
	1137				
	1183				
1258		**1259**		**1259**	**1259**
1331		**1333**		**1333**	**1333**
1407		**1406**		**1406**	**1406**
		1426		1426	1426
			1605		
1690		**1690**	**1691(polyk)**	**1690**	**1690**
	1380		1710		
	1400		1739		
			1807		
	1602		1861		
			1945		
		2343		2343	2343
		2359		2359	2359
2916		**2913**		**2913**	**2913**
		3196		3196	3196

Table 7 I.R. Data from the solid samples obtained from
Run (xii) $[Ni(dppe)_2](OTs)_2$
Run (xiii) $[Ni(dppe)_2](OTs)_2$ + excess HOTs
Run (xiv) $[Ni(dppe)_2](OTs)_2$ + dppe + excess HOTs

Polyketone	$Ni(OTs)_2$ anhydrous	HOTs	Run (xii)	Run (xiii)	Run (xiv)
		676,707		678	678
806		815, 861	**812**	**813**	**813**
	1016	*1010*	*1011*	*1010*	*1010*
	1040	*1042*	*1039*	*1037*	*1037*
1055			**1055**		
	1064				
	1105				
	1137	1124	1126	1124	1124
	1183	*1176*	*1182*	*1178*	*1178*
1258					
1331			**1334**	**1334**	**1334**
	1380	1370			
	1400				
1407			**1406**	**1406**	**1406**
		1451			
	1602				
1690			**1690**	**1690**	**1690**
2916			**2910**	**2910**	**2910**

Table 8 I.R. Data from the solid samples obtained from
Run (xv) $[Ni(dppe)_2](OTs)_2 + PPh_3$
Run (xvi) $[Ni(dppe)_2](OTs)_2 + 2PPh_3$
Run (xvii) "$[Ni(dppp)_2](OTs)_2$" + dppp

The polyketone samples obtained from these runs were relatively pure and did not contain $Ni(OTs)_2$ as an impurity.

Polyketone	Run (xv)	Run (xvi)	Run (xvii)
806	806	806	806
1055	1055	1055	1055
1258	1258	1258	1258
1331	1331	1331	1331
1407	1407	1407	1407
1690	1690	1690	1690
2916	2916	2916	2916

Table 9 I.R. Data from the solid sample obtained from Run (xviii). The solid sample was not polyketone and was found to be a combination of $Ni(OAc)_2$ and HOTs.

$Ni(OAc)_2$	HOTs	Run (xviii)
	676,707	678
	815,	813,
	861	861
	1010	1010
	1042	1037
		1110
	1124	1124
	1176	1176
	1370	
1414		
		1436
	1451	
1516,		
1540		
2341		2341
2360		2360

Appendix 6

Colloquia, Lectures and Seminars Attended

6.1 Lectures and Colloquia At Durham

1995

November 1	Prof. W. Motherwell, UCL London New Reactions for Organic Synthesis
November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada New Indium Coordination Chemistry

1996

January 10	Dr Bill Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a new sporting technique
February 12	Dr Paul Pringle, University of Bristol Catalytic Self-Replication of Phosphines on Platinum(0)
February 21	Dr C R Pulham , Univ. Edinburgh Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes
March 6	Dr Richard Whitby, Univ of Southampton New approaches to chiral catalysts: Induction of planar and metal centred asymmetry
March 13	Prof. Dave Garner, Manchester University Mushrooming in Chemistry
October 14	Professor A. R. Katritzky, University of Gainesville, University of Florida, USA Recent Advances in Benzotriazole Mediated Synthetic Methodology
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 12	Professor R. J. Young, Manchester Materials Centre, UMIST New Materials - Fact or Fantasy? Joint Lecture with Zeneca & RSC
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 3	Professor D. Phillips, Imperial College, London "A Little Light Relief" -
December 11	Dr Chris Richards, Cardiff University Sterochemical Games with Metallocenes

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January 15	Dr V. K. Aggarwal, University of Sheffield Sulfur Mediated Asymmetric Synthesis
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
January 29	Dr Julian Clarke, UMIST What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?
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 25	Professor A. G. Sykes, University of Newcastle The Synthesis, Structures and Properties of Blue Copper Proteins
February 26	Dr Tony Ryan, UMIST Making Hairpins from Rings and Chains
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
October 15	Dr R M Ormerod, Department of Chemistry, Keele University Studying catalysts in action
October 21	Professor A F Johnson, IRC, Leeds Reactive processing of polymers: science and technology
October 22	Professor R J Puddephatt (RSC Endowed Lecture), University of Western Ontario Organoplatinum chemistry and catalysis
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 19	Dr G Morris, Department of Chemistry, Manchester Univ. Pulsed field gradient NMR techniques: Good news for the Lazy and DOSY
November 20	Dr L Spiccia, Monash University, Melbourne, Australia Polynuclear metal complexes
December 2	Dr C J Ludman, University of Durham Explosions
October 27	Professor W Roper FRS. University of Auckland, New Zealand

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January 21	Professor D Cardin, University of Reading
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 3	Dr J Beacham, ICI Technology The chemical industry in the 21st century
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

6.2 External Colloquia and Events Attended

1. 5th ICI-Katalco Symposium on Catalytic Chemistry, Darlington May 1996 (Poster Contribution).

2. 6th ICI-Katalco Symposium on Catalytic Chemistry, Darlington May 1997 (Poster Contribution).

3. 1st Anglo-Dutch Symposium on Organometallic Chemistry, Sheffield September 1996.

4. 2nd Anglo-Dutch Symposium on Organometallic Chemistry, Amsterdam September 1997.