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STUDIES RELATING TO THE COUPLING OF CARBON DIOXIDE AND PROPENE AT NICKEL(0).

by

Graham Eastham, B.Sc

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Finally my thanks to my family and friends who have endured and encouraged me throughout, particularily my sincerest thanks to Andrea.

MEMORANDUM

The work described in this thesis was carried out in the laboratories of I. C. I. Acrylics, at Wilton between July 1992 and June 1994. It has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

ABSTRACT

The work described in this thesis is concerned with the regioselective coupling of carbon dioxide and propene in the presence of nickel catalysts to give methacrylic acid, the catalytic cycle for which is given in Figure 1.0. An important aim of the work is to obtain information which can lead to a better understanding of the chemistry involved and to a viable process for the industrial production of methacrylic acid.

Carbon dioxide is a remarkable source of carbon both as gas or bound in carbonate rocks. The total amount of carbon existing in the atmosphere as carbon dioxide is estimated to be 720 x 10^9 tons[1]. The chemical utilisation of carbon dioxide as a resource for the production of useful substances has been rather limited, however. The large quantities of carbon dioxide available at relatively inexpensive cost is one driving force for the development of the use of carbon dioxide in industry. Another pressure to find ways to use carbon dioxide is related to its perceived role in the greenhouse effect.

The important result of this work is the demonstration that the complexes of the type [$L_2Ni\{CH_2CH(CH_3)COO\}$] (I) and [$L_2Ni\{CH(CH_3)CH_2COO\}$], (II) can be synthesised from methacrylic acid (I) and crotonic acid (II) respectively via an extension of the chemistry developed by Yamammoto et al and reviewed in chapter four(1). The same complexes can also be synthesised from propene and carbon dioxide via an oxidative coupling reaction at phosphine liganded nickel(0). The synthesis of the intermediates (type I and II) from the corresponding carboxylic acid is a two step process. The oxidative addition of methacrylic/crotonic acids to nickel(0) only occurs in the presence of one molar equivalence of tricyclohexylphosphine, a highly electron donating sterically demanding phosphine. The second reaction to form complexes of the type [$L_2Ni\{CH_2CH(CH_3)COO\}$] (I) and [$L_2Ni\{CH(CH_3)CH_2COO\}$] (II) is a ligand displacement reaction. The following compounds have been synthesised. Type (I) [$L_2Ni\{CH_2CH(CH_3)COO\}$] where L_2 = DPPE(1B), DCPE(1C), DCPP(1D), DCPy(1G), Bipy(1H), Phen(1J), TMEDA(1I). Type (II) [$L_2NiCH(CH_3)CH_2COO$] where L_2 = DPPE(1E), DCPE(1F).

The complex [(DCPE)$Ni\{CH_2CH(CH_3)COO\}$] has been used for further reaction studies, chosen because it has been shown that it can be synthesised from methacrylic acid as well as from propene/carbon dioxide mixtures. Ways were sought to destabilise the metallacycle to liberate methacrylic acid, the use of maleic anhydride and heat/pressure are reported.

The final section of this work involved the oxidative coupling of propene and carbon dioxide at liganded nickel(0). Sucessful coupling in high yield was obtained using the ligands DCPE and DCPy only to yield complexes of the type [$L_2Ni\{CH_2CH(CH_3)COO\}$] and [$L_2Ni\{CH(CH_3)CH_2COO\}$]. A small degree of coupling was indicated using DCPP but this was only a minor component of the nickel containing species isolated at the end of the reaction. The amine ligands tried all appeared to form carboxylates and/or carbonates as indicated by the IR spectra of the solids isolated.

CONTENTS

ABBREVIATIONS

Bipy	2,2'-Bipyridine
THF	Tetrahydrofuran
DCPE	1,2-bisdicyclohexylphosphinoethane
DCPP	1,3-bisdicyclohexylphosphinopropane
DCPy	2-{2-(dicyclohexylphosphino)ethyl}pyridine
DPPE	1,2-bisdiphenylphosphinoethane
DPPP	1,3-bisdiphenylphosphinopropane
DPPB	1,4-bisdiphenylphosphinobutane
COD	1,5-cyclooctadiene
Phen	1,10-phenanthroline
TMEDA	N,N'-tetramethylethylenediamine
MAA	Methacrylic acid
MMA	Methylmethacrylate
mNBA	m-Nitrobenzylalcohol
PCy_3	Tricyclohexylphosphine
PEt_3	Triethylphosphine

PREFACE

The work described in this thesis is concerned with the regioselective coupling of carbon dioxide and propene in the presence of nickel catalysts to give methacrylic acid, the catalytic cycle for which is given in Figure 1.0. An important aim of the work is to obtain information which can lead to a better understanding of the chemistry involved and to a viable process for the industrial production of methacrylic acid. The proposed catalysis has four basic steps:-

I An active catalyst (I, Figure 1.0) forms from a convenient starting complex.

II Coordination and oxidative coupling of propene and carbon dioxide within the coordination sphere of the metal to generate the intermediate III. Very little is known about the exact mechanism of this reaction. Questions remain about whether it is the alkene or carbon dioxide which coordinates first to the metal and becomes activated toward coupling with the other molecule. The effects of concentration and pressure on this reaction are factors which need to be studied.

III β hydrogen migrates to the metal centre. This generates the necessary unsaturation in the organic part of the molecule which will become methacrylic acid . A metal hydride is also generated. These tend to be short lived and difficult to detect.

IV Methacrylic acid is reductively eliminated, and the active catalyst is regenerated. This may involve delivery of the hydride to the oxygen α to the carbonyl group. Little is known of the exact mechanism of this process.

The thesis consists of ten chapters, the early chapters consisting of reviews of the chemistry relating to the components of the coupling reaction. Later chapters are concerned with oxidative coupling in general and industrial routes to methacrylic acid and methyl methacrylate. Final chapters are concerned with the experimental chemistry undertaken with this work.

Specifically chapter one gives a brief review of the known industrial uses of carbon dioxide and its advantages as a source of carbon. It deals mainly, though, with the bonding of carbon dioxide to transition metals. Known bonding modes are reviewed using known complexes as examples. The requirements for the activation of carbon dioxide are also discussed.

In chapter two the chemistry of alkenes is reviewed together with a section on alkynes and their interactions with transition metals. It includes (i) bonding description, (ii) results of bonding, (iii) reactions of coordinated alkenes. The aim is to outline the key parameters in the bonding of alkenes and transition metals and the types of reactions (and conditions in which they occur) which alkenes undergo in the coordination sphere of transition metals.

Chapter three introduces nickel as the transition metal of choice for studying this chemistry. Some of the relevant chemistry and known catalysis of Nickel is reviewed and the advantages of this metal discussed. Nickel-alkene chemistry in particular is reviewed, with special emphasis on the features and structures of active complexes, e.g. stereochemistry, oxidation states, degree of coordinative saturation.

In chapter four the area of oxidative coupling is reviewed. This is the linking of alkene/alkyne and CO2 to give type III intermediates. Also reviewed are the following areas relevant to the development of a catalytic cycle: (i) oxidative addition of methacrylic acid to nickel complexes to generate type II intermediates (reverse catalysis), and (ii) the utilisation of phenyl isocyanate as an analogue of CO2 where catalysis has been developed.

Known industrial routes to methacrylic acid and methyl methacrylate are reviewed in chapter five. As stated previously, the overall aim is to develop a catalysis to achieve the synthesis of methacrylic acid. A route to methacrylic acid and ultimately methyl methacrylate from propene and carbon dioxide would be desirable.

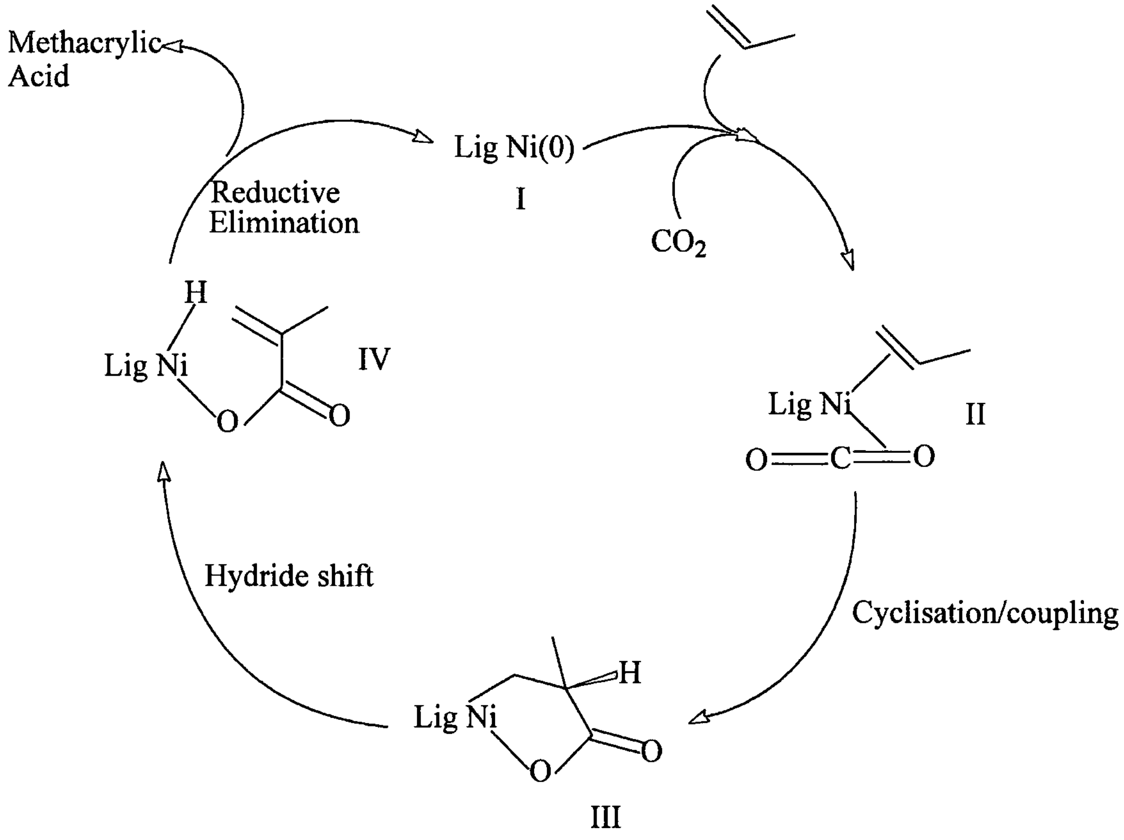
In chapter six the experimental approach adopted in this studied is outlined, the experimental protocols followed in this work are described and the spectroscopic data generated from the study of compounds synthesised in this thesis is detailed. The chapter is divided into four sections which deal with the following areas relevant to the study of the catalytic cycle: (i) the synthesis of precursor materials not available commercially, (ii) the synthesis of type III intermediates from methacrylic and crotonic acids utilising the oxidative addition chemistry of Yamamoto et. al. reviewed in chapter four of this thesis, (iii) reactions of type III intermediates generated in this thesis, and (iv) oxidative coupling of propene and carbon dioxide.

In chapter seven the experimental data relating to the oxidative addition of methacrylic and crotonic acids to nickel(0) is discussed. The synthesis of a number of oxanickellacyclopentanones (type III intermediates) is demonstrated by reference to spectroscopic data. Where relevant this is compared to published data.

Chapter eight discusses the experimental data relating to the post reaction of selected oxanickellacyclopentanones. Both chemical and thermal methods are tried to liberate methacrylic acid from a type III intermediate. The results obtained are discussed in terms of equilibria occuring at the metal centre.

In chapter nine the experimental data relating to the oxidative coupling of propene and carbon dioxide is discussed. Successful coupling is demonstrated in a number of cases. Where coupling has not occured or products resulting from oxidative coupling are only minor components the resultant chemistry is discussed

Finally in chapter ten conclusions are drawn relating to the work as a whole. Trends are sought in the model compounds synthesised and attempts are sought to relate these to ligand and structure of the metallacycle. The proposed catalysis is discussed in light of the experimental results and recommendations made for further work.



Proposed catalytic cycle for the propene and carbon dioxide oxidative coupling reaction

FIG. 1.0

CHAPTER ONE

THE USES OF CARBON DIOXIDE AND ITS BONDING TO TRANSITION METALS

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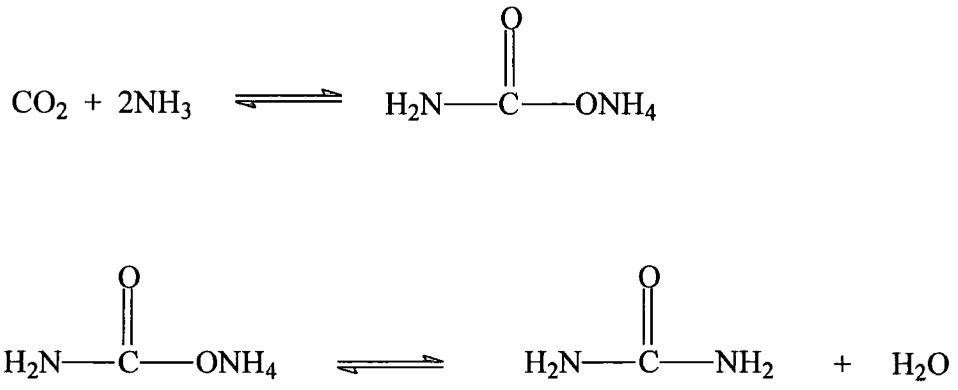
THE USES OF CARBON DIOXIDE AND ITS BONDING TO TRANSITION METALS

Carbon dioxide is a remarkable source of carbon both as gas or bound in carbonate rocks. The total amount of carbon existing in the atmosphere as carbon dioxide is estimated to be 720 x 10^9 tons[1]. The chemical utilisation of carbon dioxide as a resource for the production of useful substances has been rather limited, however.

The large quantities of carbon dioxide available at relatively inexpensive cost is one driving force for the development of the use of carbon dioxide in industry. Another pressure to find ways to use carbon dioxide is related to its perceived role in the greenhouse effect. Continuous measurements at Mauna Loa (Hawaii) and at the south pole have showed that the CO_2 content in the atmosphere increased from a presumed 250ppm in the preindustrial era to 315ppm in 1958 and to 340ppm in 1984. If this trend continues, CO_2 concentrations in the atmosphere will reach values of 600ppm in the next century[1]. Numerous indications are that an increasing CO_2 concentration in the atmosphere changes the radiation intensity and the global climate on earth.

A small contribution to reducing the build up of CO_2 in the atmosphere would be made if carbon dioxide produced industrially could be transformed into useful products via chemical reactions. The main current industrial uses of carbon dioxide are listed below:-

(i) Urea Synthesis - Currently the largest use of carbon dioxide as a starting material in organic synthesis is in the production of Urea, the diamide of carbonic acid. This reaction of ammonia and CO_2, discovered as far back as 1870 by Bassarov, proceeds at elevated pressure (150 - 250 Bar) and temperature (150 - 200°c) via the intermediate stage of ammonium carbamate according to the equations shown.

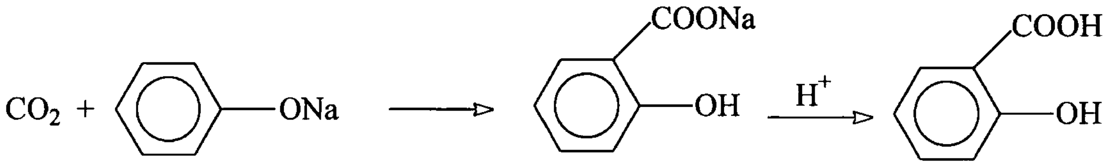


$$CO_2 + 2NH_3 \rightleftharpoons H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4$$

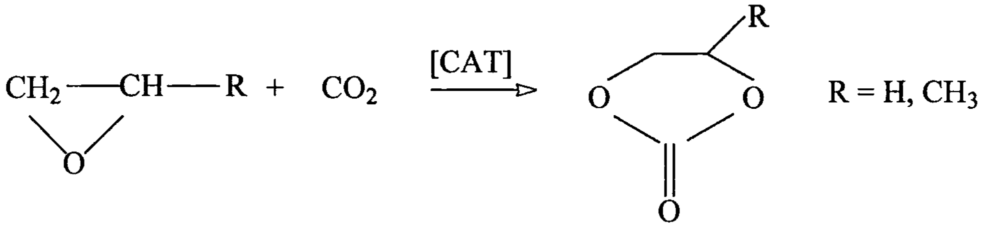
$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4 \rightleftharpoons H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2O$$

The first industrial synthesis plant was built in 1922; in 1985 worldwide production was estimated to be 42 x 10^6 t/a.

(ii) Salicylic acid - Mainly used in the production of acetylsalicylic acid (aspirin). In 1980 in the USA, the production of salicylic acid was 25,000t/a(1). In 1874, it was manufactured by Kolbe by carboxylation of sodium phenolate according to the equation shown below. In 1884, Schmitt increased the yield from ca.50 to 90% when he introduced carbon dioxide under pressure (ca.5 BAR). Nowadays, salicylic acid is produced in industry almost exclusively by this "Kolbe-Schmitt process", usually in batchwise operation (1).



(iii) Cyclic Organic Carbonates - ethylene and propylene carbonates are produced from the respective oxide and CO_2 according to the equation shown.



The two cyclic carbonates are used as high boiling solvents. Their ability to dissolve a wide range of substances has led to their extensive use in the production of polyacrylic fibres and paints.

(iv) Methanol Synthesis - Methanol is made commercially from synthesis gas (CO + $2H_2$). If gas of composition (CO + $3H_2$), produced by steam reforming of dry natural gases, is used instead of synthesis gas, carbon dioxide must be added to counterbalance the "surplus" hydrogen and it also reacts to form Methanol with the formation of water according to the equations shown below.

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

Addition of carbon dioxide to the reactant gas is practised in many industrial methanol plants. With about 16 x 10^6 t/a (1986) being produced worldwide a considerable amount of carbon dioxide is being converted into an organic bulk chemical.

A few industrial processes do exist then where carbon dioxide is utilised as a raw material. Carbon dioxide though is often classified as a stable, almost inert compound in as much as it is the thermodynamic end product of many energy producing processes (e.g. the combustion of hydrocarbons, see below).

$C_2H_6 + {}^7/_2O_2 \rightarrow 2CO_2 + 3H_2O(l)$ ΔH_{298^oC}=1560.1 kJmol^{-1} (ref1)

Increased use of carbon dioxide will only be possible if the relatively inert carbon dioxide molecule can be activated. This goal can be achieved with the aid of transition metal catalysts that lower the activation energy of carbon dioxide reactions and thus considerably increase the reaction rate.

A. Behr (1) has proposed a theoretical catalysis cycle (fig. 1.1) involving carbon dioxide and a substrate. It shows how a metal catalyst might influence the reaction of CO_2 to an arbitrary substrate (Su). Of interest here is the coordination of carbon dioxide to the transition metal complex (step 5). Coordination of the substrate to the metal, where the substrate is an alkene/alkyne followed by CO_2 insertion and oxidative coupling of substrate and CO_2, again where substrate is an alkene/alkyne, will be reviewed in later sections:

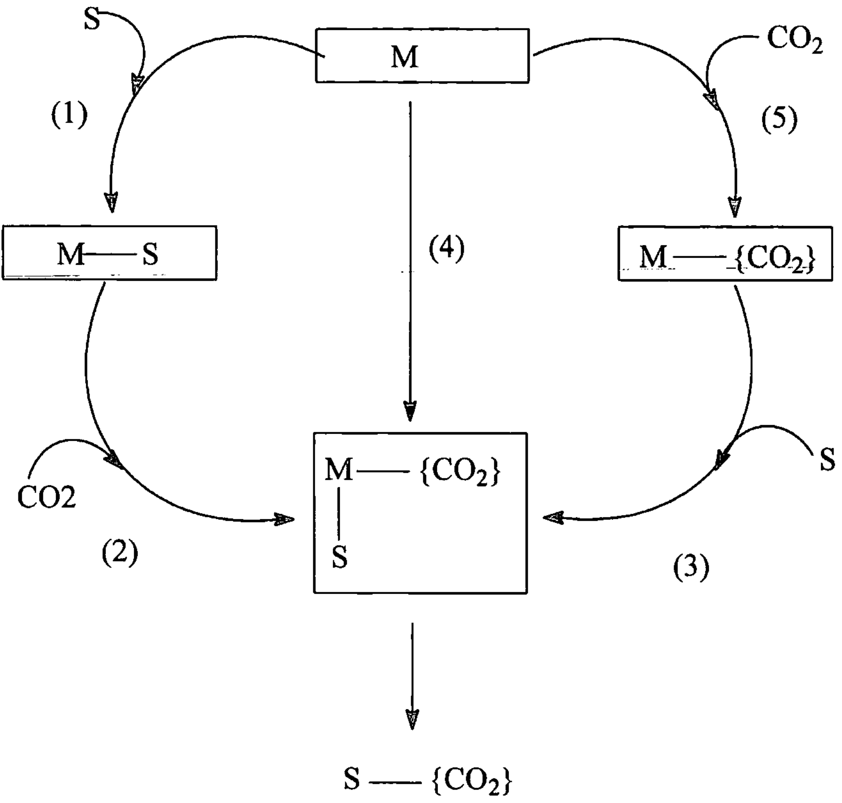
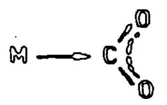
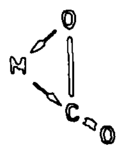
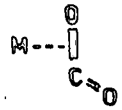
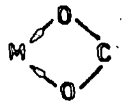
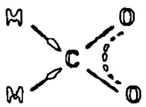
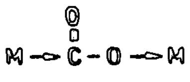
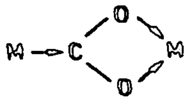
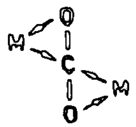
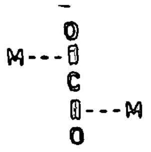
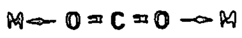
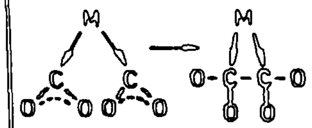
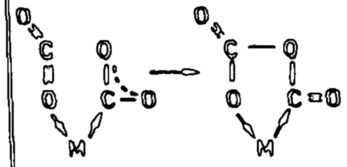
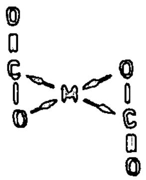
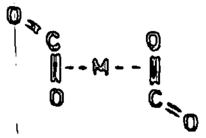
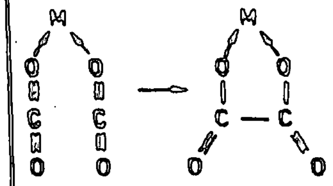
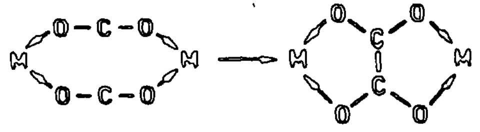
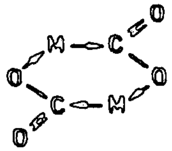
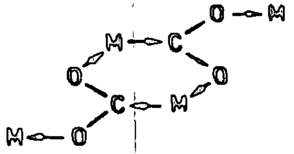
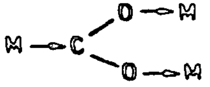


FIG. 1.1
Possible routes for interaction between carbon dioxide(CO_2), substrate(S), and transition metal(M).

Figure 1.2(1)

Carbon dioxide and transition metals: modes of coordination.

Ratio metal: CO_2	Electron transfer metal → C	Electron transfer metal → C and O → metal	Formation of π-complexes	Electron transfer O → metal
1 : 1	 I	 II	 III	 IV  V
2 : 1	 VI	 VII  VIII  IX	 X	 XI
1 : 2	 XII XIII	 XIV XV  XVI	 XVII	 XVIII XIX
n : m	 XX XXI	 XXII	 XXIII		 XXIV

Carbon dioxide can interact with transition metals in three ways (1.6), (i) via the carbon atom which is a Lewis acid centre and is therefore the most electrophillic centre in the carbon dioxide molecule, (ii) via the terminal oxygen atoms which are Lewis base sites and therefore the most nucleophillic centres of the carbon dioxide molecule and (iii) via a carbon-oxygen π bond. Fig. 1.2 taken from (1) shows the wide variety or potential transition metal-carbon dioxide complexes possible because of the polyfunctionality of the carbon dioxide molecule. The different bonding modes of carbon dioxide to transition metals are reviewed with reference to the various theoretical types (I-XXIV) shown in fig. 1.2. Additional examples are given in references 25-39.

Bonding Modes of Carbon Dioxide

Type I where a molecule of carbon dioxide is bound to a transition metal via a metal-carbon bond ($\eta 1$ type interaction) is often termed a metallacarboxylate (1). The first reported example was; $[Rh(\eta 1\text{-}CO_2)(Cl)(diars)_2]$: (diars = σ-phenylenebis(dimethylarsine)[12], (see Fig. 1.3)

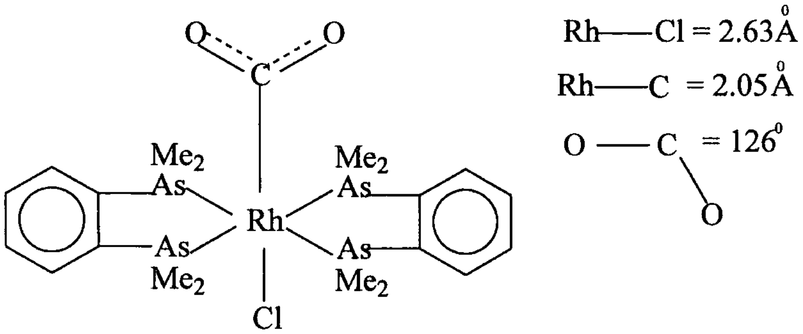


Figure 1.3

X-Ray Crystal Data for $[Rh (\eta 1\text{-}CO_2)(Cl)(diars)_2]$

It was prepared from the complex $Rh_2Cl_2(C_2H_4)_4$, which when reacted with 4 equivalents of the diarsine ligand in THF, gave first the 16-electron complex $Rh(diars)_2$ Cl, which when reacted with carbon dioxide even at low temperatures gave $[Rh (\eta 1\text{-}CO_2)(Cl)(diars)_2]$ (14).

In the complex the carbon dioxide molecule is distorted from its linear geometry in the free state and it is likely that η^1 bonding of the carbon dioxide is stabilised by additional C-H....O interactions with the diarsine ligand (12).

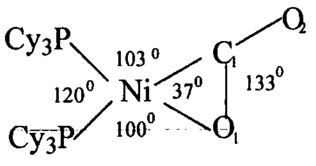
The coordination about the rhodium is essentially octahedral with the n^1-bonded CO_2 ligand trans to the chloride. The Rh-Cl distance 2.634Å is longer than the average Rh-Cl distance. (2.4Å) observed for a series of related structures (12). The CO_2 is therefore having a bond weakening trans influence on the Rh-Cl bond in this complex.

In the above Type I example, the intermediate reacting with CO_2 is of the form $[ML_4]X$ where M = metal, L = ligand, X = halogen. A whole group of η^1-CO_2 bonded complexes have been reported (12,10) where; M = Rh, Ir, L = PMe_3; dmpe/$_2$; depe/$_2$; diars/$_2$ and X = Cl, I. All are reported to form 1:1 M-CO_2 adducts with η1 -CO_2M binding evidenced by infrared bonds at ~1600 (νCO_2 asym) and ~1200 (νCO_2 sym)cm-1. The η^1-CO_2 complex $[Rh(CO_2)(Cl)(diars)_2]$ whose structure has been determined by X-ray crystal analysis has infrared vibrations at 1610(strong)cm^{-1} and 1210(strong)cm^{-1}.

The η^1-carbon dioxide found in these complexes resembles a carboxylate group. Evidence for this comes from the reaction of $Ir(CO_2)(Cl)(dmpe)_2$ with $MeFSO_3$ to give $Ir(CO_2Me)(Cl)(dmpe)_2$, whose structure has been characterised by X-ray crystallography and was claimed as the first transformation of a well defined CO_2 ligand into an organic species (16).

Examples of type II/III are more common in the literature. Three representative examples will be discussed here to illustrate the spread across the transition metal series and to show the effect on the carbon dioxide molecule of bonding in this manner:

1. Aresta and Nobile were able to assign the structure $Ni(CO_2)(PCy_3)_2$ 0.75(toluene) to crystals isolated from the reaction of $Ni(PCy_3)_3$ or $Ni(PCy_3)_2(N_2)$ with carbon dioxide in toluene at room temperature (3) (see fig. 1.4). The carbon dioxide is bound side on as shown:



$Ni—C = 1.84 \overset{0}{A}$

$Ni—O_1 = 1.99 \overset{0}{A}$

$C_1—O_1 = 1.22 \overset{0}{A}$

$C_1—O_2 = 1.17 \overset{0}{A}$

Figure 1.4
Selected X-Ray Crystal Data for $Ni(CO_2)(PCy_3)_2$ 0.75(toluene)

Coordination about the metal is planar. The CO_2 molecule is markedly bent (OCO 133°) on coordination from the O-C-O 180° in gaseous CO_2. Comparison of the bond lengths of the complex with those in free CO_2 (1.16 A) shows a slight but not significant lengthening of the C-O bonds but there is a significant difference in the Ni-C Ni-O bond lengths of the coordinated carbon dioxide.

Addition of triphenylphosphite at room temperature yields CO_2 quantitatively. Further evidence for the instability of the complex is the liberation of CO_2 if argon is bubbled through the toluene solutions of the complex. The starting complex can be reformed on re-exposure to CO_2. Rapid heating also liberates

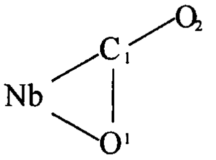
CO_2 from the complex, further adding to the evidence that the CO_2 is acting as a very labile ligand able to bond reversibly with the electron rich coordinatively unsaturated metal centre.

Interestingly, a chelating phosphine, 1,2-bis(diphenylphosphino)ethane does not give isolatable complexes of formula Ni(CO_2)(dppe). It was suggested by Aresta and Nobile⁽⁴⁾ that chelating phosphine decreased the P_1-Ni-P_2 angle to less than 120° and increased P_1-Ni-C close to 180°. The result of these changes in the distorted square planar structure is to weaken the trans influence of P_1 of the dppe ligand on the Ni-Carbon bond, the result being a weaker Ni-CO_2 interaction.

It is not clear if this is also true with more highly basic chelating phosphines such as 1,2 Bis (dicyclohexylphosphino) ethane (DCPE). More highly basic phosphine should increase the strength of the Ni-CO_2 bond because of the greater electron density at the metal available for backbonding into the p-π orbitals of the carbon-oxygen bond.

Aresta and Nobile found the Ni-CO_2 interaction (infered from $\nu_{C=O}$ CO_2 stretching frequencies) to be greater in Ni(CO_2)(PET_3)$_2$, [PKa (PET_3) = 8.69] and Ni(CO_2)(PBu_3)$_2$, [PKa (PBu_3) = 8.43] than in Ni(CO_2)(PCy_3)$_2$, [PKa (PCy_3) = 9.70]. This arises from steric effects of PCy_3 on the coordination symmetry around the metal. The bulky cyclohexyl group is having an effect outweighing its high basicity on the Ni-CO_2 interaction, giving a weaker Ni-CO_2 interaction than that predicted.

2. At the opposite end of the transition series, niobium, a hard oxophylic transition element, forms a type II/III 18-electron complex [Nb(η-C_5H_4Me)$_2$(CH_2SiMe_3)(η^2-CO_2)]⁽⁹⁾ via the reduction of [Nb(η-C_5H_4Me)$_2$(CH_2SiMe_3)Cl] with sodium amalgam in THF under 1 atmosphere of CO_2 (see Figure 1.5).



Nb—C = 2.14Å

Nb—O_1 = 2.17Å

C_1—O_1 = 1.28Å

C_1—O_2 = 1.22Å

O_1—C_1—O_2 132.4°

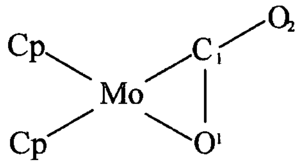
Figure 1.5

Selected X-Ray Crystal Data for [Nb(η-C_5H_4Me)$_2$(CH_2SiMe_3)(η^2-CO_2)]

It is worth noting here that the niobium-carbon and niobium-oxygen bond lengths are almost identical, whereas in the nickel-CO_2 complex, the nickel-carbon bond length is significantly shorter than the nickel-oxygen bond. In other respects, the complexes are very similar. The carbon-oxygen bonds are

slightly longer, but not significantly different and the O-C-O angles are virtually identical.
The niobium complex is much more stable than the nickel complex, and is attributed to the fact that it is a coordinatively saturated 18-electron species. The nickel complex in solution is a coordinatively unsaturated 16-electron species.

3. The third example of a type II/III transition metal - CO_2 complex is the molybdenum complex, $Cp_2Mo(CO_2)$ (Cp = cyclopentadiene) produced from $Cp_2Mo(PhC{\equiv}CPh)$ (14) (see Figure. 1.6). Carbon dioxide displaces diphenylacetylene from the complex in toluene at room temperature.



$Mo—C = 2.11$ Å
$Mo—O_1 = 2.16$ Å
$C_1—O_1 = 1.29$ Å
$C_1—O_2 = 1.20$ Å

Figure 1.6
Selected X-Ray Crystal Data for $Cp_2Mo(CO_2)$

The bond distances compare closely with those reported for the niobium complex discussed earlier. Both complexes are coordinatively saturated 18-electron systems.

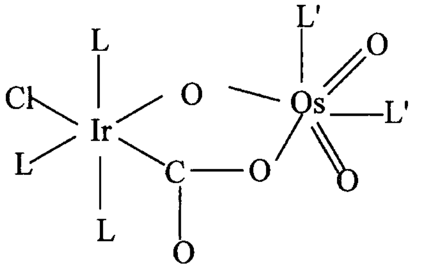
This is an example of a non-phosphine containing transition metal-CO_2 complex. The Cp ligands are displaced to make a cavity in the equatorial plane for the CO_2 unit (14). There is also evidence (IR ν(C=O) stretching frequencies solution → solid) that the Cp hydrogen atoms interact with the oxygen atoms of the carbon dioxide. The I.R. stretching frequency ν(C=O) of $Cp_2Mo(CO_2)$ in the solid state is $1705cm^{-1}$ versus $1745cm^{-1}$ in the solution state. This has been interpreted as the weakly acidic hydrogen atoms of the cyclopentadiene interacting at the oxygens of the carbon dioxide in the solid state(hydrogen bonding) . This has been dubbed bifunctional activation. In the crystal structure analysis of $Cp_2Mo(CO_2)$ it is found that the metal-bonded oxygen atoms are involved in the formation of one hydrogen bond and the uncoordinating oxygens form two hydrogen bonds with the Cyclopentadiene. It is also found that there are two crystallographically independent molecules, whose geometries are not significantly different. The two molecules differ in the structure taken up as a result of hydrogen bonding.

Other Molybdenum-CO_2 complexes have been reported but they are structurally of a different type and will be reviewed later.

Until now, no complexes having structures of type IV and V, (ie exclusive bonding of carbon dioxide via the oxygens to a transition metal centre) have been isolated and

characterised by X-ray analysis. This type of bonding has been suggested for ruthenium in the complex [Ru(CO$_2$)(NH$_3$)$_5$]X$_4$ (1). Infrared stretching frequencies in the range 2320cm^{-1} - 2340cm^{-1} are close to the infrared signal in unbound linear CO$_2$ 2349cm^{-1}. However, alternatively it is possible that the CO$_2$ in the Ruthenium complex is also linear, making it a type IV complex.
Moving on to complexes involving two transition metal centres. Structures VI to XI are theoretically possible (Figure 1.2).

Structure type VII has been assigned for an iridium-osmium complex (see fig. 1.7) prepared from Vaska's complex [IrCl(CO)(PPh$_3$)$_2$] and Osmium tetroxide in the presence of 4-tert-butylpyridine (15).



L = Triphenylphosphine

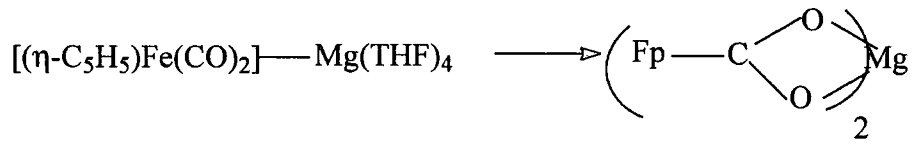
L' = 4-tert-butylpyridine

Figure 1.7
Proposed structure of the complex obtained from reaction of [IrCl(CO)(PPh$_3$)$_2$] with osmium tetroxide in the presence of 4-tert-butylpyridine.

The bridging CO$_2$ unit in this complex arises from oxidation of CO and is not a result of reaction with molecular Carbon Dioxide. It is an example of in situ synthesis of carbon dioxide.

Reaction of this complex with methyl trifluoromethane sulphonate leads to methylation of the exocyclic oxygen of the CO$_2$, giving a complex with a bridging methyl ester ligand. An X-ray analysis has been obtained of this compound (15) and with supporting NMR and IR data the structure given above (Figure 1.7) for the dinuclear Carbon Dioxide complex deduced.

Structure type VIII differs from type VII in that both oxygens coordinate to the metal. A type VIII structure has been proposed for a compound produced according to the equation shown below(20).



Fp = (η-C$_5$H$_5$)Fe(CO)$_2$

In this complex, the carbon is η^1 bound to the iron in the same way as the rhodium complex (type I, Figure 1.3). In addition, the Carbon Dioxide is further stabilized by coordination to the magnesium cation. In the rhodium complex (Figure 1.3),

stabilization of the η¹ bonding was postulated to be by the cyclopentadiene ligand C-H interactions with the CO_2 Oxygens.
The structure proposed in the iron case is an interesting example of CO_2 activation by a combination of basic and acidic metal centres. The structure is assigned on the basis of spectral interpretation and chemical reactivity analysis.

A structurally related complex has also been proposed by Bianchini for the cobalt complex shown in Figure 1.8.

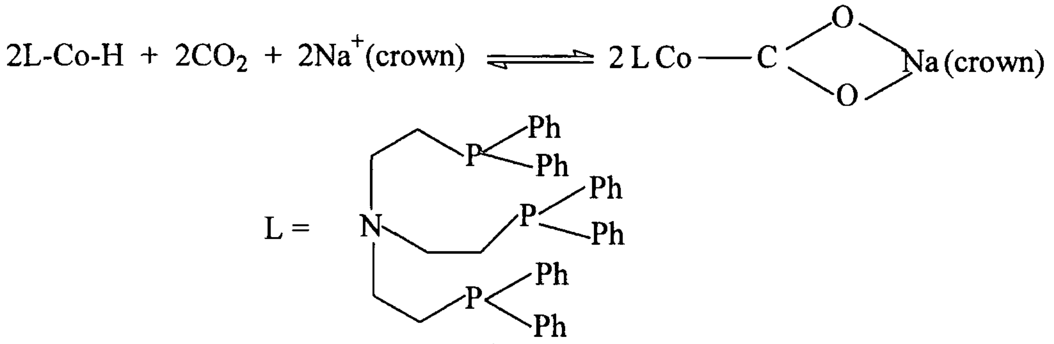
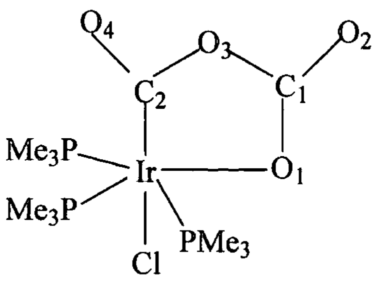


Figure 1.8
Synthesis of LCoCOONa(crown)

In both of these examples, the counterion intercepts and stabilizes the 1:1 CO_2 adduct as a metallacarboxylate and blocks CO_2 dissociation and 2:1 CO_2 binding pathways. The oxygen atoms of the CO_2 are not as accessible as those in the η¹-CO_2 Rhodium complex but reaction with trifluoromethane sulphonate leads to alkylation and methoxycarbonyl formation to give (η-C_5H_5) $(CO)_2FeCOOMe$. Reaction with trifluoromethane sulphonate suggests that the CO_2 has been activated. The oxygen atoms have more nucleophillic character in the complex than as free CO_2 molecules.

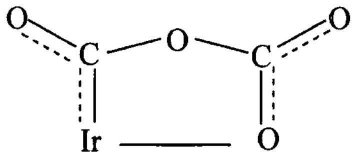
Examples of fully characterised complexes where two carbon dioxide molecules are bonded to the same transition metal are few in number . One such example is an iridium complex formed by exposing benzene solutions of $Ir(Cl)(C_8H_{14})(PMe_3)_3$ to a carbon dioxide atmosphere. White crystals of $Ir(Cl)(C_2O_4)(PMe_3)_3 0.5C_6H_6$ are formed. The crystal structure of this complex has been determined and the structure shown in fig. 1.9 assigned (16) (21).



C_1—O_2 1.23Å
C_2—O_4 1.23Å
C_2—O_3 1.35Å
C_1—O_3 1.35Å
C_1—O_1 1.24Å
Ir —Cl 2.36Å
Ir —O_1 1.99Å

Figure 1.9
Selected X-Ray Crystal Data for $Ir(Cl)(C_2O_4)(PMe_3)_30.5C_6H_6$

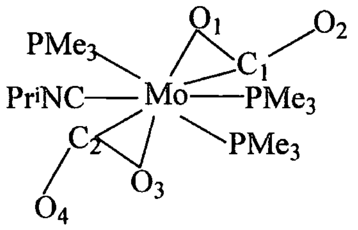
This is an example of a type XV transition metal - CO_2 complex. T. Herokovitz et al described the unusual CO_2 coordination using the valence bond approach shown below.



The carbon oxygen multiple bonds (C_1-O_1, C_1-O_2 and C_2-O_4) are like the short bonds in carboxylic acids and esters and the carbon oxygen single bonds (C_1-O_3 and C_2-O_3) are like the C-O single bonds in carboxylic acids and esters. For comparison the C-O distance in CO_2 is 1.16A and in carbonates about 1.29A (16) where C-O bonds are of equal length.

The mechanism for its formation is presumed to be addition of CO_2 to $Ir(Cl)(C_8H_{14})(PMe_3)_3$ forming initially $Ir(Cl)(CO_2)(PMe_3)_3$. The CO_2 and chloride are trans to each other. The activated CO_2 molecule and more specifically the more basic oxygen (O3) binds a second CO_2 molecule through C_1. Iridium-oxygen bond formation affords the product. Of interest here is that the first bound CO_2 molecule is sufficiently activated to react with the nucleophillic carbon centre of another CO_2 molecule. There are also similarities to η^1 - CO_2 complexes discussed earlier. Here, reaction with CO_2 and cyclization stabilize the reactive η^1-CO_2 complex. This is known as "Head to Tail" bonding.

A further example of the double co-ordination of CO_2 and an example of type XVI/XVII structure is provided by the molybdenum complex $Mo(CO_2)_2(PMe_3)_4$ (8, 22, 17)formed in the reaction of CO_2 with the Molybdenum dinitrogen complex Cis $Mo(N_2)_2(PMe_3)_4$. This material has been well characterised spectroscopically but no crystals have been obtained. Reaction of this material with isopropylnitrile ($CNPr^i$) yields the complex $Mo(CO_2)_2(PMe_3)_3(CNPr^i)$ of which crystals have been obtained and the X-ray crystal structure determined (Figure 1.10).



C_1—O_1 1.26Å C_2—O_3 1.26Å

C_1—O_2 1.22Å C_2—O_4 1.22Å

Mo—O_1 2.15Å

Mo—C_1 2.11Å

O_1—C_1—O_2 134°

O_3—C_2—O_4 133°

Figure 1.10
Selected X-Ray Crystal Data for $Mo(CO_2)_2(PMe_3)_3(CNPr^i)$

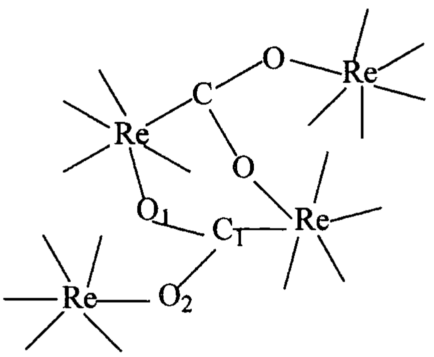
Both CO_2 molecules are bound almost identically as judged by bond distances and angles. The molecule is essentially octahedral at molybdenum with the CO_2 ligands trans to one another. The CO_2 ligands are bonded side on through one of the C=O bonds. The carbon-oxygen and molybdenum-carbon, molybdenum-oxygen bond lengths are very similar to those found in the type II/III $Nb(CO_2)(C_5H_4Me)_2(CH_2SiMe_3)$ and $Mo(CO_2)(Cp)_2$.

The molybdenum-CO_2 bonding is relatively strong. Evidence for this comes from a comparison with the diethylene species trans-$Mo(C_2H_4)_2(PMe_3)_4$. In this complex, the average Mo-C (ethene) distance is 2.27Å as compared with Mo-C (CO_2) 2.105Å and Mo-O (CO_2) 2.147Å. The metal carbon and metal oxygen bonds are significantly shorter in the CO_2 complex than in the ethylene complex.

The strong bonding helps explain the surprising thermal stability of the $Mo(CO_2)_2(CNPr^2)(PMe_3)_3$. The solid can be heated for several hours in air or under nitrogen at 80°C without noticeable decomposition (8). Carmona et al (22) attributes the remarkable strength of the Mo-CO_2 bonds as compared to other transition metal-carbon dioxide bonds to intense back bonding from the molybdenum centre to the coordinated CO_2 molecules and to the oxophillic nature of molybdenum.

The final group of complexes are those where several metal centres are involved in binding and activating carbon dioxide. From Figure 1.2, these are structure types XX to XXIV.

A η^3-CO_2 bridge of type XXIII was reported in a rhenium complex by Beck et al (11) (1). This complex, like the type VII iridium-osmium complex, is not formed by direct reaction with CO_2. Reaction of $(OC)_5ReFBF_3$ with aqueous NaOH gives in 95% yield a compound formulated as "$Re(CO)_5OH$", but is in fact a tetranuclear Rhenium cluster $Re_4(CO)_{18}(CO_2)_2$ formed by self condensation with the elimination of water to give the structure shown in Figure 1.11. The carbon-oxygen bond lengths of the CO_2 group are like those in the carboxylate anion.



C_1—O_1 1.28Å

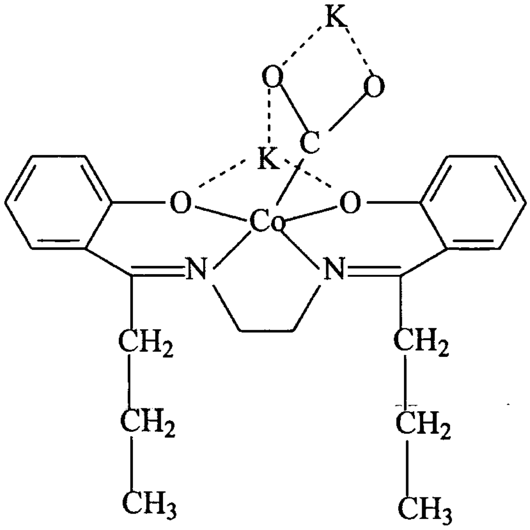
Re—C_1 2.0A°

Re—O_1 2.16Å

Re—O_2 2.13Å

Figure 1.11
Selected X-Ray Crystal Data for $Re_4(CO)_{18}(CO_2)_2$

An example of structure type XXIV synthesized by Floriani et al (18) and determined by X-ray analysis is shown in Figure 1.12. The complex is formed by reducing N,N'-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), or a substituted Co(salen) with potassium and exposing the complex formed [Co(salen)K] to CO_2 at room temperature.



C_1—O_1 1.24Å

C_1—O_2 1.22Å

Co—C_1 1.99Å

K —O_1 2.69Å

K —O_2 2.73Å

Figure 1.12
Selected X-Ray Crystal Data for $Co(pr\text{-}salen)K_2CO_2.THF$

This is related to the type VII structures discussed earlier. Interestingly the complex functions as a reversible CO_2 carrier, the metal-carbon sigma bond is easily formed and broken. It is an example of bifunctional activation of CO_2 involving basic and acidic metal centres. Florioni et al (18) hypothesize that the bifunctionality is important in CO_2 fixation. The hypothesis stems from the observation that some reactions of CO_2 require in addition to a basic centre the assistance of an acidic partner (Lewis acid centre).

The presence of a basic metal centre is certainly important for interaction with the carbon atom Lewis acid site of carbon dioxide. Acidic partners can also play a role in stabilizing structures of η^1-CO_2 in some cases.

The above structure is thought to be formed by concerted attack of the nucleophillic cobalt (I) on the eletrophillic carbon of the CO_2, whilst the acidic M^+ interacts with the basic oxygens of the carbon dioxide.

The best example is of a type XXIV transition metal-CO_2 compound. The compound is formed from the reaction of $Os_6(CO)_{18}$ with $[Os_3(CO)_{11}H]^-$ to give $[HOs_3(CO)_{10}O_2{\cdot}C{\cdot}Os_6(CO)_{17}]^-$. Two osmium clusters are bonded by a bridging CO_2 unit formed in situ and not from gaseous CO_2.

Conclusions

Activation of CO_2 occurs by two basic mechanisms:-

(i) Interaction of a basic metal centre with the lewis acid carbon to form a metallacarboxylate. These materials on their own seem unstable or prone to further reaction, possibly by interaction with another CO_2 molecule and subsequent disproportionation to carbonyl and carbonate. Some stabilization or bifunctional activation is required. This can come from interactions with ligand C-H groups, basic metal ions or other transition metals. No known complex exists where η^1 - CO_2 bonding is present without some stabilization or bifunctional activation: The closest to this is the $Rh(\eta^1\text{-}CO_2)(Cl)(diars)_2$ complex. Depending on either stabilization or bifunctional activation, the oxygens of the CO_2 are activated for further reaction. The CO_2 in these complexes is isostructural with/closely analagous to a carboxylate group ($M\text{-}COO^-$, $R\text{-}COO^-$).

(ii) Carbon dioxide couples laterally to the transition metal and a metal-carbon and a metal-oxygen bond are formed. It is claimed from MO calculations (6) that η^2-CO_2 bonding is most favoured when large back donative stabilization is present. It should also be noted that this π backbonding component decreases in the CO_2 coordination modes $\eta^2\text{-}C_1O >> \eta^1\text{-}C > \eta^1\text{-}O$. η^2-CO_2 complexes are the most highly stabilised.

Bonding through the carbon alone (η^1) may be anticipated in species where the metal is electron rich and where simultaneous side on coordination is not possible for some reason, such as coordination saturation. Additionally, it is apparent that when η^1-C and η^1-O binding modes are simultaneously present in a complex, this represents a favourable situation (net stabilisation occurs).

An examination of the X-ray analysis data for the complexes reviewed shows that the geometry of complexed carbon dioxide does not deviate greatly for the various bonding modes. For example, the oxygen-carbon-oxygen bond angle ranges from 126^{O} in $Rh(CO_2)(Cl)(diars)_2$ to 134^{O} in $Mo(CO_2)_2(CNPr^{i})(PMe_3)_3$.

The coordinated CO_2 molecule has a calculated minimum bonding energy reached at an O-C-O angle of 138^{O} (6). The energy required to distort the CO_2 from its equilibrium geometry is more than compensated for by the metal-CO_2 interaction energy, primarily backbonding from the metal to the π^* orbital of CO_2.

Carbon-Oxygen bond distances in the transition metal-CO_2 complexes discussed vary from 1.17Å in $Ni(CO_2)(PCy_3)_2$ 0.75 (Toluene) to 1.35Å in $Ir(C_2O_4)(Cl)(PMe_3)_3$. The C-O bond length in carbon dioxide is 1.16Å. In the nickel complex, the C-O bond not interacting with the nickel remains virtually unchanged. In the iridium complex, the C-O bond reflects the carboxylate nature of the CO_2 in this complex.

Another important point to note is that the majority of methods to synthesise transition metal-CO_2 complexes employ low temperature and atmospheric pressure conditions, ie, the activation of carbon dioxide can be achieved at low pressures and temperatures. The known routes to transition metal-CO_2 complexes in general are:-

1. Substitution of Labile Ligands

Even under mild conditions, phosphines can dissociate from an electron rich complex and be replaced by carbon dioxide. The nickel complex $Ni(CO_2)(PCy_3)_2$ is synthesized by this route. Nitrogen and alkenes are other ligands which have been displaced by carbon dioxide to give stable complexes at low temperatures and pressures.

$$Mo(N_2)_2(PMe_3)_4 + 2CO_2 \rightarrow Mo(CO_2)(PMe_3)_4 + 2N_2$$

$$Ir(C_8H_{14})Cl(PMe_3)_3 + 2CO_2 \rightarrow Ir(CO_2)_2Cl(PMe_3)_3$$

2. Addition to 16-electron Complexes

This method is used in the synthesis of $Rh(CO_2)(diars)_2(Cl)$. The 16 electron intermediate is synthesized $[(Rh(diars)_2Cl)]$ and reacted in situ with carbon dioxide. The 16-electron compound is a very reactive intermediate and reaction occurs at low pressure.

3. Insertion Into Binuclear Complexes

Basic transition metal centres can react with alkali metal ions which act as Lewis-acid centres forming binuclear complexes. The cobalt complexes of Floriani are good examples of this.

$$[Co(Pr\text{-}salen)K] + CO_2 \rightarrow [Co(Pr\text{-}salen)K(CO_2)THF]$$

4. Reduction of Complexes

This is perhaps the most severe synthetic route to transition metal-CO_2 complexes. The reduction of $Nb(Cl)(C_5H_4Me)_2CH_2SiMe_3$ using a sodium amalgam occurs at room temperature and 1 atmosphere CO_2 to give $Nb(CO_2)(C_5H_4Me)_2(CH_2SiMe_3)$.

5. In Situ Synthesis of Carbon Dioxide

Some complexes discussed earlier were not formed by reaction with CO_2 but by formation of CO2 in the coordination sphere of the metal, eg.

$$Re(CO)_5OH \rightarrow [(CO)_5Re]_2(CO_2)[Re(CO)_4]_2$$

The two most important reactions involve either the substitution of labile ligands or additions to 16 electron compounds. These two reactions are obviously closely related. Substitution of labile ligands most likely occurs via a two step mechanism, dissociation of the labile ligand followed by reaction of a 16-electron coordinatively unsaturated intermediate with carbon dioxide. These two types of reaction also play a role in homogeneous catalysis. Thus, from our review of the types of Metal-CO_2 complexes and the way they form, there is abundant evidence to suggest that catalysis involving CO_2 should be possible.

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CHAPTER TWO

TRANSITION METAL-ALKENE/ALKYNE INTERACTIONS

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Alkene/alkyne complexes of the transition metals are essential intermediates in a variety of homogeneous catalytic processes. Consequently, because of their importance, the bonding in these complexes, activation of the ligands and their reactions have been extensively studied. The purpose of this review is to discuss the bonding principles and the effect of coordination of alkenes and alkynes to transition metals on the chemistry of these ligands and in particular their activation for further reaction. Examples of alkene and alkyne complexes will be discussed (where relevant) along with typical reactions. This subject is reviewed in references 1-26 which is by no means an exhaustive list.

Bonding Description of Alkenes to Transition Metals

The classical description of the bonding between a transition metal and an alkene was first proposed by Dewar (1) and later refined by Chatt and Duncanson (2) in the 1950's, and is known as the "Dewar, Chatt, Duncanson" model.

The alkene is bound laterally to the metal, with the two alkene carbon atoms equidistant from the transition metal centre. The bonding between a transition metal and an alkene has two different components which reinforce one another in a synergic process. A forward bonding component results from transfer of electron density in the π bonding molecular orbital of the alkene to a suitable σ-orbital on the metal. The second component, a backbonding component, results from transfer of electron density from a filled metal d-orbital into the π* antibonding molecular orbital of the alkene. Thus, the carbon-carbon π bond is serving as a σ donor to the metal and the π* molecular orbital is serving as a π acceptor.

This leads us to two extremes of bonding (see Figure 2.1). In complexes where the metal bears a positive charge (usually high formal oxidation state), alkene ligands act predominantly as σ donors (Type I). The effect of this on the alkene and its reactivity is discussed later. At the opposite extreme, where the metal retains more electron density (usually low formal oxidation state), alkene ligands act predominantly as π acceptors (Type 2). If backbonding is carried far enough, the olefinic carbons change to sp3 hybridization and the complex can be described as a metallacyclopropane.

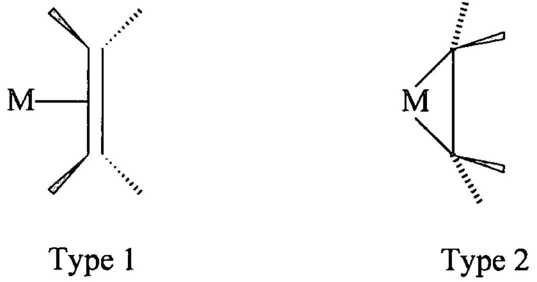


Figure 2.1

Extremes of Metal-Alkene Bonding

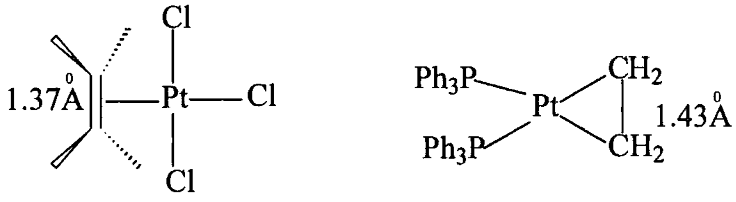
The majority of transition metal-alkene complexes fall midway between these two extremes.

Changes in Alkene Structure

1. The carbon-carbon bond increases in length. this is as a result of the decrease in electron density in the π carbon-carbon bonding molecular orbital and the increase in electron density in the π* antibonding molecular orbital. The carbon-carbon bond is weakened and this shows itself as an increased bond length. The C=C bond length of complexed alkenes lies between that of the free alkene and the saturated hydrocarbon e.g.

   CH2=CH2 1.337Å,
   CH3-CH3 1.534Å

   The two extremes are best understood by reference to the examples shown below (see Figure 2.2):-



(I) (II)

Figure 2.2
Transition Metal-Alkene Complexes

In Zeises salt (I, Figure 2.2) a PtII complex, the σ donor component predominates and the carbon-carbon bond length more closely resembles the free alkene. In a complex of a transition metal in a lower valency state where the metal is strongly π basic (II, Figure 2.2), the carbon-carbon bond distance is much longer and is considered as approaching the metallacyclopropane extreme. This is because of significant d - π* back donation offloading the build up of electron density at the metal centre.

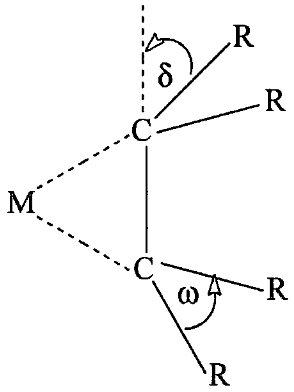
In Zeises salt, it has been estimated that 75% of the total binding energy comes from the forward donation component and 25% from the back donation component (2).

2. The substituents on the coordinated alkene bend away from the metal on coordination. These changes are again a result of the alteration in the electron density in the π and π* orbitals of the coordinated olefin. The two extremes are again type I and type II (Figure 2.2) . In type I where d - π* back bonding is minimal, the alkene carbon atoms closely resemble sp^2 hybridized carbon and bending away from the metal is minimal. In type II where the coordinated olefin is approaching the metallacyclopropane extreme, the substituents on

carbon are strongly folded back away from the metal as the carbons rehybridize from sp^2 to something approaching sp^3 (tetrahedral) .

The effect is shown in Figure 2.3 below. The angles δ and ω are known for two nickel complexes.

(i) $(CH_3)_2C = C(CH_3)_2\ NiP(\text{cyclo-}C_6H_{11})_2C_2H_4P(\text{cyclo}C_6H_{11})_2$
a bisdicyclohexylphosphinoethanenickel (hexene) complex
(ii) $(CN)_2C = C(CN)_2\ Ni(CN\text{-tert-}C_4H_9)_2$
tetracyanoethylenenickel complex.



1) $\delta = 26^{o}$, $\omega = 111.8^{0}$

2) $\delta = 28.4^{o}$, $\omega = 114.7^{0}$

Figure 2.3
Extremes of Transition Metal-Alkene Bonding Effect on Hybridization of carbon

The tetracyanoethylene complex has a much greater d - π^* backbonding component and this is observed in the greater bending back of the olefinic carbon substituents towards sp^3 hybridization of the carbon atoms. It should be noted that electron withdrawing substituents on the alkene encourage backdonation leading to a substantial increase in the π^* antibonding orbital electron density. This weakens and lengthens the alkene multiple bond and causes a greater bending back of the substituents on the alkene carbons as shown for the greater angle σ in the tetracyanoethylene nickel complex.

3. The alkene molecule is twisted out of the plane formed by the metal and the remaining ligands. This is shown in the diagram Figure 2.4 below as the angle α.

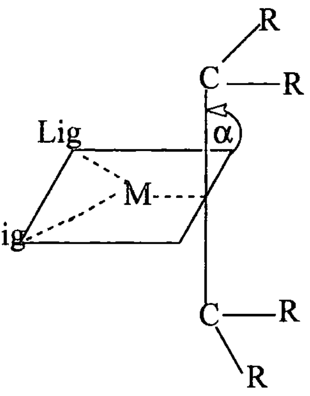


Figure 2.4
Out of Plane Twisting of Substituted Alkenes

This effect occurs when unsymmetrically substituted alkenes coordinate to transition metals. Depending on the substituents (R), the metal carbon bond lengths can differ significantly. In the square planar Platinum II - alkene complexes (2), the metal carbon bond length to the olefinic carbon atom carrying the substituent is invariably longer than that to the unsubstituted carbon atom. The effect is independent of whether the substituent is a net π donor or π acceptor.

RESULTS OF ACTIVATION : SPECTRAL & CHEMICAL:

Coordination of an alkene to a transition metal is accompanied by changes in its spectroscopic properties. The position of vinyl protons and vinyl carbons in the ^1H and ^{13}C NMR change on coordination. For example, at the type II metallacyclopropane extreme (Figure 2.1) vinyl protons can resonate 5ppm and the vinyl carbons 100ppm to high field of their position in the free ligand, as is consistent for a change of hybridization from sp^2 to $\equiv$ sp^3 at carbon (4). An example of the upfield shift of the vinylic carbon atom is in the complex $Ni(PPh_3)_2(Ema)$ Ema = ethylmethacrylate (5). The complex has the structure shown below in Figure 2.5.

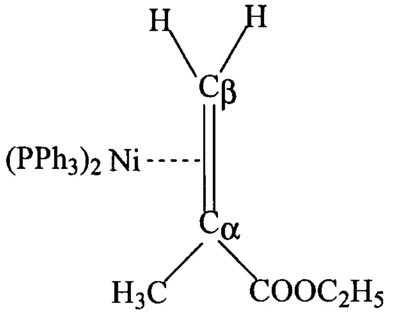


Figure 2.5
Structure of $Ni(PPh_3)_2(Ema)$, Ema = ethylmethacrylate

The vinylic carbon Cα is shifted upfield to a chemical shift of 57.6ppm (136.4 free Ema). The vinylic β carbon is shifted to a chemical shift of 53.1 (124.6 free Ema).

The chemical shift change as a result of coordination of the alkene is Cα 79.8ppm, Cβ 71.5ppm. In complexes of this type, the large shift is attributable to the basic phosphine ligands enhancing Ni-Ema backbonding increasing the electron density in the π* orbital thus increasing the shielding of the olefinic carbons.

Changing the phosphine ligand affects the chemical shifts of the vinylic carbon atoms. Increasing basicity further shifts the vinylic carbons upfield for the same reason as above ie. further increased backbonding. The increasing basicity of the ligand affects the α carbon to a greater extent than the β carbon. This effect can also be accounted for in terms of Ni-Ema backbonding. The α carbon of Ema in the uncoordinated state has less electron density than the β carbon because of the effect of the electron withdrawing ethoxycarbonyl group. Back donation of electron density from nickel to the double bond would therefore increase electron density at the α carbon to a relatively greater extent.

The infra red properties of coordinated alkenes are less diagnostic (6). The coordinated C-C stretching frequency occurs around 1500cm^{-1} but is weak and may be mixed with CH_2 deformation modes. This bond is not related in any simple way to the coordinated alkene C-C bond length.

Chemical significance of alkene coordination comes from assessing the two extremes of bonding type I and typeII (Figure 2.1) . Type I, where the σ donor contribution to the bond is greatest, results in a δ+ve charge on carbon. This is because the ligand to metal σ donation depletes the charge on the ligand and, in the type I extreme, this is not recovered by back donation. These alkene complexes are therefore subject to nucleophilic attack, and resistant to electrophillic attack at the vinyl carbons. Since simple alkenes in the free state are generally (but not always true) subject to electrophillic but not nucleophillic attack, the effect of binding is very significant on the chemical reactivity of alkenes.

At the opposite extreme, type II (Figure 2.1), complexes are attacked by electrophiles such as protons at the electron rich metal carbon σ bonds. These reactions are discussed in a later section.

In general metals in a high formal oxidation state, e.g. Pd(II), Hg(II), Ag(I), tend to form type I complexes (electron deficient) and metals in a low formal oxidation state (e.g. Ni(O), Pd(O), Pt(O), tend to form type II (electron rich) metallacyclopropane like structures.

Coordinated alkenes can be very reactive toward other ligands in the same coordination sphere by migratory insertion. This is a key step in many homogeneous catalysis cycles and examples will be discussed. These are perhaps the most important reactions (commercial) of coordinated alkenes.

NUCLEOPHILLIC ATTACK TO COORDINATED ALKENES

Unsaturated hydrocarbons such as alkenes are electron rich and as such are normally resistant to nucleophillic attack. However, upon coordination to an electron deficient metal centre, the alkene pattern of reactivity can be reversed , the metal acting as an electron withdrawing group. Not all transition metal-alkene complexes are reactive toward nucleophilles. The metal must be in a relatively high oxidation state (II to IV), have a full formal positive charge and/or have a number of remote electron withdrawing ligands. This is the opposite to the situation in the present research programme where highly electron donating ligands and low oxidation state transition metals are used. The nuceophilic addition reactions of coordinated alkenes are discussed briefly for completeness:

Nucleophilic attack usually occurs on the complexed alkene to produce σ-alkyl metal complexes. In most cases studied, the process involves trans attack (from the face opposite the metal) of the free nucleophille (see Figure 2.6).

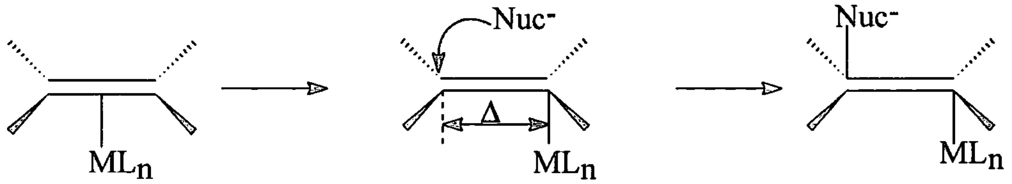
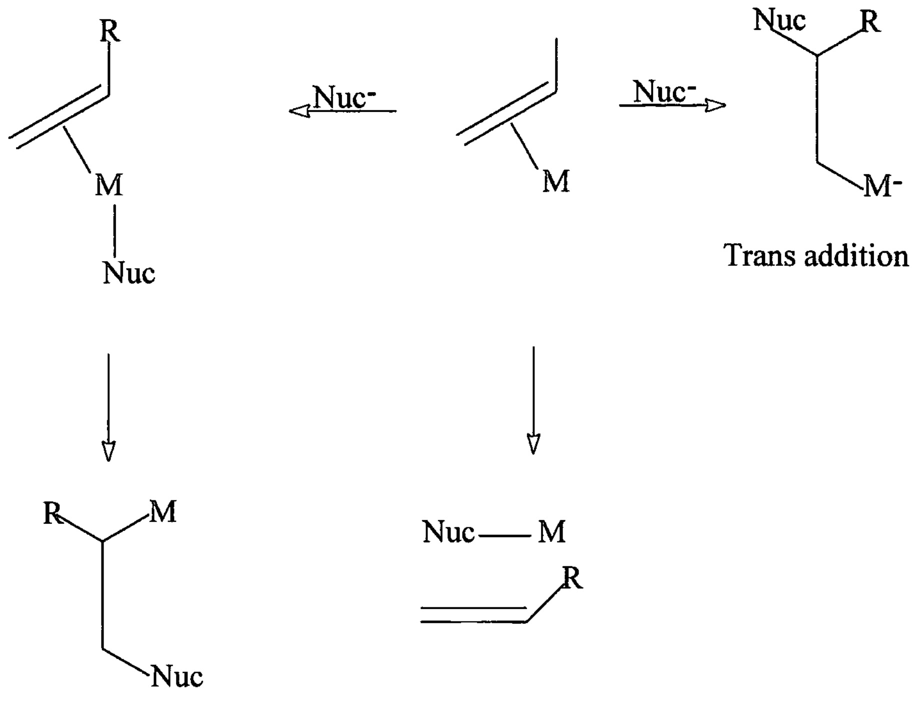


Figure 2.6

Nucleophilic Attack at Coordinated Alkene to give σ-Alkyl Metal Complexes

With substituted alkenes, nucleophillic attack occurs predominantly at the more substituted alkene carbon atom. The regiochemistry and overall activation are attributed to the out of plane twisting of the alkene discussed earlier for substituted alkenes. Displacement of the alkene from an $\eta^2(\pi)$-bonding mode toward an $\eta^1(\sigma)$-bonding mode follows.

Some nucleophilles attack the metal first, this is followed by insertion of the olefin into the metal nucleophille bond resulting in overall cis addition (see Figure 2.7).



Cis addition Displacement

Figure 2.7
Modes of Nucleophilic Attack at Metal-Alkene Complexes

In the absence of unusual electronic effects, attack (insertion) occurs at the least substituted alkene carbon.

Reactions of both types are restricted to mono or disubstituted alkenes since more highly substituted species coordinate only weakly and are easily displaced. Displacement of the olefin by the nucleophille is the major competing reaction particularly if the nucleophille is a good ligand for the metal.

An example of nucleophillic attack at coordinated ethene is shown for the iron II complex (see Figure 2.8) below (6).

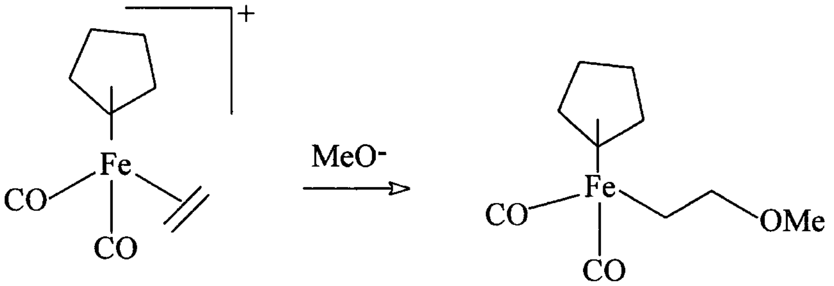


Figure 2.8
Nucleophilic Attack at Coordinated Ethene in Fe(Cp)$(CO)_2$(ethene)

ELECTROPHILLIC ATTACK AT COORDINATED ALKENES

When coordinated to transition metals alkenes are in general not electron rich and are thus less susceptible to electrophillic attack than the free uncoordinated alkene. At the type II extreme (Figure 2.1), the metallocyclopropane-like structure, coordinated alkenes are susceptible to electrophillic attack at the electron rich metal-carbon σ bonds (6). Electrophillic attack is frequently indirect occurring by an insertion reaction into the bond formed by initial electrophillic attack at the metal. See (see Figure 2.9) below.

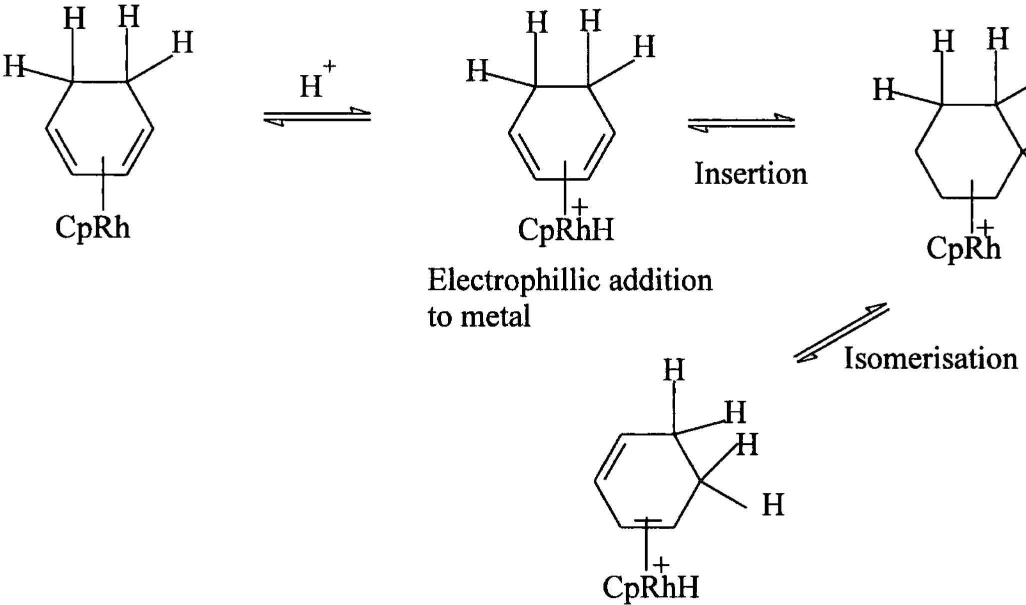


Figure 2.9
Electrophilic Attack at Coordinated Alkene

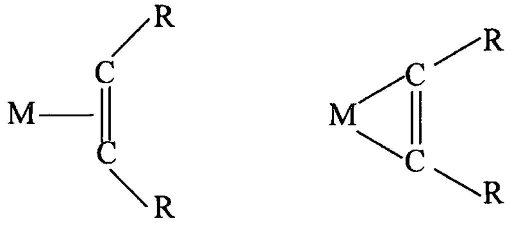
Bonding of Alkynes to Transition Metals

Upon coordination to a metal, the acetylenic group is distorted toward the geometry of a cis olefin as shown in Figure 2.10 (type I). The degree of distortion is highly variable, so that a range of structures is possible. The bonding in metal-alkyne complexes is similar to that in alkenes and can be treated by the Dewer Chatt Duncanson model. Alkynes have two bonding and two anti bonding π* orbitals that can in principle interact with metal d orbitals. These are:-

(i) Those lying in the metal:alkyne bond plane (parallel orbitals 1σ and 1π) which are analagous to the orbitals used by alkenes in π complexes and

(ii) Orbitals lying perpendicular to the metal:alkyne bond plane (1π).

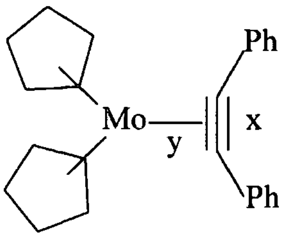
Alkynes may be formally neutral two electron σ donors (using the parallel π orbital) but can also act as two electron π donors (using the perpendicular π orbital). The parallel π* acceptor orbital is also important- sufficient π donation into it creates a structure best described as a metallacyclopropene. In this limit the metal alkyne carbon bonds are strengthened, the carbon-carbon bond is weakened and becomes longer, and the substituent groups are bent away from the metal. The two extremes of transition metal:alkyne bonding are shown in Figure 2.10 below.



Type I Type II

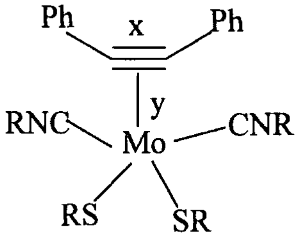
Figure 2.10
Extremes of Metal-Alkyne Bonding

The effect of increased π donation are to move from type I to type II character. This is illustrated by the following examples .



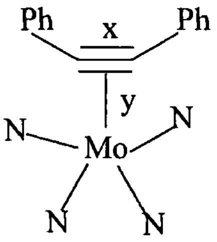
A

x = 1.27Å, y = 2.05Å



B

x = 1.28Å, y = 1.95Å



C

x = 1.32Å, y = 1.86Å

The alkyne carbon-carbon distance x increases across the series, whereas the distance y from the midpoint of the carbon-carbon triple bond to molybdenum decreases. The porphyrin complex (C) shows greater π donation than in A and B and therefore the longest acetylenic carbon-carbon bond and the shortest molybdenum-acetylene bond distance. It most closely approximates to the metallacyclopropene extreme whereas complex A most closely approximates to the metal π bound extreme. These structural extremes ae exactly analagous with the alkene-transition metal bonding discussed earlier.

Coordination of an alkyne to a transition metal causes the carbon-carbon triple bond stretching frequency to become infra red "allowed" and to shift to lower frequencies. This shift is highly variable - from 150 to 450 cm^{-1} below the Raman active vibration for the uncoordinated alkyne. (Symmetrical alkynes do not have an allowed infra red bond because the stretching motion does not result in a change in dipole moment.)

As for alkenes, coordinated alkynes are readily attacked by nucleophiles but they have been studied less. Also, alkynes are known to readily bridge two metals. In these cases, the alkynes are acting as two electron donors to each metal.

In conclusion, no new concepts need to be introduced to understand the bonding of alkynes to transition metals and the types of reactions which occur.

INSERTION REACTIONS OF COORDINATED ALKENES

Coordinated alkenes can be very reactive toward other ligands in the same coordination sphere by migratory insertion or electrocyclic reactions. The insertion of coordinated alkenes into metal-hydride bonds is a key step in a variety of catalytic reactions. Those that will be discussed here are (i) oligomerization and cooligomerization of alkenes, (ii) isomerization of alkenes, (iii) hydrogenation of alkenes, (iv) hydrosilyation of alkenes and (v) hydrocyanation of alkenes. Each reaction will be discussed with reference to coordination of the alkene to the metal, activation and post reaction (insertion) and factors affecting these processes.

OLIGOMERIZATION AND COOLIGOMERIZATION OF ALKENES:

The polymerization or oligomerization of simple alkenes involves three basic steps:

a) Initiation
b) Propogation
and c) Termination.

A schematic view of alkene oligomerization is shown below (see Figure 2.11) for a nickel catalysed reaction (7).

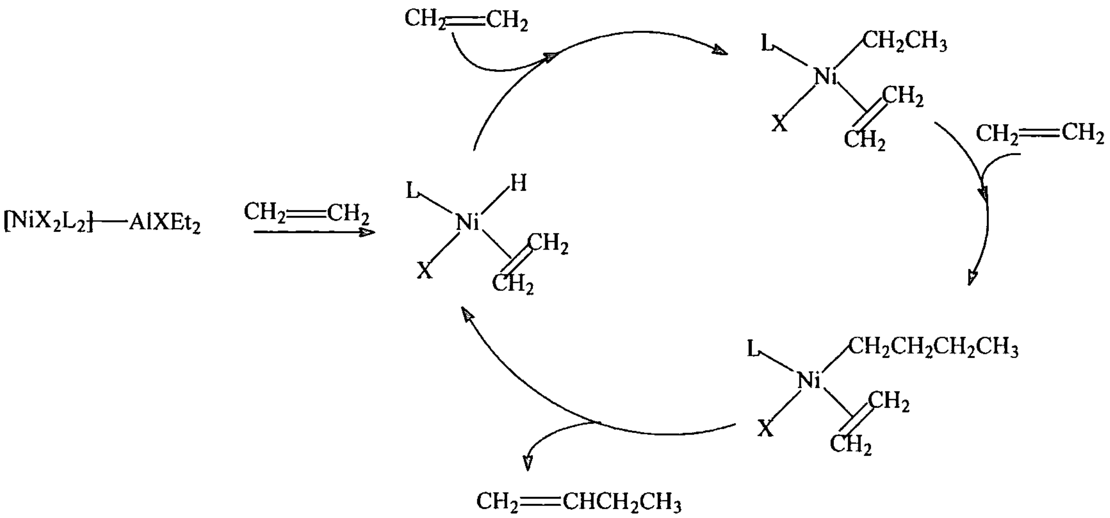


Figure 2.11
Schematic View of Alkene Oligomerization

The key step of interest is the coordination of alkene and insertion into either the metal hydride or metal alkyl bond. A vacant 2-electron coordination site is required for the alkene to bind before insertion can take place. For an effective oligomerization, the alkene must be a good ligand. Amongst simple monoenes these oligomerizations/polymerizations are usually limited to ethene and other unhindered terminal alkenes (ethene>propene>1-butene). Internal alkenes are normally not polymerized by these catalysts. (6).

The second stage is the formation of the new carbon-hydrogen or carbon-carbon bond. The majority of evidence suggests this occurs by a simple migratory insertion (6,8,9) of the coordinated hydride or alkyl to the coordinated alkene (see mechanism Figure 2.11).

The reverse of the migratory insertion is the ubiquitous β-hydride elimination. This is thought to be the termination step, regenerating the starting hydride and producing oligomers with terminal alkene bonds. β-hydride elimination blocks the 2-electron coordination site for incoming alkene and therefore prevents further alkene binding. The transition state for insertion (see Figure 2.12) is thought to occur via coplanarity of the metal-carbon and carbon-hydrogen or alkylcarbon bonds.

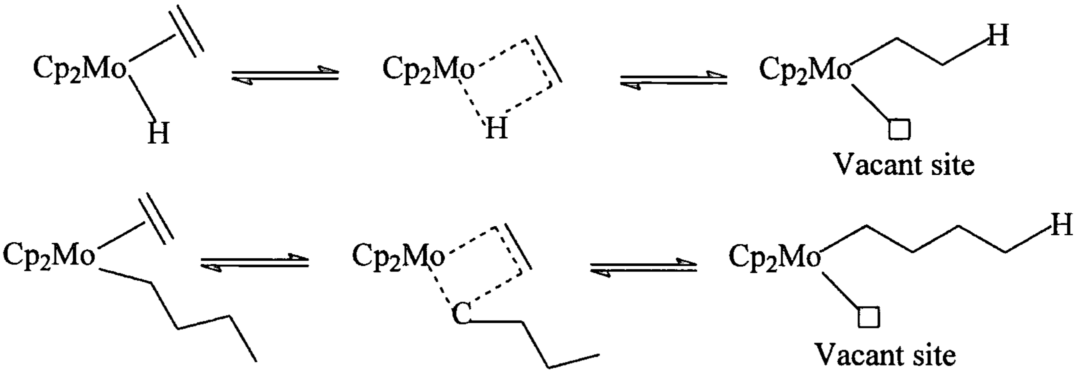


Figure 2.12
Theoretical Mechanism of Insertion into Metal-Hydride Bond

By the theory of microreversibility, β-hydride elimination also requires the same coplanarity. This effect can be used to stabilize metal alkyls and metallacycles. If for example, coplanarity is not possible for steric reasons, decomposition by *β*-elimination cannot occur.

Directly relevant to the current research programme is the oligomerization of propene at nickel catalyst systems. The reaction of propene is more complex than that of ethene since a mixture of primary products can be formed depending on the regiochemistry of addition. The sense of addition seems to be controlled by steric factors (7).

HYDROGENATION

Hydrogenation catalysts add molecular hydrogen to the C=C group of an alkene to give an alkane. Three types of hydrogenation have been distinguished according to the way each activates hydrogen. The cycle in Figure 2.14 shows the hydrogenation of alkenes by a catalyst that activates hydrogen by an oxidative addition mechanism.

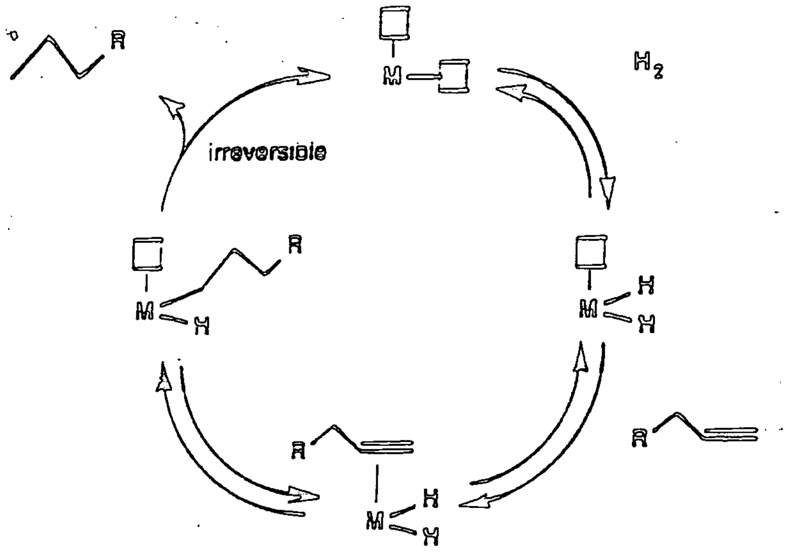
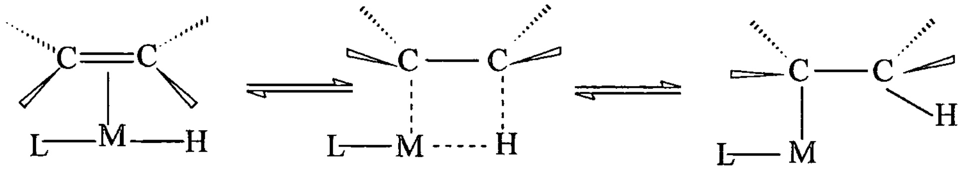
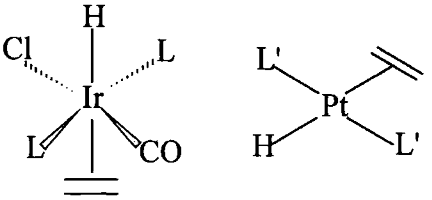


Figure 2.14
Schematic View of Alkene .

A very useful and widely used hydrogenation catalyst is Wilkinsons catalyst $Rh(Cl)(PPh_3)_3$. This is a 16-electron stable species. In order to bind two hydrides and the alkene, a total electron count of 4-electron, the 16-electron catalyst needs to disassociate a 2-electron donor ligand. Alkene binding is into a 2-electron vacant coordination site. The common feature of the hydride alkene insertion, whereby the hydride, the metal and the alkene must all be coplanar, is important. The consequence of this sterochemical requirement is that catalytic hydrogenations of alkene double bonds are usually cis (see below). Examples of compounds which contain coordinated alkene and hydride ligands in the same compound are not common, and generally occur when both ligands are mutally trans. Isomerization would need to occur before migratory insertion.



Cis Relationship Between Alkene And Hydride
Necessary For Insertion



Mutually Trans- No Insertion

The selectivity of reaction for hydrogenation of alkenes, is determined by how easily the alkene can bind to the metal, the poorer ligands among them being reduced only slowly, if at all. The hydrogenation rates charge in the order monosubstituted > disubstituted > trisubstituted > tetrasubstituted ≅ O.

A study by Tolman and Seedel,(10)who measured the stability constants of various alkene-nickel-ligand complexes (ligand = tris-o-toly phosphite) showed that the equilibrium constant for the formation of the complex from free alkene and liganded nickel could vary by as much as 10^{12} depending on the nature of the alkene. The results showed a one thousand fold difference in equilibrium constant between ethylene and propylene. These results suggest that the rate determining step in transition metal alkene reactions can often be coordination of the alkene and not further reaction, ie. whatever happens once the alkene is in the coordination sphere of the metal.

Alkene Isomerization

Many transition metal complexes are capable of catalysing the migration of hydrogen substituents in alkenes, a reaction that has the net effect of moving the C=C group along the chain of the molecule. Many hydrogenation and oligomerization catalysts also isomerize to some extent the alkenes they coordinate. This is because the migratory insertion of the coordinated alkene is the first step in hydrogenation and oligomerization reactions. Reverse β elimination to give either the starting alkene or an isomer of it are possible competing reactions with elimination of the alkene (see Figure 2.15).

The diagram below shows how isomerization is a competing process in some hydrogenation catalysts.

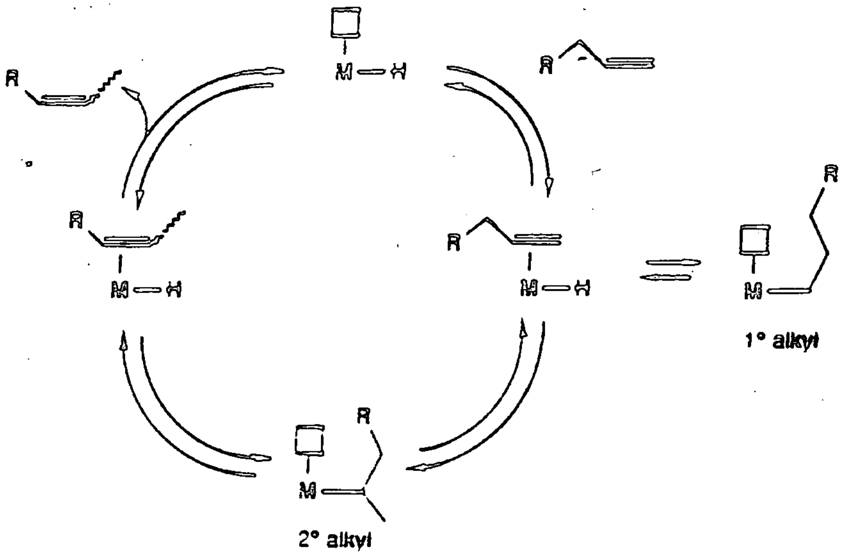


Figure 2.15
Schematic View of Alkene Isomerization

The example serves to show that a given catalyst is capable of more than one type of reaction.

Many alkene isomerization catalysts are nickel based systems (7), which will be discussed later.

Hydrocyanation/Hydrosilyation

Hydrocyanation and hydrosilyation of alkenes are closely related to each other and to homogeneously catalysed hydrogenation. Though detailed mechanisms are not fully understood, plausible steps can be written down which account for a large number of these catalysis cycles. These are (i) Oxidative addition of the cyano or silyl compound accross the metal to give a metal hydride in both cases, (ii) Coordination of the alkene to the metal. (iii) Migratory insertion of hydride to give a metal alkyl and generate a vacant coordination site. (iv) Reductive elimination of the hydrosilyation/ hydrocyanation product. There is nothing new to glean from these reactions in terms of the coordination of alkenes and their reaction in the coordination sphere of a transition metal.

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CHAPTER THREE

Nickel Chemistry Relevant to Homogenious Catalysis Involving Alkenes/Alkynes

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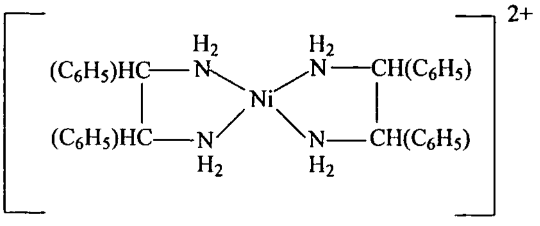
General Aspects of Nickel Chemistry

In nature nickel occurs mainly in combination with arsenic, antimony and sulphur, for example as millerite (NiS) as a red nickel ore that is mainly NiAs. In general, the ore is transformed to Ni_2S_3 which is roasted in air to give NiO and this is reduced with carbon to give the metal.

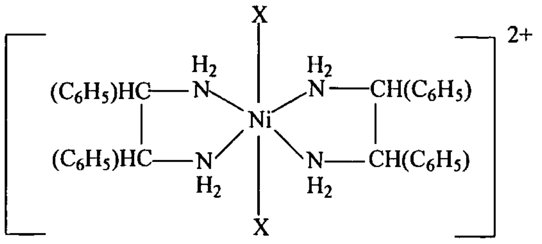
The most common oxidation state of nickel is +2, the maximum coordination number of nickel II is 6 and these complexes are octahedral. These compexes are exemplified by $[Ni(H_2O)_6)^{2+}]$ hexaaquonickel ion. A considerable number of both trigonal bipyramidal and square pyramidal complexes of five coordinate nickel (II) are known also. Examples of these are $[Ni(CN)_5]^{3-}$ and $[Ni(Ph_2MeAsO)_4(ClO_3)]^{+}$. The most common form of nickel (II) is four coordinate which can be either square planar or tetrahedral.

Tetrahedral complexes are generally strongly coloured and tend to be blue or green unless the ligands also have absorbtion bands in the visible region. They also tend to be paramagnetic with two unpaired electrons. The $[NiCl_4]^{2-}$ ion is a representative tetrahedral complex. For the vast majority of four coordinate nickel (II) complexes, planar geomoetry is preferred. This is a material consequence of the d^8 configuration, since the planar ligand set causes one of the d orbitals (dx^2-y^2, dz^2) to be uniquely high in energy and the eight electrons can occupy the other four d orbitals but leave this strongly non-bonding one vacant. In tetrahedral coordination on the other hand, occupation of antibonding orbitals is unavoidable. Planar complexes of nickel (II) are thus invariably diamagnetic. They are frequently red, yellow or brown. Important examples of square planar four coordinate nickel (II) complexes are the phosphine complexes $Ni(PR_3)_2X_2$(P=alkyl) reported as yellow to brown diamagnetic compounds.

An interesting property of nickel (II) is its ability to alter its confirmation relatively easily.The complex of nickel (II) with substituted ethylenediamines, below was observed to be blue and paramagnetic at times but yellow and diamagnetic at others. This was dependent on many factors such as temperature, identity of anions present, solvent used, exposure to atmospheric water vapour and the diamine used. It is now recognised that the yellow species are square planar complexes and the blue ones are octahedral complexes derived from the square planar complexes by coordination of two additional ligands - solvent molecules, water molecules or anions - above and below the plane of the square planar complex (1a).



Yellow Square Planar



Blue Octahedral eg. X= H_2O

This may be relevant to the current research where it is envisaged intermediates of square planar nickel (II) are possible products and the above stereochemical change may be possible. Another phenomenon to be aware of is the association or clustering of four coordinate complexes or ions to give species in which the nickel becomes five or six coordinate, an example is shown below (1a).

A third phenomenon is square planar:tetrahedral isomerism. For example, in the NiL_2X_2 cases where L-triphenylphosphine, tetrahedral structures are found, whereas the complexes with trialkylphosphines generally give square planar complexes. Perhaps it is not surprising that a number of NiL_2X_2 complexes in which L represents a mixed alkylaryl phosphine exist in solution in an equilibrium distribution between the tetrahedral and square planar forms. In some cases, it is possible to isolate two crystalline forms of the compound, one yellow to red and diamagnetic, the other green or blue with two unpaired electrons. One example is $Ni[C_6H_5CH_2)(C_6H_5)_2P]_2Br_2$ in which both tetrahedral and square planar complexes are found in the same crystalline material (1a).

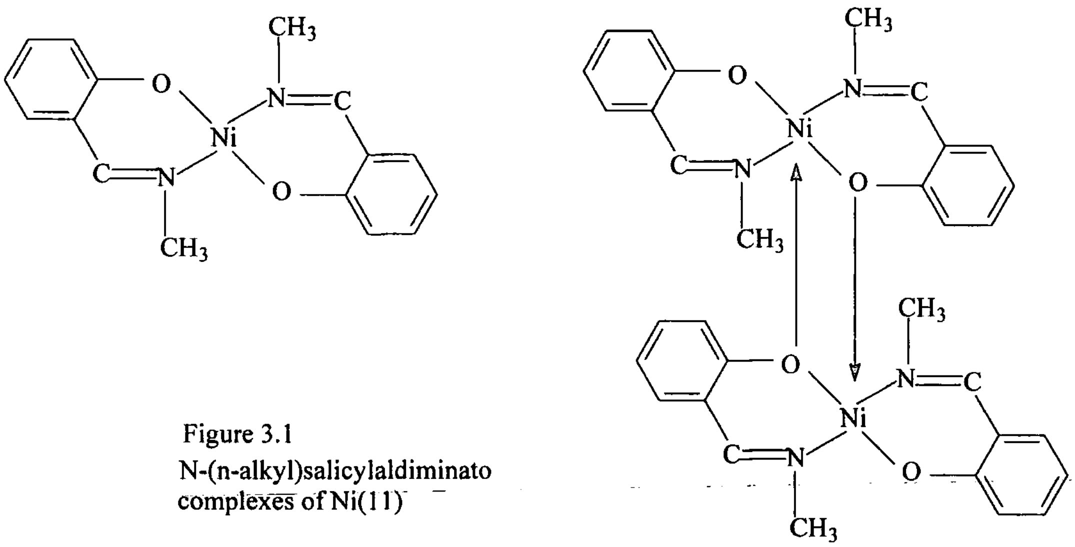


Figure 3.1
N-(n-alkyl)salicylaldiminato
complexes of Ni(11)

Complexes of nickel(O) are quite common and are formed mainly with ligands having strong π acceptor properties. Nickel(O) forms either 3 or 4 coordinate complexes. The 4 coordinate complexes undergo oxidative addition reactions easily to form nickel (II) complexes. We propose to take advantage of the reactivity of nickel (O) species in our current reasearch, utilizing nickel (O) species as starting reactive compounds. We also propose a $L_2Ni(O)$ species as a reactive intermediate in our proposed catalysis. The role of nickel in catalytic cycles and alternating oxidation state is discussed later.

Nickel as a Transition Metal in Homogeneous Catalysis

In addition to cobalt, which is mainly used in hydroformylation reactions, nickel is probably the most frequently used metal in homogeneous transition metal catalysis. There are two main reasons for this: (i) The relatively low price of nickel as compared with the price of other transition metals, (ii) The wide range of reaction possibilities and selectivites demonstrated for nickel. This part of the review comprises (i) historical uses of nickel, (ii) a review of the current industrial uses of nickel in homogeneous catalysis and other processes not yet exploited industrially. Additional material relevant to the use of nickel in homogeneous catalysis can be found in references 9-28

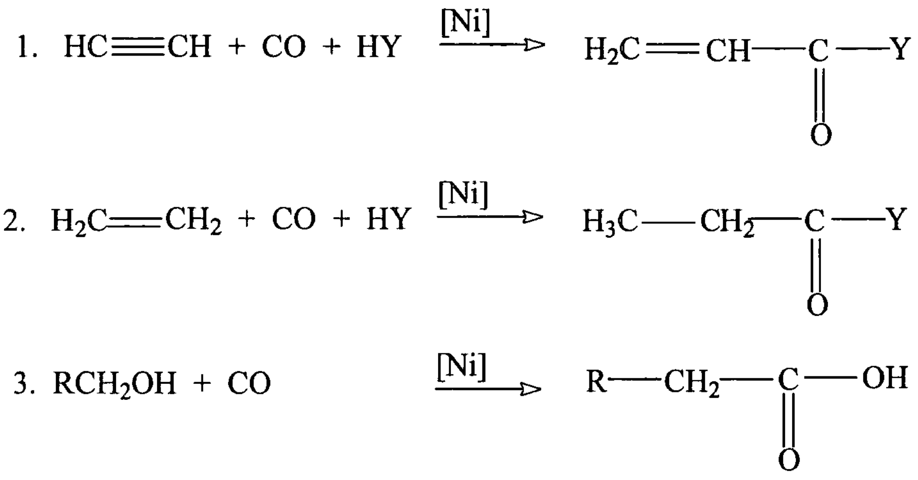
Organonickel chemistry was born with the discovery of nickel tetracarbonyl $Ni(CO)_4$ by Mond, Langer and Quincke in 1890 (2), during studies of corrosion in the ammonia soda process (solvay process). It was found that traces of carbon monoxide in the cabon dioxide used to sweep out the ammonia attacked the nickel valves attached to the reaction vessel. This discovery initiated a vigorous development of organonickel chemistry. Mond immediately recognised the importance of this discovery and, within two years, construction started on a large pilot plant for the production of pure nickel (Mond Nickel Process).

In 1906, Sabatier reported the nickel catalysed hydrogenation of carbon monoxide to methane (1b). This reaction is still used today on an industrial scale to remove carbon monoxide from a stream of hydrogen gas as, for example, in the production of ammonia. The reverse reaction, the cleavage of methane (steam reforming) also proceeds via nickel based catalysts. Sabatiers biggest contribution to chemistry was the recognition of these hydrogenation properties, thus paving the way for further catalysis reactions. One of the oldest hydrogenation catalysts was Raney nickel, first used industrially in 1925 and which subsequently became one of the most important industrial catalysts. Many of the inherent drawbacks of highly dispersed nickel catalysts were overcome by supporting the catalyst on various carriers. Examples of those used are $NiMo/Al_2O_3$ and Ni/AlO_3. These catalysts were used industrially for:-

(i) Hydrogenation of carbon-carbon double bonds primarily in oil conversions but also in fats,
(ii) Hydrogenation of carbonyl groups,
(iii) Hydrogenation of nitrogen containing compounds.

The development of homogeneous nickel catalysis began over half a century ago with the work of Reppe.

During and after the second world war, Reppe's group in Germany was developing a vast array of organic reactions catalysed by soluble organotransition metal compounds. Reppe discovered a series of carbonylation reactions (see equations below) whilst researching the uses for carbon monoxide (1b).



$$1.\ HC\equiv CH + CO + HY \xrightarrow{[Ni]} H_2C=CH-C(=O)-Y$$

$$2.\ H_2C=CH_2 + CO + HY \xrightarrow{[Ni]} H_3C-CH_2-C(=O)-Y$$

$$3.\ RCH_2OH + CO \xrightarrow{[Ni]} R-CH_2-C(=O)-OH$$

$Y = OH, OR, NR_2, RS, O_2CR$

Reaction 1 above represents an important route to acrylic acid used right up until the end of the 1960's. The use of ethene, equation 2, leads to propionic acid, a process employed by BASF. The carbonylation of methanol to give acetic acid developed into a most important process. nickel catalysts were first developed but, industrially, cobalt and rhodium catalysts are now used. The Monsato process using rhodium catalysts is currently the preferred process for acetic acid synthesis.

The variety of potential applications of reactions 1-3 is immense. It can be anticipated that many further uses of carbonylation reactions may evolve in the future.

Perhaps the most impressive reaction discovered by Reppe is the nickel catalysed tetramerization of ethyne to cyclooctatetraene (3). It is a striking example of the capabilities of organometallic chemistry. Its importance lies not in exploitation as an industrial process, but that it has been the subject of many experimental and theoretical investigations. The mechanism of this reaction has still not been conclusively determined.

The development of nickel homogeneous catalysis continued with the work of Wilke. He studied the possibility of using Ziegler catalysts prepared from nickel acetylactonate and $AlEt_2OEt$ for the polymerization of butadiene. A mixture of products was obtained 1,5 Cyclo octadiene (COD) 25%, 4 vinylcyclohexene (VCH) 10% and 1,5,9 Cyclododecatriene (CDT) 65%. Had Wilke only tried the Ziegler system $NiCl_2/Et_2AlCl$ which produces polybutadiene, an interesting area of organonickel chemistry may have been overlooked. Wilke observed that the ratio of COD:CDT:VCH could be altered by the addition of R_3P phosphine ligands. One of Wilke's greatest accomplishments was to have recognised for the first time the route to controlling the distribution of oligomers by ligand variation. This so called ligand tailoring is of critical importance to all scientists working in this area of chemistry. Two noteworthy examples of industrial uses of ligand tailoring are; (i) Shells hydroformylation reaction for converting alkenes into linear alcohols and (ii) Duponts hydrocyanation of butadiene to adiponitrile (see later for explanation).

The diagram Figure 3.2 below shows the range of possibilities discovered by Wilke and coworkers using Butadiene and nickel catalysts (1, 2) to investigate the impact of ligands on product formation and selectivity.

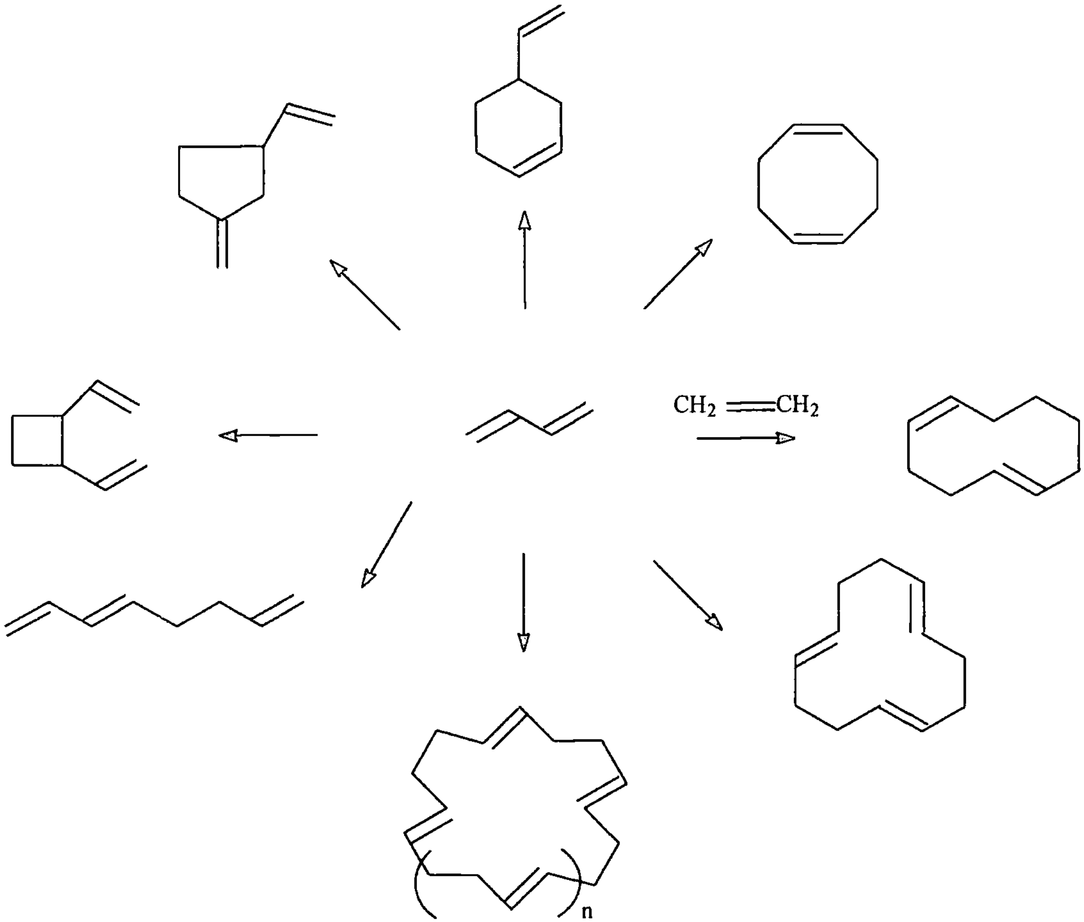
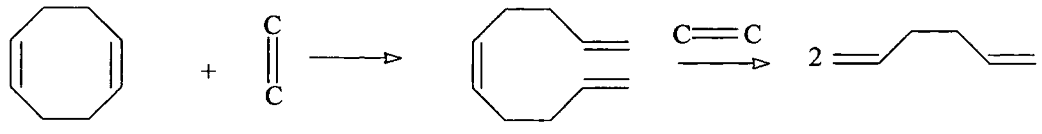
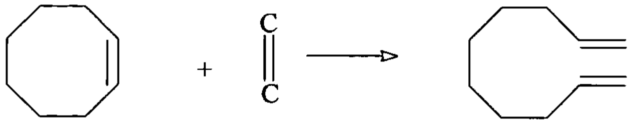


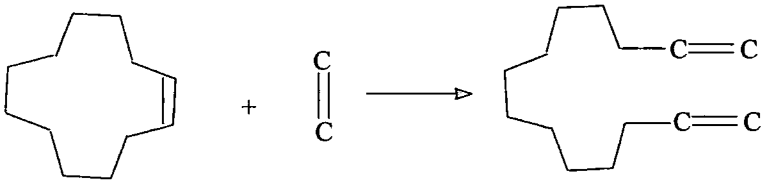
Figure 3.2
Ring Synthesis from Butadiene

Cyclododecatriene is used for the preparation of Nylon 12 as practiced by Huls AG and Dupont (1b). Two commercially valuable products Duponts Quiana and Huls AG's Vestamid are produced.

Shell produces a selection of industrially interesting olefines based on cyclooctadiene and cyclododecatriene by the Feast process. See equations below (5,6):







The large ring systems synthesised by Wilkes reactions of organonickel complexes with dienes have lead to whole new areas of chemistry.

Another impressive example of ligand nickel control was first reported by Bogdanovic and Wilke who drastically influenced the products from the dimerization of propene. Hexenes, 2 methyl-pentenes or 2,3-dimethylbutenes can be produced, depending on the substituent on the phosphorus ligand (see Table 3.1).

R_3P	n-hexenes %	2 methyl-pentenes %	2,3-dimethyl-butenes %
Ph_3P	21.6	73.9	4.5
Me_3P	9.9	80.3	9.8
iPr_2tBuP	0.1	19.0	80.9
$iPrtBu_2P$	1.0	81.5	17.5

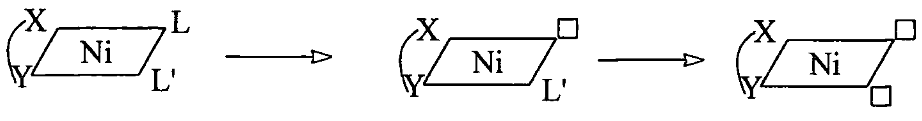
Table 3.1
Control of Oligomerization using R_3P Ligands and Nickel Catalysts

The possibilities for controlling the regioselectivity of carbon-carbon bond formation via nickel phosphine ligand systems are key points to investigate in this research involving the coupling of carbon dioxide and C_3 feedstocks. Using nickel as the transition metal to investigate catalytic coupling opens up this whole area of product selectivity control more so than most other transition metals. This may be simply because more work has been done with nickel based systems than with any other transition metal.

With Wilke's discoveries, a whole new area of chemistry developed based on homogenous catalysis utilizing organonickel catalysts and phosphine ligands. Two examples will be discussed. The two largest applications of homogenous nickel catalysis are Shells Highers Olefines Process (SHOP) and DuPonts hydrocyanation of butadiene to adiponitrile, a Nylon intermediate.

Shell Higher Olefines Process

The Shell higher olefines process is a large-scale industrial process based on homogeneous nickel catalysis discovered by Keim, who was given the task of developing catalysts to convert ethene into value added chemicals such as α-alkenes. The model of Keim shown below (Figure 3.3) perhaps best demonstrates the usefulness and versatility of nickel as a metal in homogeneous catalysis and its ability to interact with a wide variety of ligands in known ways, and demonstrates its usefulness to the transition metal chemist seeking catalysis .



X-Y = Chelate ligand

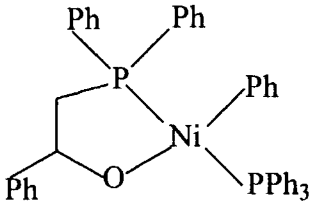
Figure 3.3
Proposed Model for the Formation of Free
Coordination Sites in Nickel-Chelate Systems

Chelates X-Y were chosen for the following reasons (4);

(i) Exploitation of the chelate effect,
(ii) Selection of distinct structures, i.e. chelates favour square planar structures with potentially free coordination sites for formation of an octahedral system,
(iii) Impact on redox properties,
(iv) Ease of reductive elimination. Cis configuration of other ligands.

According to the model, Keim envisaged displacement or exchange of ligands L and L' (Figure 3.3) for ethene and the tailoring of the chelating phosphine to create the electronic and steric environment for linear oligerimization, i.e. migratory insertion, recoordination and β hydride elimination. The course of the investigation of this concept led to the formation of linear α-alkenes of various lengths, which were used in the SHOP process.

The full SHOP technology involves additional stages to the oligomerization of ethene to α alkenes. A typical example using the nickel catalyst illustrated below will be used to illustrate this:



If the above nickel catalyst is dissolved in the toluene and allowed to react with ethene, oligomers are produced which are up to 99% linear, of which about 98% are formed as α-alkenes. The directly marketable α-alkenes produced in the oligerimization part of the SHOP process are separated by distillation. These are the C_{10} - C_{18} linear α olefines. The remaining unmarketable α-alkenes $<C_{10}$ and $>C_{18}$ are isomerized to a mixture of internal alkenes over a heterogeneous catalyst and converted in a third step over a heterogeneous metathesis catalyst into linear alkenes with internal double bonds in the C_{10} - C_{18} range are separated the remainder being returned to step 2 or 3. The C_{10} - C_{18} alkenes are hydroformylated (not part of SHOP) using a cobalt catalyst which simultaneously isomerizes the internal double bonds. The resulting C_{11} - C_{19} primary alcohols are used as plasticizers.

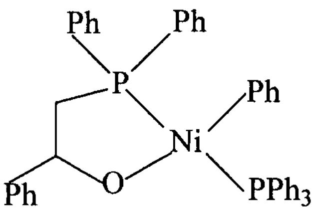
The catalysts used in the ethene oligomerization stage of SHOP have a lot in common with those used in the current research program;

(i) they are nickel based systems;
(ii) they utilise chelating phosphorus containing ligands;
(iii) the ligand/nickel complex is proposed to be square planar;
(iv) interaction with a linear alkene is desirable but oligomerization is undesirable;
(v) the principle of catalysis is by generation of vacant coordination sites .

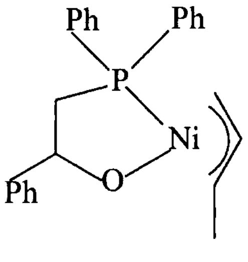
Keim undertook a mechanistic study of the SHOP oligomerization catalyst. Based on the original model, he varied (i) L and L^1 keeping X and Y identical, (ii) the identity of X and Y in an attempt to answer two general questions:-

(i) Do alkenes other than ethene react in these systems and, if so, under what conditions?
(ii) Can control be exercised over the ratio of linear to branched products?

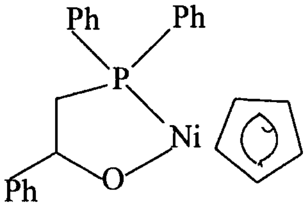
Keim took the three systems shown below labelled A,B and C.



A

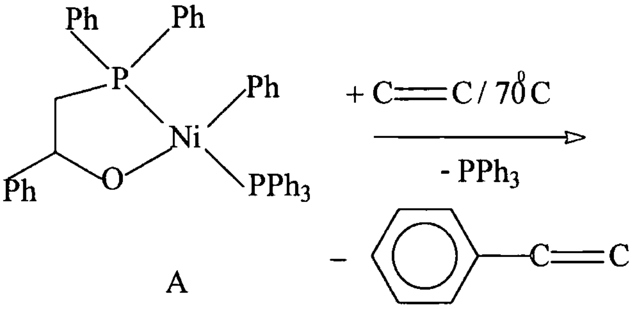


B

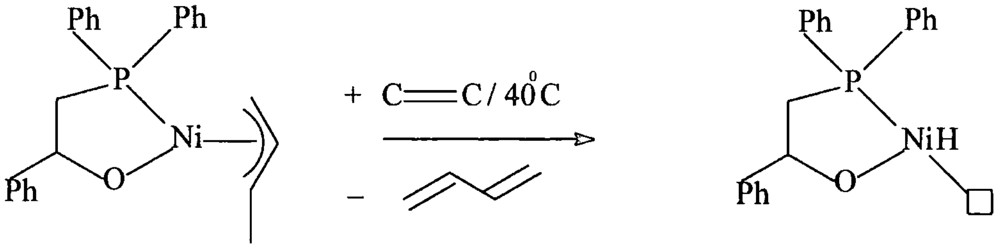


C

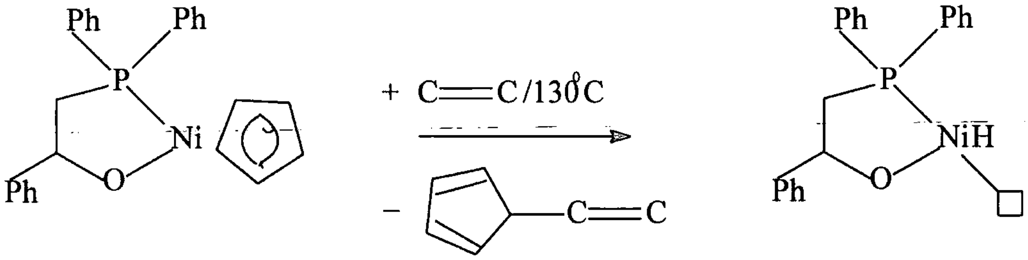
For each system polymerization of ethylene occurred under the following conditions; A - 70°C, B - 40°C, C - 30°C. It was concluded that the temperature was directly related to the conditions under which the active catalytic intermediate nickel hydride formed in each system. This demonstrates the point that starting materials and isolated complexes may only be precursors from which true catalysts are derived (see equations below).



A

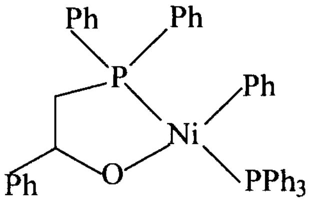


B

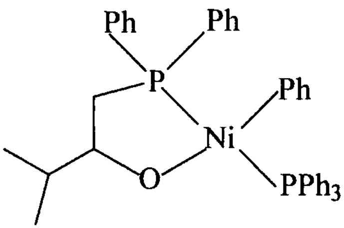


C

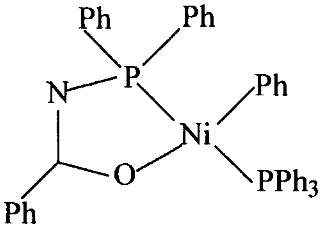
When the complexes A,D and E shown below were studied with propene, the results shown in Table 3.2 were obtained.



A



D



E

	conversion %	n-hexenes %	2 methyl-pentenes %	2,3-dimethyl-butenes %
A	10	29	67	4
D	20	4	92	4
E	35	27	66	7

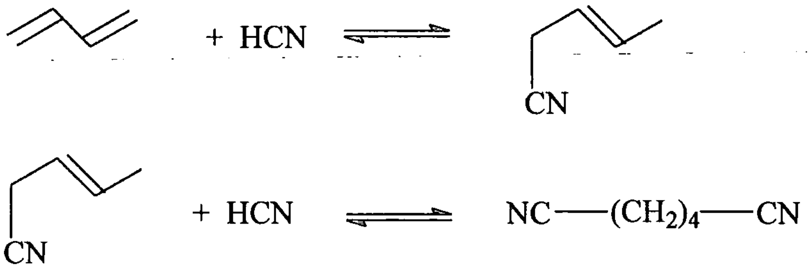
Table 3.2

Products Formed in the Oligomerization of Propene using Nickel Catalysts A,D and E.

It is significant that quite small changes in the nature of the phosphine ligandcan have a marked effect on the selectivity. The P-O chelated complexes have promise as highly selective dimerization catalysts. However in the context of the catalytic coupling of alkenes and CO_2 the electron density requirements at the metal may be quite different in the SHOP process to those required for reaction with CO_2. There are, though, a number of pointers in the ligand tailoring work and general chemistry of nickel complexes which may be of assistance.

Hydrocyanation of Butadiene

The nickel catalysed addition of hydrocyanic acid to mono and di-alkenes is an elegant method for the synthesis of alkyl nitriles. Hydrocyanation of Butadiene was first discovered by Drinkard of DuPont as a route to adiponitrile. The reaction proceeds according to the equations shown below. It is currently used on a large scale by DuPont for production of the nylon intermediate Adiponitrile.



The proposed mechanism shown below in Figure 3.4 involves oxidative addition of HCN to NiL_4 ($L=P(OC_6H_5)_3$), with disassociation of two phosphite ligands to yield complex A.

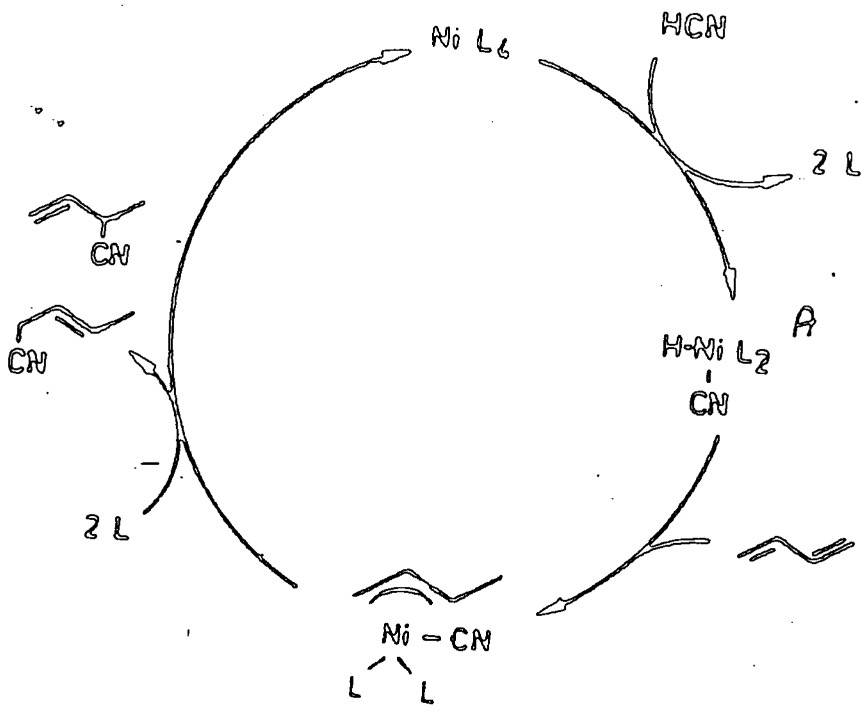


Figure 3.4
Proposed Mechanism of Butadiene Hydrocyanation

Complex A then reacts with butadiene to yield an η^3-allyl nickel cyanide complex from which the products are released through reductive elimination. The reductive elimination gives the straight chain nitrile as the major species. This internal alkene cannot be directly hydrocyanated to give adiponitrile but has to be isomerized first. The species $HNiL_{3+}$ present in reaction mixtures (formed by loss of ligand from NiL_4 followed by protonation) is a very active isomerization catalyst functioning by the hydride mechanism. The internal alkene is therefore isomerized to the terminal alkene which once formed, is rapidly and selectively hydrocyanated to the linear adiponitrile product; all other possible dinitriles are formed at a much slower rate.

The reductive elimination also generates the branched isomer. This can isomerize to the linear isomer by reoxidative addition to the nickel to give back the η^3-allyl nickel cyanide complex.

The features of this catalysis of interest and relevance to the current research program are:-

(i) The active species are square planar liganded systems. An important step at several points in the catalytic cycle is loss of ligand to generate a vacant coordination site at the metal. It is thought that these disassociative steps are controlled by the bulk of the ligand. Using PPh_3 instead of $(PhO)_3P$ results in catalyst death. $(PPh_3)_2Ni(CN)_2$ precipitates and no nickel hydride is formed.

(ii) Ligands strongly π-acidic in character are required to facilitate the reaction chemistry in the cycle. One of the best ligands is tolylphosphite which combines steric bulk(involved in selectivity and rate of ligand disociation) with π-acidic character(gives necessary electronic environment). This highlights the dilemma in looking for systems which will catalyse reactions of carbon dioxide. Activation of carbon dioxide requires electron donating ligands in the metal complex, but migratory insertion/reductive elimination in some systems are favoured by ligands having π-acidic character(able to back accept electrons from the metal). This also highlights the beauty of using nickel based systems for the investigation. Much work has been done on ligand modification of square planar nickel systems and ligand tailoring, whilst not predictive, can be done in a reasoned manner. When looking for a balance of steric and electronic effects to achieve a result, nickel based systems have proven useful.

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CHAPTER FOUR

Oxidative Coupling of Alkenes or Alkynes and Carbon Dioxide

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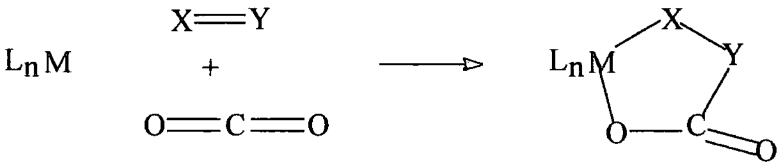
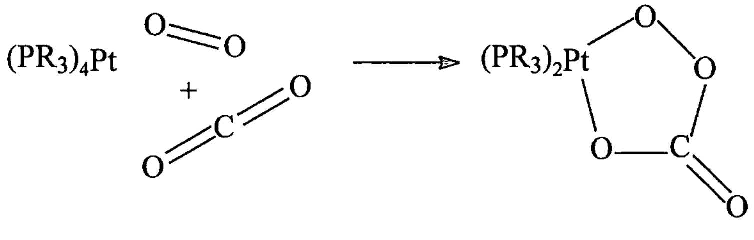
Oxidative Coupling of Alkenes or Alkynes and Carbon Dioxide

Oxidative coupling is a key basic reaction in carbon dioxide chemistry. It leads to products that have been postulated as intermediates in catalytic processes. For the purpose of this review, oxidative coupling will be concerned with the reaction of carbon dioxide or an isoelectronic moiety e.g. phenyl isocyanate with an unsaturated compound, X=Y, at a metal centre, M, to form a metallacycle as illustrated below (24).

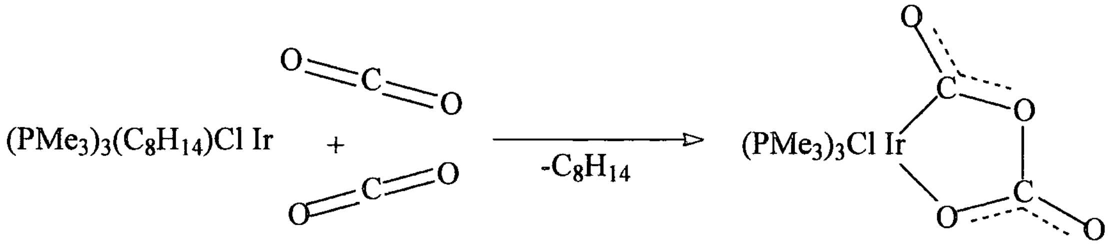


Mechanistically, this reaction can be regarded as a (2π+2π+2π) cycloaddition in which the electron-rich metal and the two unsaturated π compounds make an electron pair available each to form three new σ bonds.

The principle of oxidative coupling has been known for a long time; Wilkinson and his coworkers described the reaction of platinum phosphine complexes with oxygen and carbon dioxide in 1967. They obtained the peroxycyclocarbonate complex illustrated below(24).



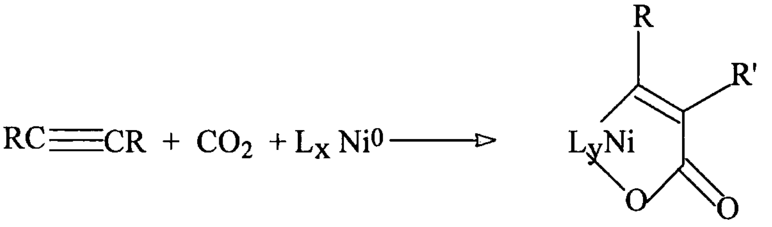
A reaction discussed previously in this review as a head to tail joining of two CO_2 molecules at an electron-rich Iridium centre can also be regarded as an oxidative coupling of the above type (see Figure 2.15). The process is illustrated in the following equation.



Detailed investigations of oxidative coupling with CO2 and related molecules has been in progress since the early '80's. This review section concentrates primarily on the work of H. Hoberg and D. Walther in this area. This body of work is directly analogous in many respects to the topic of current research. Its aims are essentially the same-to research catalytic routes to value-added organic molecules utilizing carbon dioxide as a C_1 feedstock. Additional information can be found in refs 39 - 44.

OXIDATIVE COUPLING OF ALKYNES AND CO_2 (1, 2, 3, 5, 22)

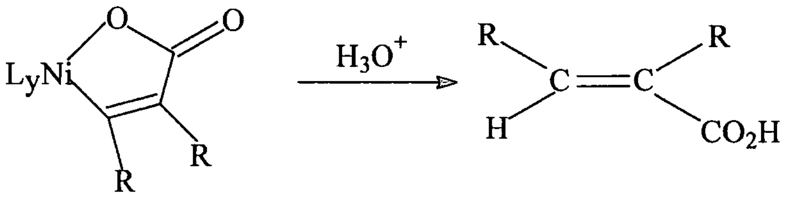
Carbon dioxide and alkynes undergo 1:1 coupling in the presence of Ni(O) complexes to give five membered cyclic nickel complexes. The reaction occurs readily according to the equation below.



R, R' = Alkyl, Aryl

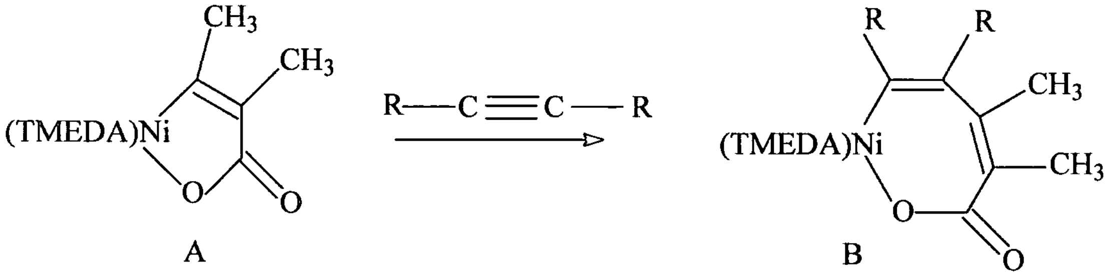
In the absence of the alkyne and where L = TMEDA, disproportionation of CO_2 to $(TMEDA)Ni(CO_3)$ and $Ni(CO)_4$ occurs . In the presence of 2-butyne, disproportionation does not occur, and the oxanickelacyclopentene is formed in 65% yield. Protonolysis of the metallacycle led to 2-methylcrotonic acid. Formation of the ring structure can be monitored by infra red spectroscopy. The conjugated carbonyl in the above type of metallacycle absorbs at $1580cm^{-1}$ -$1650cm^{-1}$.

Another method of showing that oxidative coupling has occured is via acid hydrolysis of reaction products which generates the carboxylic acid according to the following equation .



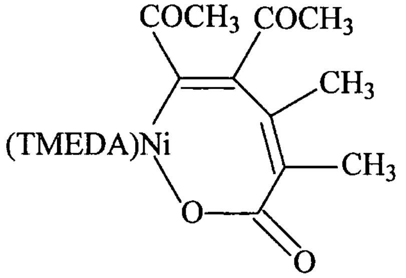
The intermediate metallacycle structure can be inferred from the nature of the hydrolysis products .

The metallacycle produced as a result of oxidative coupling of CO_2 and alkynes , specifically 2-butyne, is a potentially reactive material and can undergo a whole range of insertion reactions with further 2-butyne. Perhaps the most interesting of these is the insertion of another alkyne molecule to give a seven membered metallacyclic ring according to the following equation.



Compound B above is thought to be an intermediate in the nickel catalysed synthesis of 2 Pyrones investigated by Walther (22) and first discovered by Inoue (27).

A crystal structure has been resolved for a type B compound illlustrated below.



Points of interest:

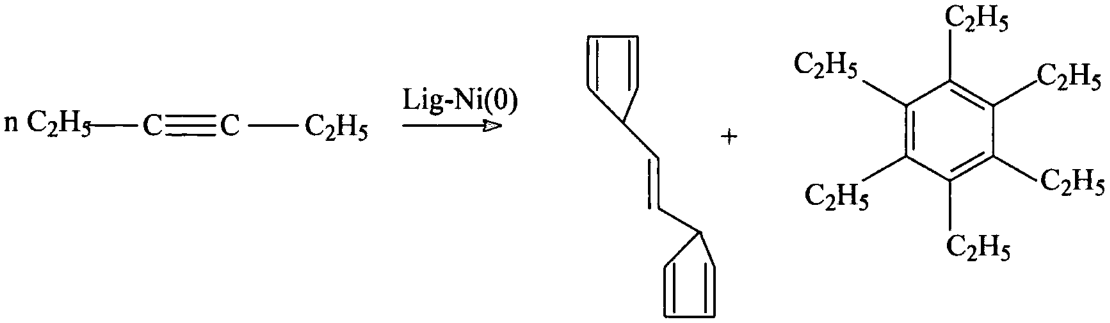
(i) Trans influence: the Ni-N bond trans to carbon is shorter than the Ni-N bond trans to oxygen δ= 0.06Å.
(ii) The plane O_1 - Ni - C is bent 5° out of the TMEDA - Ni plane.
(iii) Square planar (distorted) nickel II.

The body of literature concerning alkyne/CO_2 oxidative coupling is quite small. Only a limited number of alkynes have been looked at and only one crystal structure of a molecule resulting from such a reaction exists. This itself is not a 1:1 coupling product (alkyne:CO_2) but a 2:1 coupling product. The oxidative coupling proceeds relatively easily at nickel(O) centres of high electron density. Ligands which have been shown to facilitate this reaction as well as TMEDA are 2,2'-bipyridine, 1,2-dicyclohexylphosphinoethane and Tricyclohexylphosphine. D. Walther states (26) that basic monodentate phosphines satisfy especially well the precondition of producing high electron density at nickel(O) centres.

The side reactions which can occur are (i) oligomerization and/or cyclotrimerization of the acetylene at the metal centre with no CO_2 coupling, (ii) reductive disproportionation of CO_2 according to the equation below.

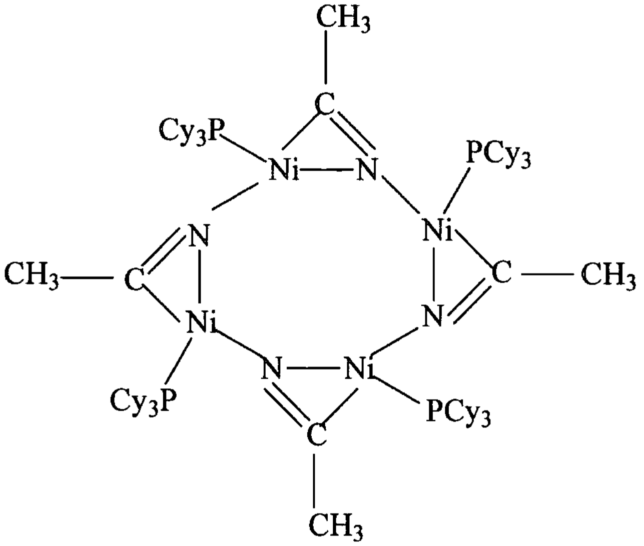
$$5[Ni^0] + 8CO_2 \xrightarrow{\text{TMEDA}} 4(TMEDA)Ni(CO_3) + Ni(CO)_4$$

Reductive disproportionation is inhibited by adding CO_2 to the metal ligand complex in the presence of the alkyne (3), and suggests that coordination of the alkyne is the first step in the oxidative coupling mechanism. Oligomerization is also inhibited by the low temperatures at which the reaction is performed. The nickel(O) complex is cooled to -60°C before the alkyne is added. Carbon dioxide is then introduced for 24 hours at -60°C. The reaction is then allowed to warm to room temperature (1-3). Even at low temperatures, cyclotrimerization and oligomerization occur to a significant degree. With acetylene (26), polyacetylene is the major product of reaction. Using hexyne and CO_2, high yields(22) of the following products form.



The cooligomerization of alkynes with CO_2 is especially subject to solvent effects (26). D. Walther reports (26) cooligomerization between hexyne and CO_2 proceeding selectively particularily when acetonitrile is used as a solvent. This seems especially true in the catalysis to 2 pyrones where turnover numbers of 52 have been achieved in THF/Acetonitrile systems.

The effect of acetonitrile in these systems has been attributed to the following three factors (6); (i) as a polar solvent, acetonitrile favours charge controlled reactions such as 1:1 coupling between CO_2 and unsaturated substrates, (ii) acetonitrile can activate CO_2 by forming an intermediate $CH_3\text{-}CN^+\text{-}COO^-$ compound, (iii) acetonitrile can have direct control at the metal centre by acting as a ligand and coordinatively interacting. This third factor seems to be most significant. Acetonitrile coordination at the nickel(O) centre has been demonstrated (26)by isolation of the tetranuclear complex illustrated below.

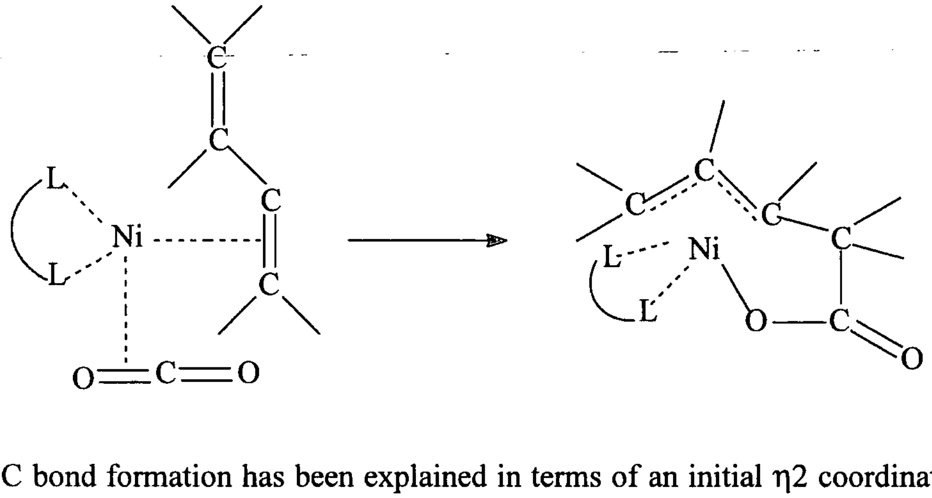


The acetonitrile is bonded like an alkyne across the triple bond. The lone pair on the nitrogen enters into a Lewis base interaction with a second nickel atom.

This reaction suggests acetonitrile is acting as a ligand. The above type complexes possibly form as intermediates and react with excess alkyne so that selective cooligomerization can then occur.

ALLENES/DIENES + CO_2 OXIDATIVE COUPLING:

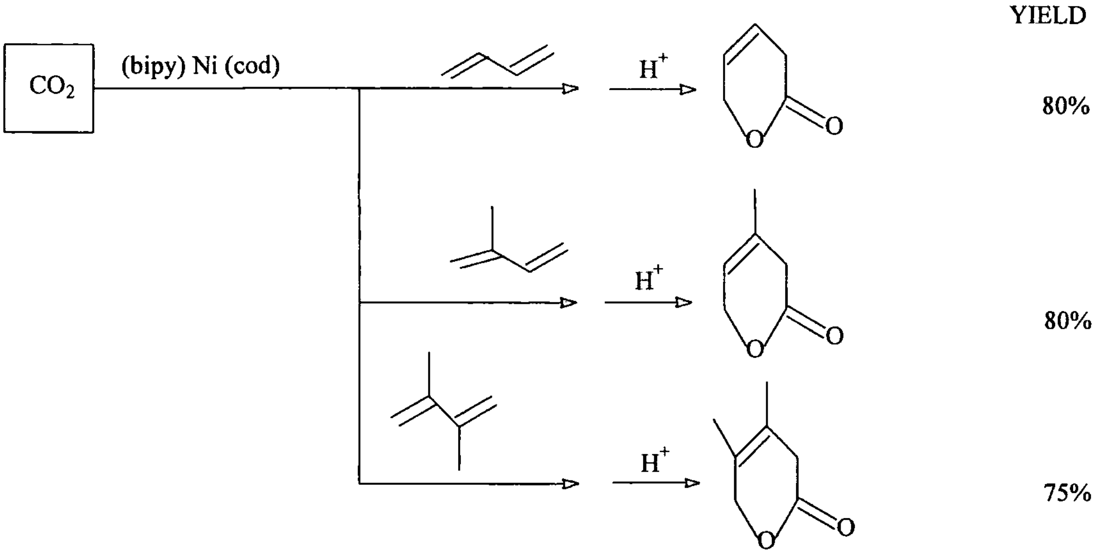
Conjugated dienes also react with carbon dioxide at nickel(O) complexes. In contrast to the five membered metallacycle described with alkynes, fragments which coordinate to the nickel atom through a η3 allyl and carboxylate moiety are formed according to the following equation.



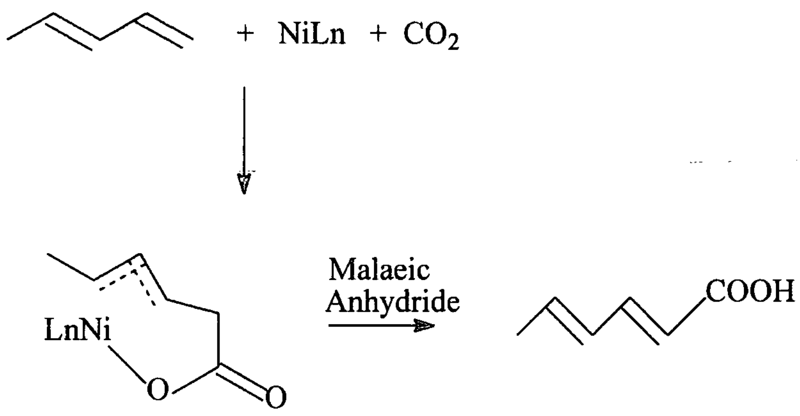
The C-C bond formation has been explained in terms of an initial η2 coordination of the 1,3 diene. With the ligand tetramethylethylenediamine and 2,3-dimethylbutadiene, a crystaline complex having the formula (TMEDA)Niη^3-$CH_2C(CH_3)C(CH_3)CH_2COO$ is obtained. A crystal structure analysis showed that the monodentate carboxylate group, the allyl system and the nitrogen atom of the chelating ligand coordinate to the nickel in a plane, but the second nitrogen atom interacts only weakly with the metal. This is a bond-weakening trans influence.

Hydrolysis of the allyl carboxylate complexes, with dilute mineral acids, usually leads to 3 -pentenoic acid. Other interesting reactions of 1,3 dienes with CO_2 illustrated below are:-

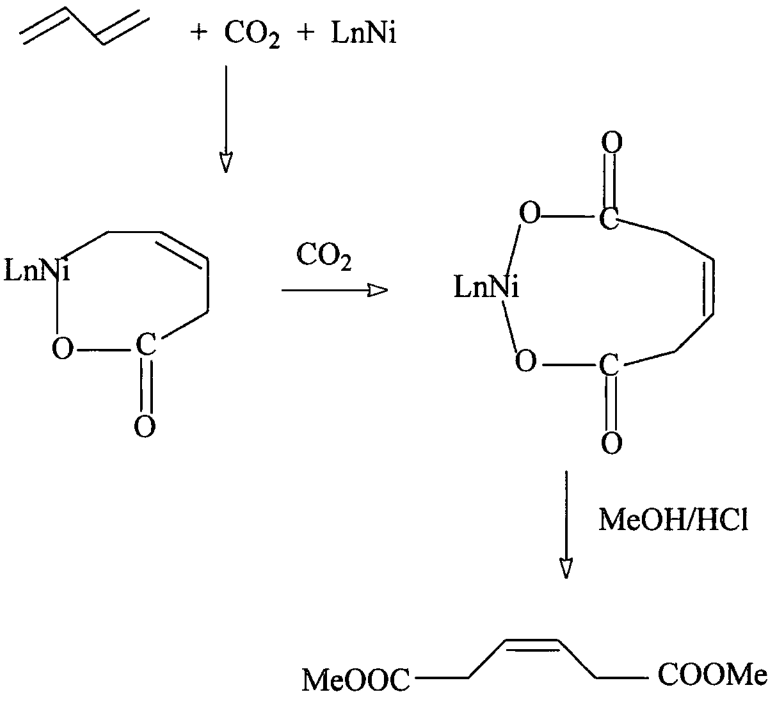
(i) Synthesis of 3-unsaturated dihydropyrones (scheme 1).
(ii) Synthesis of sorbic acid (scheme 2).
(iii) Formation of dicarboxylate complexes (scheme 3).



Scheme 1

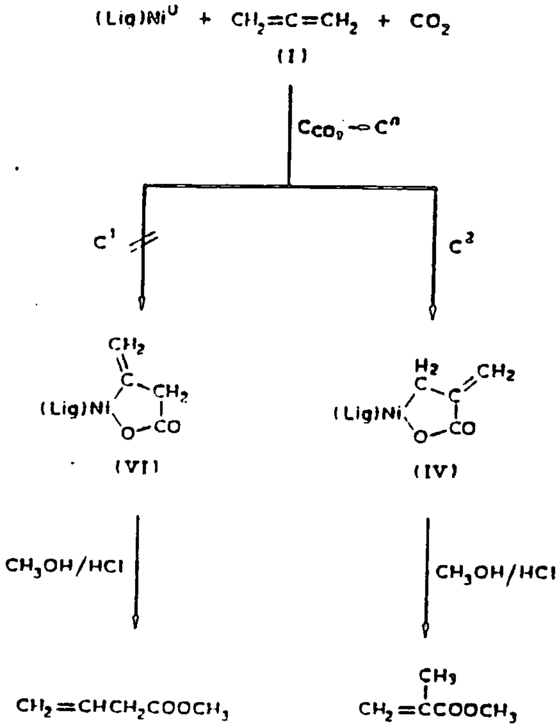


Scheme 2



Scheme 3

Besides conjugated dienes, 1,2 dienes are also reported to react with carbon dioxide in the presence of nickel complexes, yielding nickel metallacycles which can be decomposed to carboxylic acids. The reaction of allene with CO_2 has been investigated by Hoberg (5, 6, 12, 15). Allene, for example, reacts regioselectively with CO_2 to form a 5 membered ring with the methylene group α to the carbonyl group as shown below. Hydrolysis with HCl/MeOH yields only methyl methacrylate.

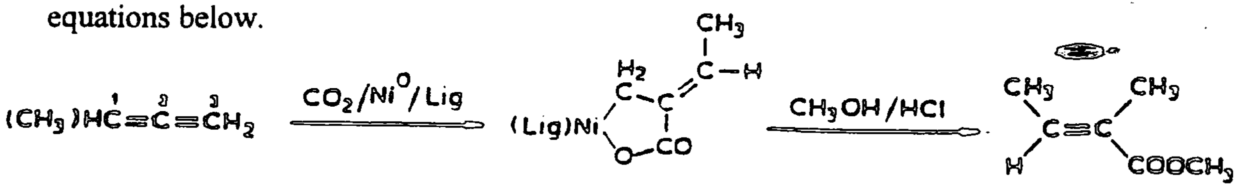


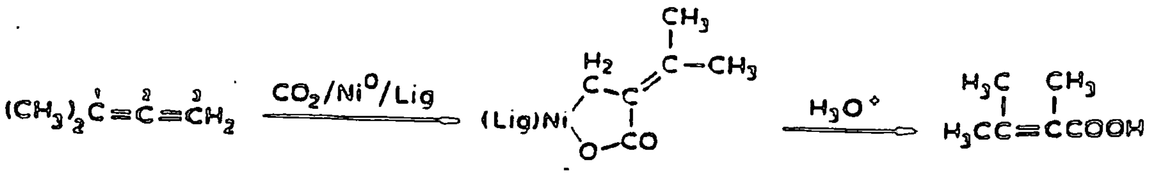
Two different regioselective couplings are conceivable and are illustrated in the above diagram:

Type (i) Coupling between the carbon atom of CO_2 and the C1 carbon atom of the allene.

Type (ii) Coupling between the carbon atom of CO_2 and the C2 carbon atom of allene.

No evidence has been reported for the type (i) coupling in this system. It has been shown (6) that using the ligands DCPE and Bipy only one ester, the methacrylic acid methyl ester, is formed. This result makes it clear that the oxidative coupling of allene and CO_2 is exclusively of type (ii). This is not only true for allene but is also true for substituted 1,2, dienes such as methylallene and 1,1 dimethylallene, reported to undergo oxidative coupling with CO_2 in this selective manner as shown in the equations below.





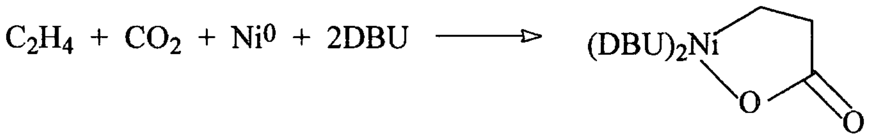
The experimental conditions and ligands used for oxidatively coupling allenes/dienes and CO_2 are virtually identical to those used for the coupling of alkynes and CO_2 discussed earlier.

MONOALKENES + CO_2 OXIDATIVE COUPLING

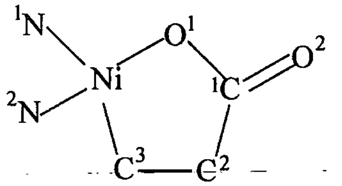
The reaction between monoalkenes and carbon dioxide will be discussed according to the nature of the alkene, to try and understand the requirements of the reaction and discuss the specific features of the alkene.

a) Coupling to ethene and other symmetrically disubstituted alkenes(5, 11, 13).

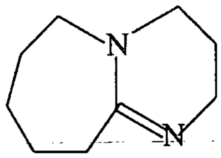
Diazabicyclo [5.4.0] undec-7-ene (DBU) has been used as the ligand in 70% yield in the oxidative coupling reaction between CO_2 and ethylene according to the following equation.



The metallacycle resulting from 1:1 coupling (13) has been subjected to an x-ray structure analysis, and shown to have the features shown in A below. The complex is formally a 16-electron with square-planar coordination of the nickel atom, two nitrogen atoms of the two DBU ligands occupying neighbouring coordination positions and the carboxylate moiety bound to the metal through both a Ni-O bond and a relatively short Ni-C bond .



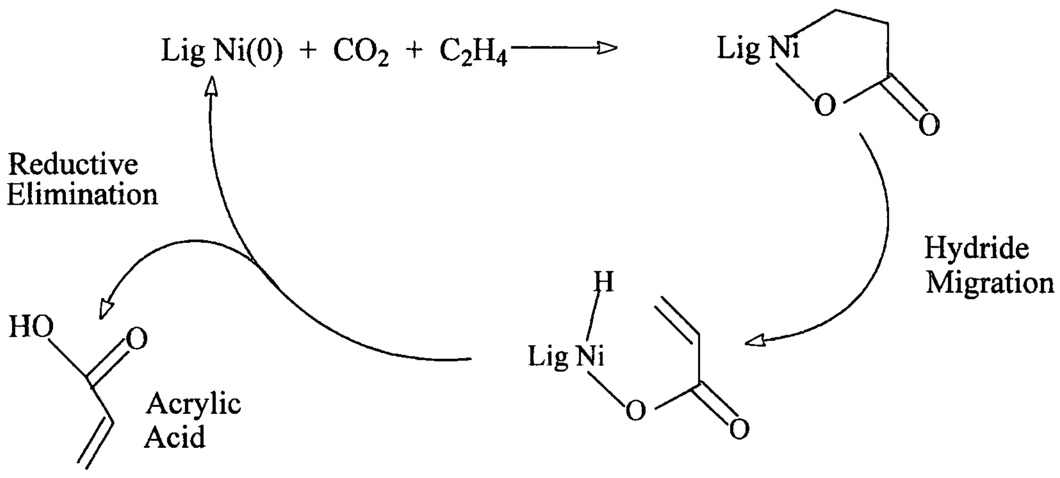
A



DBU

A strong trans influence of the nickel-carbon bond is revealed by the large $Ni-N^1$ distance (2.01Å) relative to the $Ni-N^2$ distance (1.91Å).

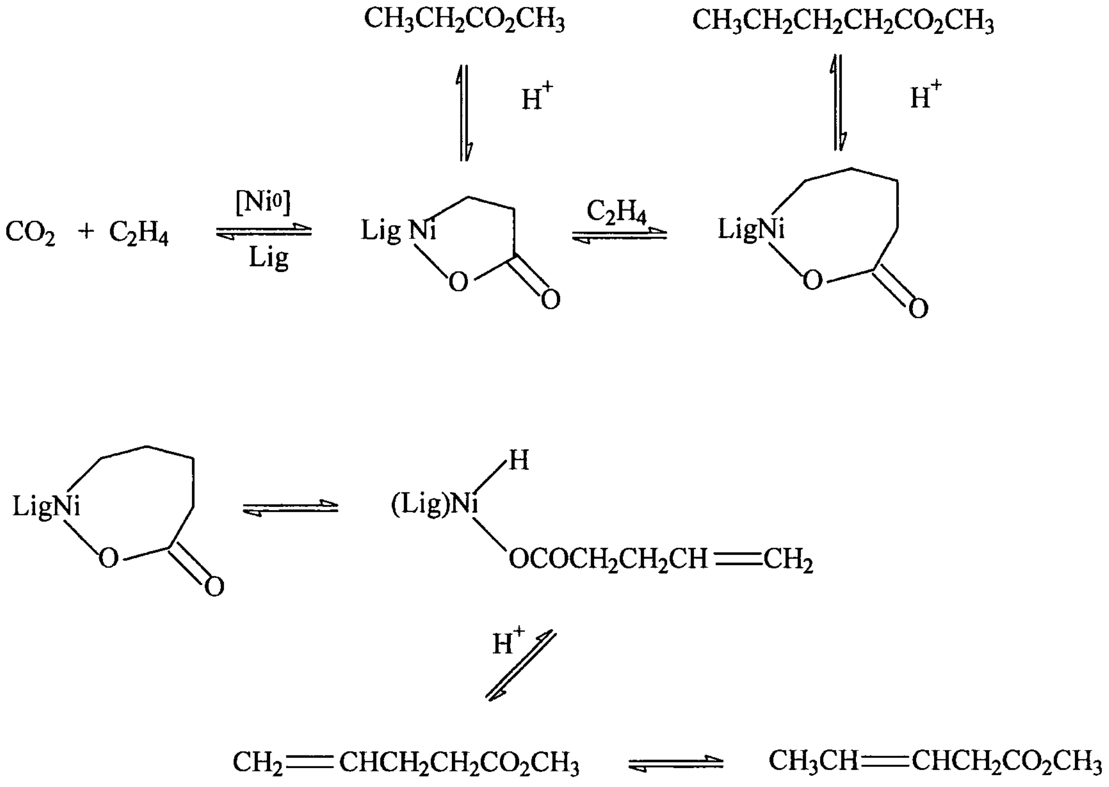
The metallacyclic ring resulting from oxidative coupling of ethylene and CO_2 is almost planar with the $Ni(DBU)_2$ unit. The torsion angle $O^1-C^1-C^2-C^3$ is 2.8°. It is thought that this planarity prevents non-bonding interactions between the nickel atom and the hydrogen atoms at C_3 and C_2. The Ni---H distances are reported as 3.6Å and 2.4Å respectively. Non-bonding interactions of this type favour hydride transfer to the metal, a proposed step in the catalytic coupling of alkenes and CO_2. Taking ethene as an example, the suggested cycle is as shown below.



The evidence provided by the crystal structure (ligand = DBU) is that the first step in this proposed catalysis above is sterically inhibited.

In a continuation of this research the reaction of ethene and CO_2 under different reaction conditions was studied. When ethene and CO_2 (1:1) react with a mixture of DBU and $Ni(COD)_2$ (3:1) in THF at 20° in a steel autoclave, the main product after esterification (CH_3OH/HCl) is reported to be methylpropanoate (55%) together with small quantities of methylesters of n-pentenoic acid (3%) and n-pentanoic acid (0.6%) (yields relative to $Ni(COD)_2$). If the partial pressure of ethene is doubled and the temperature raised to 65°C, the following product spectrum of methylesters is reported: Proprionic acid (4%), n-pentanoic acid (5%), 4-pentenoic acid (71%) and 3-pentenoic acid (16%).

Fomation of the latter three compounds can be explained according to the scheme shown below. The nickel containing five membered ring formed by 1:1 coupling reacts at the Ni-C α-bond with further ethene to form a seven membered ring by insertion. The saturated carboxylic acid ester (n-pentanoic acid methylester) is formed by direct hydrolysis/esterification of this material. The unsaturated compounds are postulated to be produced by β hydrogen elimination via a nickel hydrido intermediate. The β hydrogen migration, not possible in the five membered ring, is postulated to occur in the seven membered ring.
Hydrolysis of this intermediate gives the ester of 4-pentenoic acid . The 3-pentenoic acid derivative can form by isomerisation of the 4-pentenoic acid ester as shown in the equation below.



Several questions arise from this work.

(i) Can the five membered metallacycle be forced thermally to generate unsaturated acids ?

(ii) What precisely are the dimensional differences between the five membered metallacycle and the seven membered metallacycle that β hydrogen can migrate to the metal centre in one and not in the other? By knowing this, can we design ligands to mimic these steric requirements in five membered metallacycles? Are other electronic factors more important?

(iii) Can the intermediate nickel hydride be isolated or at least detected to add to the evidence of it being formed as an intermediate?

These questions will be addressed in the later chapters.

b) Coupling to monosubstituted alkenes .

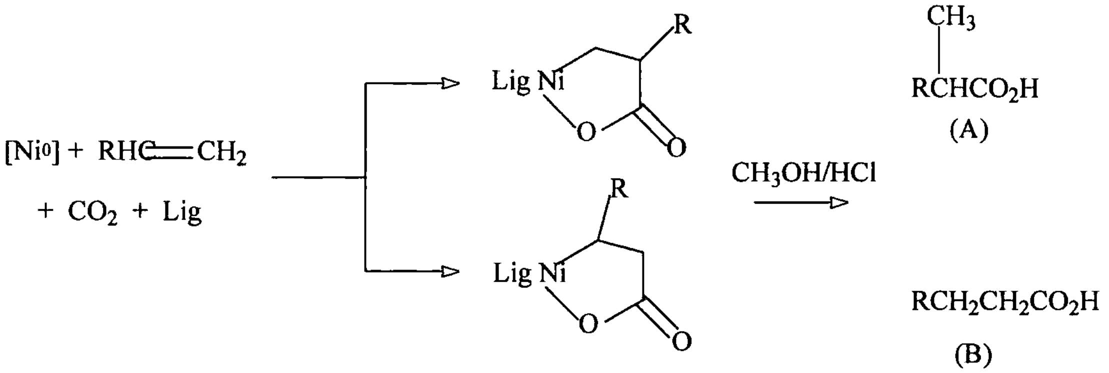
Compared with ethene or activated disubstituted alkenes, monosubstituted alkenes display weaker transition metal complexing ability. Tolman et al (10 nickel section) measured equilibrium constants for the formation of $(\text{olefin})\text{Ni}[\text{P(O-n-tolyl)}_3]_2$ complexes.

According to the equation

$$\text{NiL}_3 + \text{olefin} \xrightarrow{k_1} (\text{olefin})\text{NiL}_2 + \text{L} \qquad k_1 = \frac{[(\text{olefin})\text{NiL}_2]\,[\text{L}]}{[\text{NiL}_3]\,[\text{olefin}]}$$

For ethylene, k_1 is reported as 2.5×10^2. The values for propene and 1-butene are much lower, being 5.3×10^{-1} and 5.2×10^{-1} respectively.

The oxidative coupling of CO_2 and monosubstituted alkenes also reintroduces the possibility of regioisomers. With CO_2 and Ni(0), monosubstituted alkenes should, in principle, yield two isomeric coupling products as shown below.



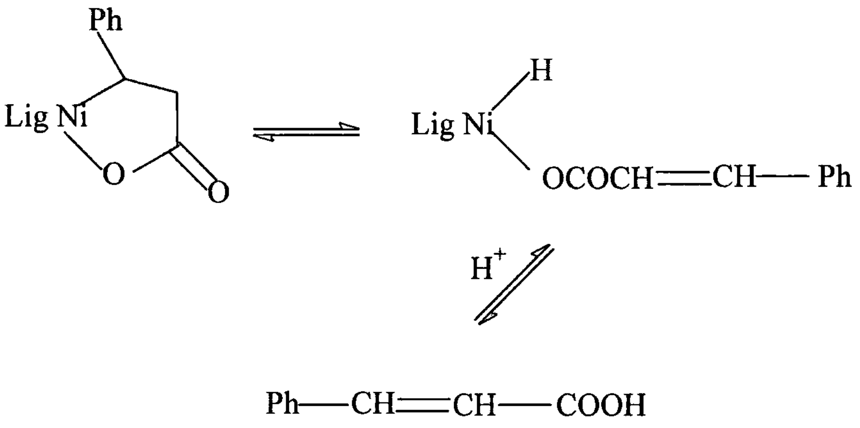
Hoberg has reported that (5) from hex-1-ene ($R=C_4H_9$) in toluene at 20°C, A and B are formed in the mole ratio 4:1, A:B. If the reaction is performed at 60°C, the ratio A:B rises to 25:1. Surprisingly, this isomer ratio is also obtained if the mixture of complexes obtained at 20°C (A/B = 4/1) is subsequently heated to 60°C in toluene (with addition of hex-1-ene and CO_2, over 40hrs). An analagous dependence of the A/B isomer ratio on temperature is observed with propene.

The effect of temperature on the regioselectivity of the C-C bond formation can be explained by the reversibility of the C-C coupling step. This leads to the preferred formation of the thermothermodynamically more stable isomer A rather than B (stability $Ni\text{-}C_{prim} > Ni\text{-}C_{sec}$) (5).

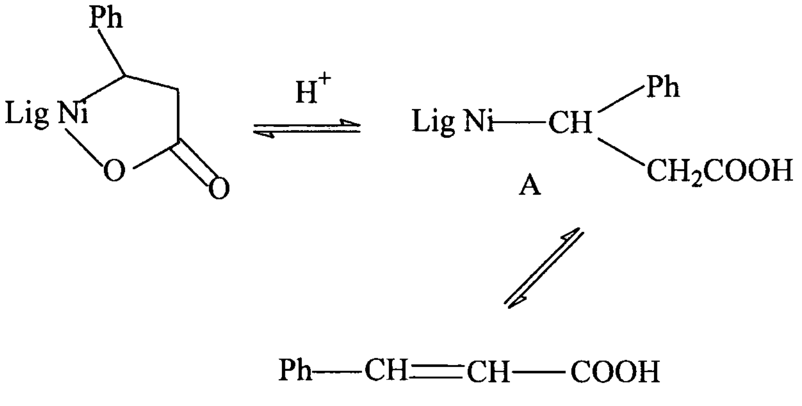
It has been found that the regioselectivity of the C-C bond formation between monosubstituted alkenes and CO_2 can be varied by changing the ligands. Using 2-diethylaminoethyl dicyclohexylphosphine as a ligand in the above oxidative coupling of hex-1-ene and CO_2, the product ratio A:B is 1:3. Subsequent heating of the mixture to 60°c produces no change in the isomer distribution.

In this example, the C-C bond formation is no longer reversible. It has been suggested the complex is paramagnetic where as the other examples were of diamagnetic complexes (5). It must be concluded therefore that the complexes have different geometries. The absence of crystal structures precludes any greater discussion of the differences.

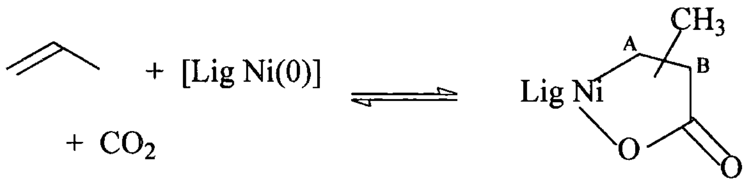
Styrene undergoes a 1:1 oxidative coupling reaction with CO_2 and $Ni(cod)_2$/DBU) to give two oxanickellacyclopentanones (regioisomers A and B 14:1 60°C). Depending on the termperature, the formation of the unsaturated cinnamic acid is observed in 70% yield (10). Production of cinnamic acid (see equation below) is proposed to be initiated by a β-hydrogen migration to the metal generating an intermediate nickel hydride which, on hydrolysis, liberates the unsaturated acid. This interaction of the β Hydrogen with the metal orbitals was proposed as not possible from the crystal structure analysis of the ethylene/CO_2 oxidative coupling metallacycle where DBU was used as a ligand.

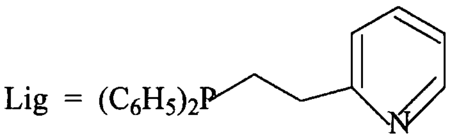


Unsaturated acids were only formed where 2:1 coupling ethylene:CO_2 occurred. It would appear that conformational changes in the metallacycle ring caused by substituents or by increase in ring size might allow interaction of the β hydrogen with unoccupied nickel d orbitals. The crystal structures of the styrene metallacycle and the ethylene:CO_2, 2:1 metallocycle have not been published. Also, spectroscopic evidence for the proposed Ni-H does not exist. The mechanism of production of unsaturated acids from CO_2 and alkenes at liganded Ni(O) is poorly understood. An alternative explanation for the formation of unsaturated acids involves protonation of the nickel bound oxygen generating the intermediate A, shown for the five membered metallacycle in the diagram below. Free rotation about the nickel-carbon bond should then be possible bringing the β-hydrogen close to the metal to enable the favourable orbital overlap for β-elimination, generating unsaturated carboxylic acids and forming a nickel hydride. The increased yield where 7-membered rings are formed may be due to the known decreased stability of 7-membered rings where the oxygen might be expected to detatch more easily.

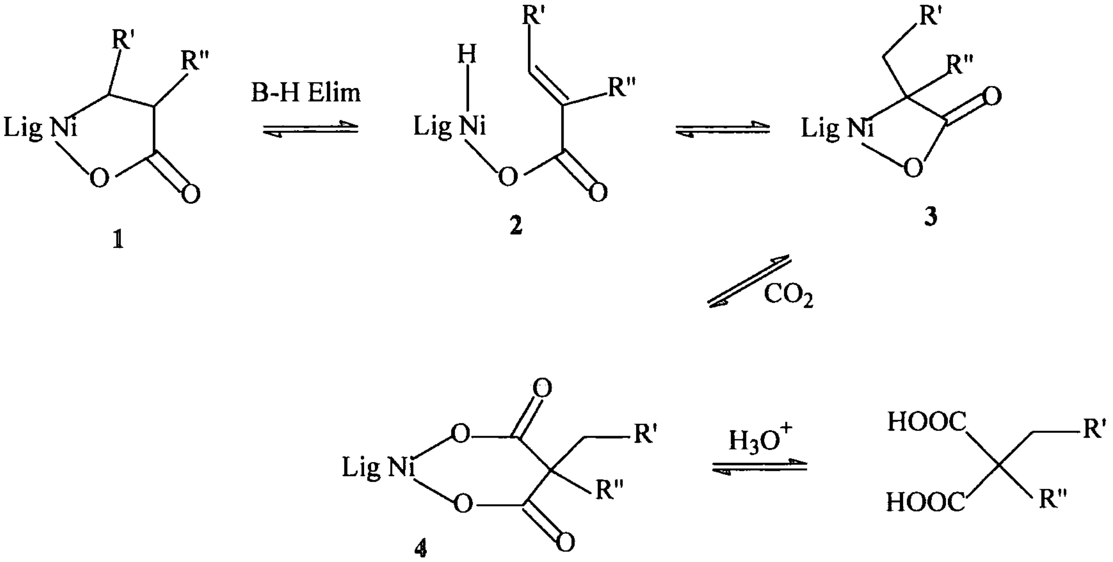


Later work with the bidentate chelating agent (cyclo-$C_6H_{11})_2PCH_2CH_2$-2-pyridine (19) provides more indirect evidence that β hydrogen migration is taking place. Propene and CO_2 can be oxidatively coupled according to the equation shown below.





A mixture of the two expected regioisomers is obtained. If CO_2 (10BAR) is reacted with the mixture of isomers in the presence of $BeCl_2$, a Lewis acid (1:1 Ni:Be) and THF/Pyridine (1:1) at 70°C for 24 hours, protonolysis gives rise to 50% dimethyl malonic acid and 15% ethyl malonic acid. The proposed mechanism for the formation of these acids is shown below .

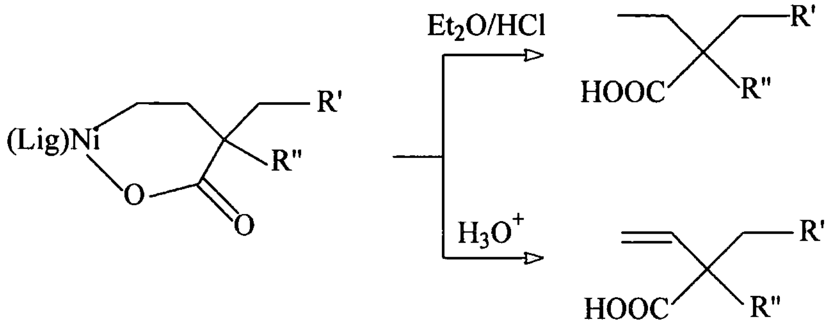


R' =H, R'' =CH_3 = Dimethyl Malonic Acid

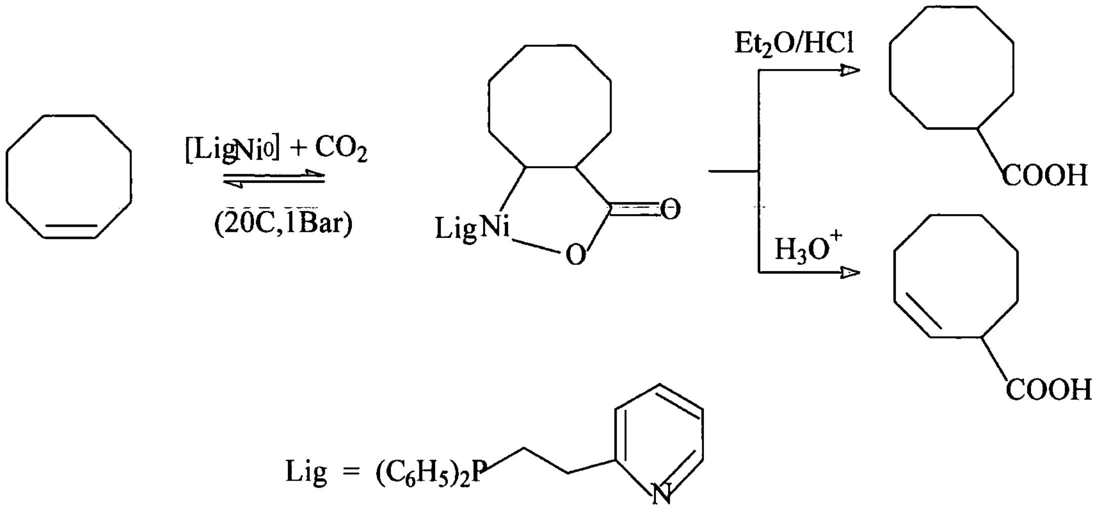
R' =CH_3 R'' =H = Ethyl Malonic Acid

It is thought that $BeCl_2$ may initiate β-hydrogen migration through possible interaction with the pyridyl Nitrogen of the ligand or the carboxylate group. A 14 electron intermediate is postulated. Readdition of the Ni-H intermediate can occur at either end of the generated double bond giving complexes 1 or 3. It is proposed that increased ring strain in 3, and the additional α-carbon substituent bring about increased reactivity. Insertion of CO_2 into the Ni-C_{sec} bond gives 4, which on protonolysis yields the found products. The increased reactivity of 3 drives the reaction equilibrium in the direction of 4.

The above argument is however based on indirect evidence derived from the structure of hydrolysis products. No direct spectroscopic evidence for the proposed nickel hydride intermediate exists and care is needed in the assignment of the exact mechanism. An observation by Hoberg et al (19, 20, 17) that the agent of protonolysis can effect the product spectrum, is relevant here. In the two equations below, protonolysis with Et_2O/HCl yields only the saturated carboxylic acid. On the other hand, if the carboxylic acids are liberated by aqueous mineral acid, then it is the unsaturated carboxylic acids which are produced .



$R' = H,\ R'' = CH_3$



It should be noted that this phenomenon has only been observed with the P-N chelate ligand where a 14-electron intemediate may be possible (due to the pyridine nitrogen flipping on and off the metal.) The nickel hydride intermediate may be favoured in the aqueous mineral acid protonolysis due to an interaction between the pyridine nitrogen and H_3O^+, favouring the 14-electron intermediate and therefore creating a vacant coordination site. In the case of the cyclooctene hydrolysis, two β-hydrogen atoms are present and it seems, from the product spectrum after protonolysis, that the β-hydrogen in the cyclooctene ring migrates to the metal centre and the β-hydrogen α to the carbonyl does not.

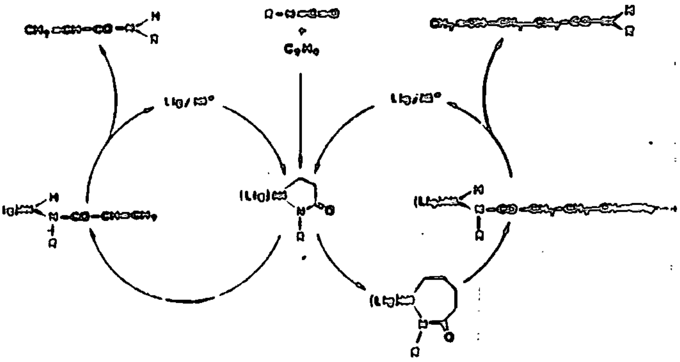
In conclusion, no known catalysis exists to produce unsaturated carboxylic acids from a 1:1 coupling of alkene and carbon dioxide. Using different ligands and alkenes, some steps in a proposed catalysis have been demonstrated, but no catalysis has been shown.

PHENYL ISOCYANATE AS A CO_2 ANALOGUE

As can be seen from the previous section, a large number of carboxylic acids can be prepared starting from carbon dioxide with the aid of nickel complexes by means of oxidative coupling, but only at present in stoichiometric reactions. If phenyl isocyanate is used, however, a molecule with a bonding structure closely related to that of carbon dioxide, a catalytic reaction with ethene does occurs in the presence of Ni(0) complexes (9). For example when a mixture of phenyl isocyanate, bis-1,5-(cyclooctadiene)nickel(0) and triphenyl phosphine is treated with ethene under pressure (3BAR) at -50°C and then heated for two days at 60°C, acrylanilide is obtained, after acid work up, in about 180% yield with respect to Ni(0). This corresponds to 1.8 catalytic cycles.

If, instead, the reaction is carried out with the basic ligand tri-n-propylphosphine and the ethene pressure is raised to 25BAR, n-pentenoic anilides are formed in yields of up to770%, corresponding to 7.7 catalytic cycles. The formation of the anilides can be explained by a common five-membered intermediate labelled A in the diagram below in which initial C-C coupling between the isocyanate and ethene is assumed. If triphenylphosphine is used as the ligand, a rapid elimination of acrylanilide occurs. In the presence of tri-n-propylphosphine, however, the insertion of a second ethene molecule into the Ni-C bond predominates and a seven membered nickel metallacycle is formed, the precursor of the isomeric pentenoic acid anilides.

Although the number of catalytic cycles is low. a noteworthy first step has been taken in the transformation of stoichometric oxidative coupling reactions into catalytic reactions.



Several important points follow from this work: Firstly, isocyanates are much more reactive than carbon dioxide. The requirement for electron density at the metal centre is less for the bonding/coordination and subsequent oxidative coupling of phenyl isocyanate than it is for carbon dioxide, hence the ligands triphenylphosphine and tri-n-propylphosphine can be used. Oxidative coupling of ethene and carbon dioxide is not possible using these ligands. They are not sufficiently basic to make the metal electron-rich to react with the electrophillic carbon of CO_2. Secondly, the intermediates, both isolated and postulated, formed from isocyanates and alkenes, are similar to those formed and suggested in the oxidative coupling reactions of alkenes and CO_2 at liganded Ni(0). In the five membered metallacycle A, β hydride migration is postulated. This process was postulated as not possible from the crystal structure analysis of the oxidative coupling product of ethene and CO_2 at DBU liganded Ni(0). Also, reductive elimination is occurring in these systems, ie. delivery of the hydride to the nitrogen atom of the phenyl isocyanate and regeneration of Ni(0) which can re-enter the catalytic cycle. It is possible that the presence of nitrogen of the cyanate in the metallacycle instead of oxygen from the CO_2 systems favours the reductive elimination process.

Hoberg et al produced a framework for catalytic reactions of alkenes with isocyanates (14). The following requirements are necessary for catalysis to occur:

(i) The presence of monodentate ligands of the type R_3P, where R=alkyl, aryl or alkoxy. Chelating agents which impose rigidity on the system are less suitable. This is related to the inability of chelating ligands to coordinate reversibly and form coordinatively unsaturated intermediates which may be necessary for β-hydride migration to occur.

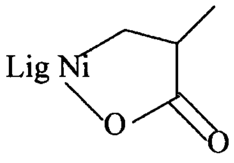
(ii) The nickel/ligand molar ratios should not exceed 1:2. This ensures that any Ni(0) regenerated by reductive elimination can react with further alkene and isocyanate and is not blocked (poisoned) by forming NiL_3 or NiL_4 complexes.

(iii) Special reaction procedures. It is essential that isocyanate is always added to the solution of Ni(0), ligand and alkene using a metering pump. Simultaneously mixing all components gives rise to the catalytic product in lower yield. Secondary reactions similar to the reductive disproportionation of CO_2 occur.

Catalysis has been extended to other C-C double bond systems using the above principles. Monosubstituted alkenes, cycloalkenes, dienes have all produced catalytic reaction products. The challenge is to transfer the catalytic principles to the carbon dioxide chemistry.

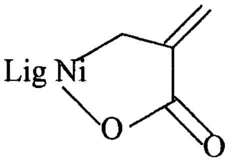
OXIDATIVE ADDITION:REVERSE CATALYSIS

The oxidative coupling of alkenes/alkynes and carbon dioxide generates intermediates of the type shown below.



A

Propene:CO_2



B

Allene:CO_2

With reference to the oxidative coupling reaction of propene and carbon dioxide at liganded Ni(0), a catalysis cycle is proposed which requires ι) β-hydride migration to the metal centre, followed by ii) reductive elimination of methacrylic acid, at the same time regenerating LigNi(0), which iii) can re-enter the cycle and oxidatively couple further propylene and CO_2. As a part of the current research, we propose synthesising intermediate compounds of type A by routes other than from propene and carbon dioxide. A small body of work exists in the literature and this is reviewed here. Synthesising these compounds by alternative routes has two purposes:-

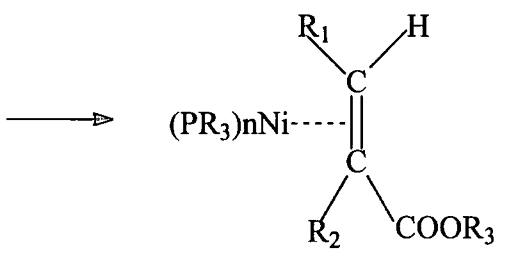
(i) These model compounds can be fully characterised to enable indentification in coupling reaction mixtures,
(ii) The reactivity of these intermediates can be studied .

T. Yamamoto et al have studied the interactions between nickel complexes, tertiary phosphines and α, β-unsaturated acids esters and amides(31-38). The products of reaction very much depend on the reaction conditions and stoichiometry and, not surprisingly, on the choice of phosphine used.

FORMATION OF Π COMPLEXES

Reactions of $Ni(COD)_2$ with methylacrylate, methyl methacrylate, ethylmethacrylate and methylcinnamate in the presence of tertiary phosphines at room temperature give orange or red nickel-phosphine complexes formulated as $Ni(PR_3)_n$ (α, β-unsaturated ester) in high yields (62-92%) (31) illustrated in the diagram below.

$$Ni(COD)_2 + PR_3 + CH(R_1){=}C(R_2)COOR_3$$



When the cone angle of the phosphine is large as in the case of tricyclohexylphosphine $(PCy_3)\sigma=179^{o}$), a complex with one phosphine ligand is obtained. In other cases where the cone angle of the phosphine is smaller, complexes with two phosphine ligands are obtained.

Evidence quoted for the side on coordination or π-type transition metal-alkene complex is:-

(i) The ^1H nmr signals of alkene protons (e.g. ethyl methacrylate) shift on complex formation to the upfield region (where the signals of alkene protons in the usual π-type transition metal-olefin complexes are observed) consistent with this type of complex.

(ii) The IR spectrum shows a shift of the $\nu_{c=o}$ frequency of ethyl methacrylate to lower values by only 43cm^{-1} suggesting no direct end on type interaction between the C=O group and the nickel atom.

A typical procedure for the synthesis of the π-type complex above is dependent upon the nature of the tertiary phosphine and for example uses (Ni(COD)$_2$, PPh$_3$, and ethylmethacrylate (ema) in a molar ratio of 1:2:1.4 respectively. Using the more basic phosphine PEt$_3$ requires a molar ratio of 1:2:4.4). Finally, using an even more basic phosphine PCy$_3$ a molar ratio of 1:2.5:8.8 is required. This result reflects the increased electron density at the metal centre as a result of using more basic phosphines, making alkene coordination less favourable.

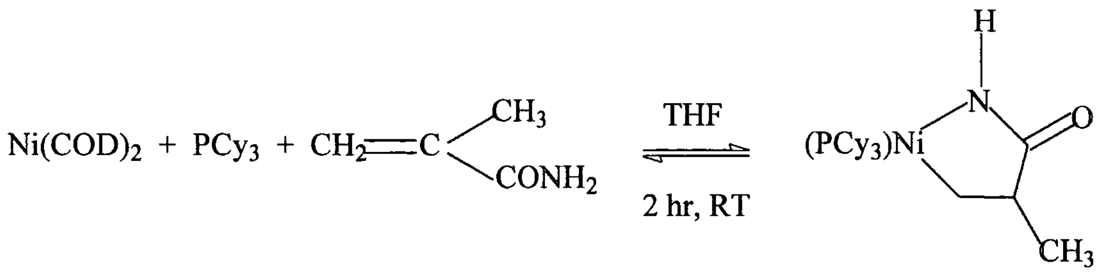
Rotation of the ligand around the Ni-alkene bond does not occur. Phosphorus NMR (^{31}P NMR) reveals that when using PPh$_3$ and PCy$_3$ the two phosphorous ligands occupy magnetically inequivalent positions.

Attempts to prepare an ethylmethacrylate-nickel complex by use of bidentate phosphine ligands, 1,2-bis(diphenylphosphino)ethane, (diphos), gave only Ni(diphos)$_2$, no π-ethyl methacrylate complex being isolated.

The complexes that are prepared and isolated are also reported to be sensitive to oxygen with sensitivity increasing with increasing basicity of phosphine ligand. Using PPh$_3$, the complex is moderately air stable, but using PEt$_3$, the complex is highly air sensitive.

METALLACYCLE FORMATION

Yamamoto et al reported the reaction of Ni(COD)$_2$ with methacrylamide in the presence of tricyclohexylphosphine (PCy$_3$) (molar ratio 1:2:1 respectively) to give a metallacycle amide complex(31-38) according to the equation below.



The spectroscopic information shows the material to be quite different from the π-type complexes discussed previously. The IR spectrum shows a sharp band ν(N-H) at 3,400cm^{-1} and only one sharp strong band at 1568cm^{-1} which is characteristic of cyclic amides. The NMR data is also consistent with the cyclic structure.

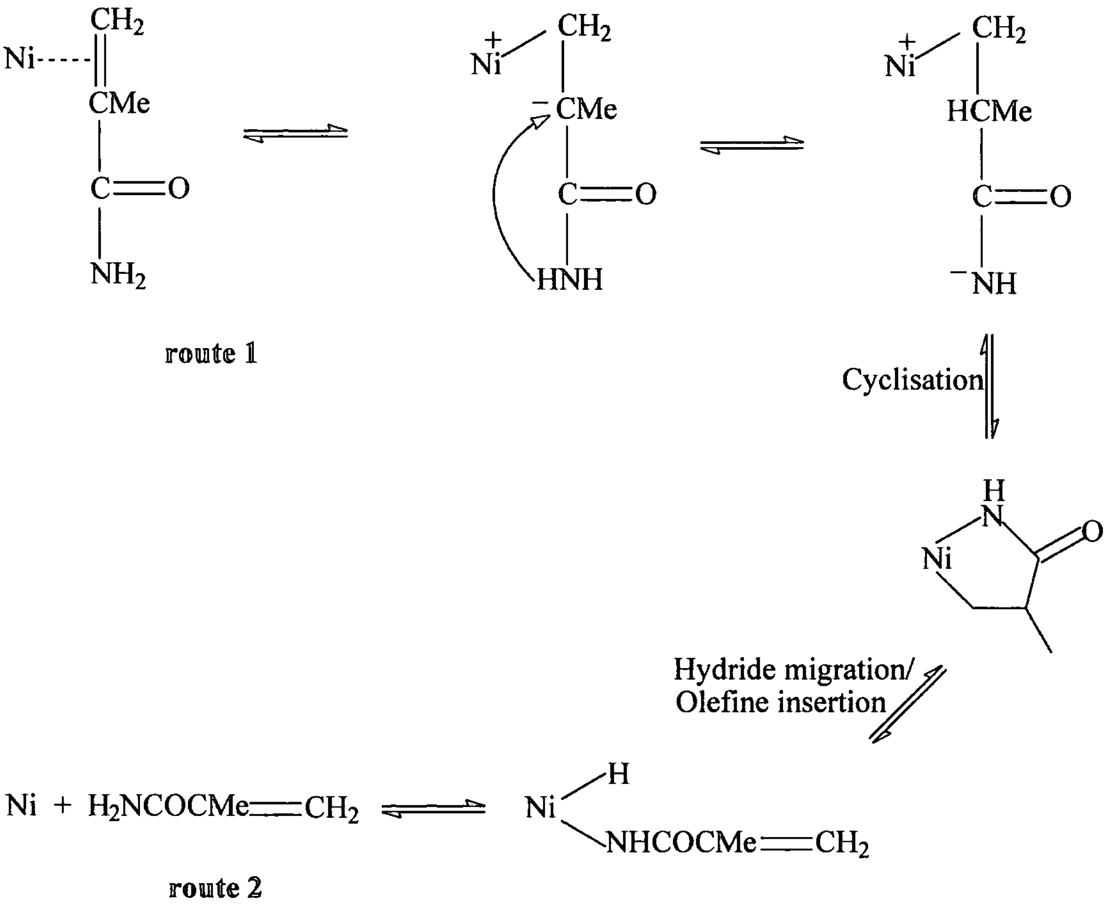
A highly basic phosphine seems to be a requirement for this reaction. A similar reaction in the presence of triphenylphosphine gave only yellow needles of a normal π-type complex.

Two mechanisms can be postulated to account for the formation of the metallacyclic amide complex, these are **route 1** and **route 2** illustrated below.

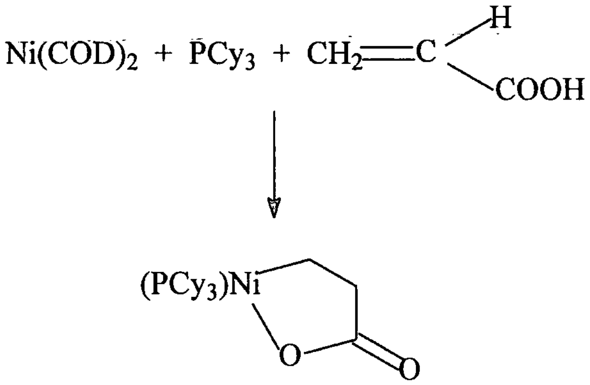
(i) Intra molecular Michael reaction type shift of H from NH_2 to the α carbon in a polarised canonical structure of a Ni-methacrylamide π complex (**route 1**),

(ii) Oxidative addition of the N-H bond of methacrylamide to nickel followed by hydride migration (**route 2**).

The same reaction using acrylic and methacrylic acid has been studied (2). A wide range of α, β-unsaturated amides and acids form analogous nickel containing cyclic complexes by reaction with $Ni(COD)_2$ in high yields under mild conditions when a highly stereo-demanding phosphine with a high basicity is employed. When a less basic and/or less stereo-demanding phosphine is employed, the reaction gives π-type olefin complexes.



Similar to the reaction of α, β-unsaturated amides with $Ni(COD)_2$, the reaction of acrylic acid with $Ni(COD)_2$ in the presence of PCy_3 affords a yellow nickel containing cyclic compound reported to be moderately air-stable according to the equation below.



The chelate groups of this molecule is the same as that of the molecule formed as a result of ethane:CO_2 1:1 oxidative coupling at liganded Ni(0).

The above reaction is reported to be temperature sensitive. Carrying out the reaction at -10°C to 0°C affords a mixture of metallacycle (A) and π-type complex (1:1), whereas carrying out the reaction at 20°C leads to polymerization of acrylic acid.

Direct evidence for the formation of the metallacycle is reported as follows:-

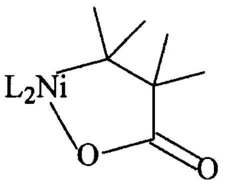
(i) Absence of the ν(O-H) stretching frequency in the IR spectra;

(ii) ν(C=O) at $1565cm^{-1}$ which is different to that expected for either the π type complex or the free acid;

(iii) Reaction with carbon monoxide yields succinic anhydride and 3-methyl succinic anhydride for the acrylic and methacrylic acid complexes resepctively.

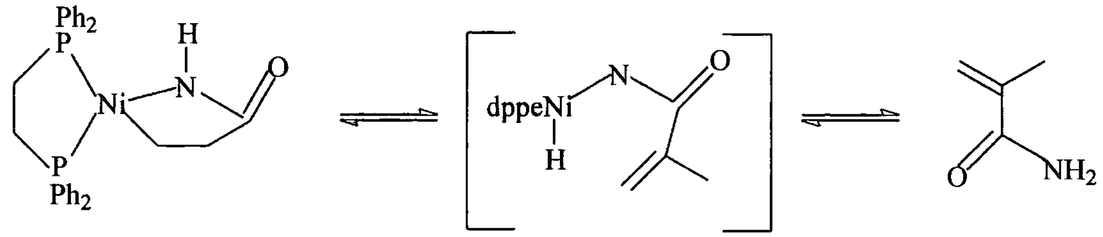
Full characterisation of the acrylic acid complex was reported not to be feasible due to difficulty in isolating an analytically pure compound.

The addition of 1,2,-bis(diphenylphosphino)ethane (dppe) to the above reaction leads to stable complexes soluble in organic solvents. This ability to add a stabilizing ligand is of interest in the current research. Adding dppe creates a coordinatively saturated square planar nickel(II) complex which has been well characterised (37, 38, 34). Other phosphine and nitrogen containing ligands can be used to stabilize these nickel complexes. This leads us to the possibility of being able to synthesize a range of compounds of the following type, illustrated below the same products as oxidative coupling of alkenes and carbon dioxide.

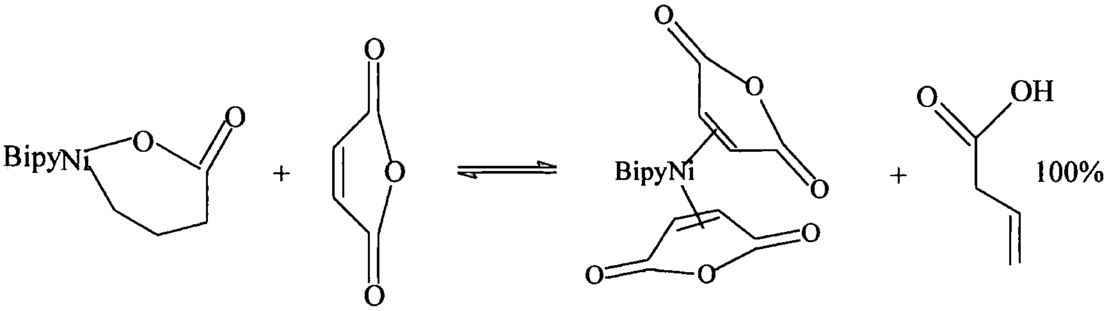


The reaction of $Ni(COD)_2$ with methacrylic acid and tricyclohexylphosphine forms a complex which can be used in phosphine displacement reactions to introduce further ligands of interest and attempt to isolate a wider range of complexes.

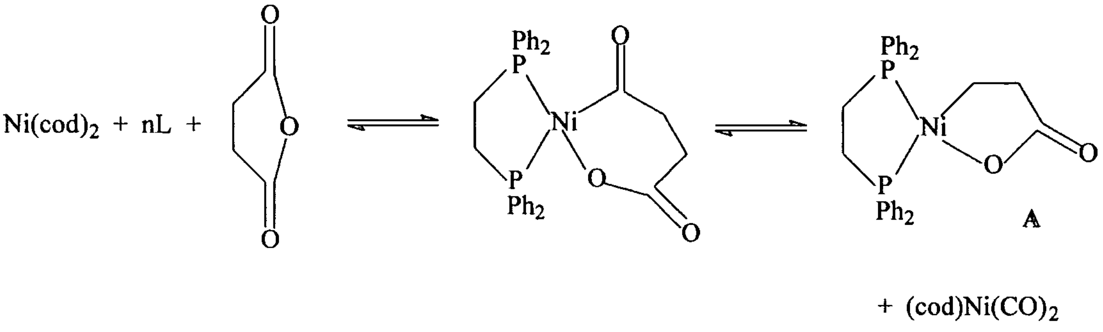
Only a limited number of chelating phosphines have been studied in these systems. Compounds have been synthesized employing 1,3,-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane with $[Ni(cod)_2]$ and methacrylamide to investigate the effect of ring size on the stability of the resulting metallacycle. It was found (36) that increasing ring size decreased the thermal stability. The dppe complex had the highest decomposition temperature, 210°C which decreased to 190°C for the dppp complex and 170°C for the dppb complex. In the case of the dppe cyclic amide complex the thermolysis product was methacrylamide which was formed by a β-elimination process illustrated below.



On thermolysis of the dppp and dppb coordinated cyclic amide complexes containing (methacrylamide), some 2-methylpropanamide, the hydrogenation product of methacrylamide, was produced in addition to the simple β-elimination product. The hydrogen source is not clear, though it could arise from orthometallation of the phosphine ligand. The β-elimination reaction of the nickel containing cyclic amide was promoted by addition of $AlCl_3$ (Lewis acid). A similar promotion effect for the β-elimination was observed when maleic anhydride was added. The hydrogenation product of methacrylamide was formed. A related nickel containing cyclic ester complex on treatment with maleic anhydride in CH_2Cl_2, gives a β-elimination product, but here 3 butenoic acid is formed according to the reaction scheme illustrated below.

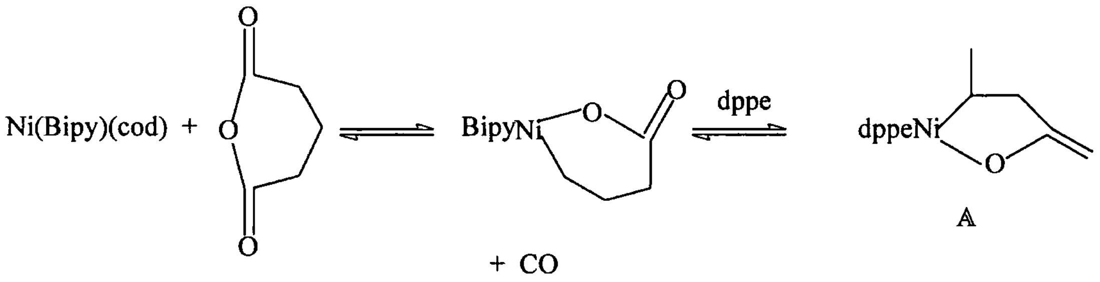


The nickel containing cyclic ester complexes have been studied less than the cyclic amide-type structures. No crystal structure analyses have been undertaken found for these complexes, though some spectroscopic data is reported for the dppe complexes of acrylic and methacrylic acid (34). The metallacycles have been studied mainly in the context of the oxidative addition of cyclic carboxylic anhydrides to liganded Ni(0). The reaction of Ni(0) complexes with succinic anhydride in the presence of the appropriate ligands such as bipyridine and PCy_3 give five membered nickel containing cyclic carboxylates as shown below.



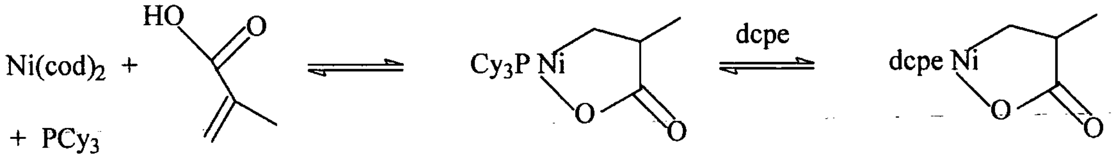
Complex A is considered to be formed through oxidative addition of succinic anhydride to nickel giving the six membered 2-oxo metallacycle, which then loses carbon monoxide.

An interesting ring contraction reaction has been observed in these systems suggesting that the 5 membered metallacycle ring is the most stable size of ring system. The reaction of Ni(cod)$_2$ with glutaric anhydride and (35)bipydridine gave a 6-membered ring compound which on addition of dppe gave a five membered complex through a ring contraction isomerisation process, as shown below.



Complex A above also decomposes above 160°c to liberate propylene and CO$_2$ in 20-30% yield.

As mentioned earlier, the work described in this thesis is based on this prior knowledge described in these review chapters, and concerns the oxidative coupling of alkenes and CO$_2$ and the subsequent ligand cleavage reactions leading to unsaturated acids or esters. Highly electron-rich phosphines are used and the work involves synthesis, structural characterisation and reaction chemistry. The initial target in the model complex programme is to use 1,2,-bis(dicyclohexylphosphino)ethane as the chelating stabilizing phosphine, as shown below.



Materials of this type have been formed from propene and CO$_2$. The attempted catalysis cycle is not complete at present because of the stability of the intermediate metallacyclic complex, and this thesis is concerned with an understanding of the chemistry of these complexes which leads to their stability. Ways are sought to destabilise these intermediates so that reaction of propene and carbon dioxide proceeds directly to methacrylic acid.

$$CH_3CH{=}CH_2 + CO_2 \rightleftharpoons CH_2{=}C(CH_3)COOH$$

The approach used here is to change the electronic and steric properties of the phosphine ligand on nickel.

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CHAPTER FIVE

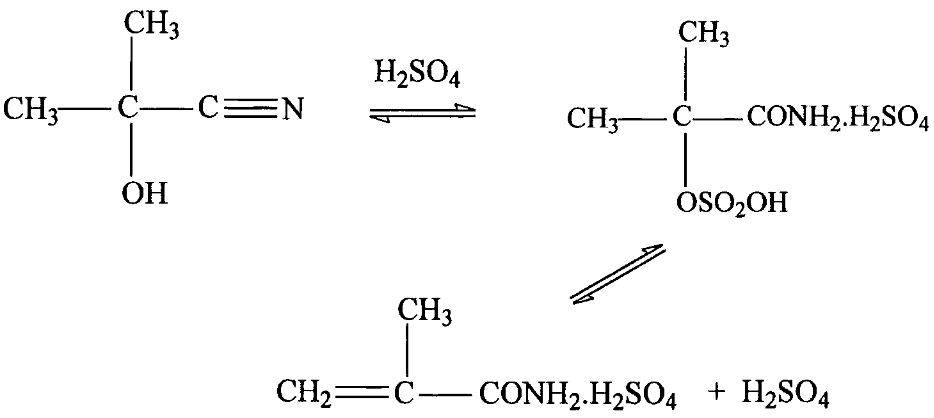
CURRENT METHACRYLIC ACID / METHYL METHACRYLATE TECHNOLOGY

CHAPTER FIVE

CURRENT METHACRYLIC ACID / METHYL METHACRYLATE TECHNOLOGY

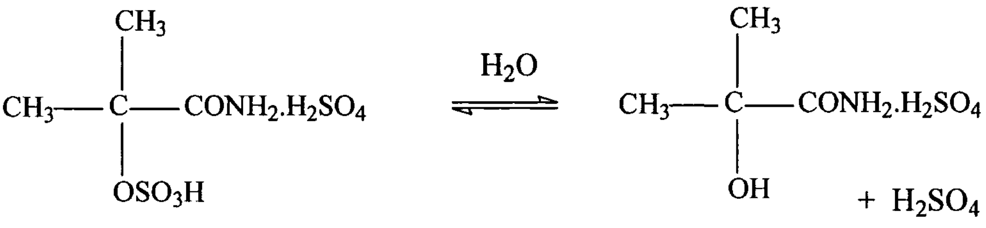
The aims of the current research are ultimately to produce methacrylic acid for conversion into methylmethacrylate from alkenes/alkynes and carbon dioxide. It is appropriate to review the existing technologies to the materials.

Methylmethacrylate can be manufactured by numerous synthetic routes from a wide variety of feedstocks. However, in commercial operations, the acetone cyanohydrin (ACH) process is the major process used all over the world. In the ACH process, dry acetone and hydrogen cyanide react in the presence of a basic catalyst to give acetone cyanohydrin, which is then reacted with excess concentrated sulphuric acid (1.4 - 1.8mol per mole of ACH) to form methacrylamide sulphate (see below).



$$CH_3-C(CH_3)(OH)-C\equiv N \xrightleftharpoons{H_2SO_4} CH_3-C(CH_3)(OSO_2OH)-CONH_2.H_2SO_4 \rightleftharpoons CH_2=C(CH_3)-CONH_2.H_2SO_4 + H_2SO_4$$

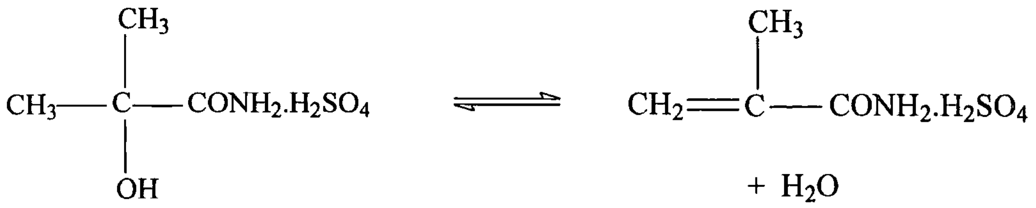
The sulphuric acid serves both as a specific reactant and as a solvent for the reaction, which appears to involve an α-sulphatoamide intermediate. If insufficient sulphuric acid is used, the reaction mass becomes a slurry or solid that is difficult or impossible to cool and pump. Both the sulphuric acid and the ACH must be anhydrous in order to minimize hydrolysis of the sulphato derivative to α hydroxyisobutanamide.



$$CH_3-C(CH_3)(OSO_3H)-CONH_2.H_2SO_4 \xrightleftharpoons{H_2O} CH_3-C(CH_3)(OH)-CONH_2.H_2SO_4 + H_2SO_4$$

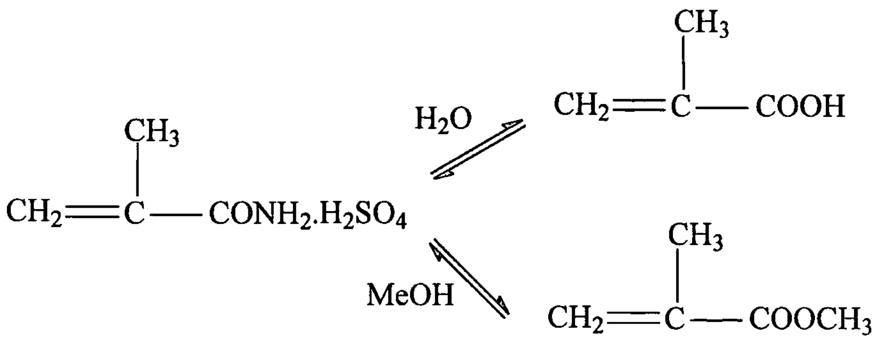
The initial reaction is carried out continuously in a series of stirred tank reactors. Good heat transfer is required to ensure removal of the heat of reaction. Thorough mixing is also necessary to avoid decomposition of the ACH to acetone and HCN, which can react to form by product acetone sulphonates and formamide sulphate.

After initial reaction is completed at 80-110°C, the mixture is subjected to brief thermal cracking at ca. 125-160°C to convert most of the α-hydroxyisobutanamide by product to methacrylamide sulphate.



Also produced at this stage are some acetone, carbon monoxide and water. Total residence time at this stage of the process is about 1 hour.

In a second stage, the methacrylamide sulphate is either hydrolysed with excess water to give methacrylic acid and ammonium sulphate, or it is treated with aqueous methanol in a combined hydrolysis-esterification step to produce a mixture of methyl methacrylate and methacrylic acid .

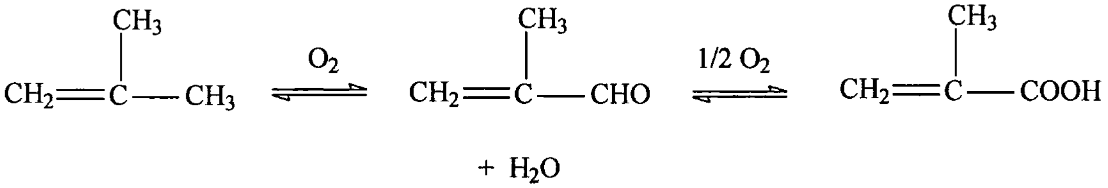


Several modifications are possible in the hydrolysis-esterification step. For example, the methacrylamide sulphate, water, methanol and recycle streams can be led through a series of continuous reactors at 80-110°C with a 2-4hr residence time. The reactor effluent then passes to a stripping column where crude methyl methacrylate, water and excess methanol are removed. The waste ammonium sulphate residue can be either treated with ammonia for conversion to fertilizer or burned to regenerate sulphuric acid. Crude methyl methacrylate is extracted with water to recover methanol, which is concentrated and recycled to the esterification reactor. Washed ester is then purified by further distillation. The overall yield based on acetone cyanohydrin is in the range of 80-90%.

A sulphuric acid regeneration plant is usually operated in conjunction with the methyl methacrylate plant, because approximately 1.6kg of sulphuric acid is required to produce each kilogram of methyl methacrylate. The presence of a regeneration facility avoids the need to dispose of large quantities of ammonuim sulphate contaminated with organic material. One of the driving forces for development of alternative routes has been the desire to eliminate the need for sulphuric acid regeneration. An additional concern is the hazard associated with transporting hydrogen cyanide which is not always generated at the methacrylate plant site. On the other hand, both acetone (from phenol manufacture) and hydrogen cyanide (from acrylonitrile manufacture) have the economic advantage that they are themselves by-products of other processes.

C_4 OXIDATION ROUTES:

The C_4 oxidation process is based on the two stage oxidation of isobutene (or t-butyl alcohol) to methacrylic acid. It is similar to the successful process for the manufacture of acrylic acid from the catalytic oxidation of propene. It is attractive because the basic hydrocarbon raw material, used to produce methacrylic acid, is obtained from the cracking of crude petroleum and the only other required reactant is air. Isobutene is oxidized in the first stage to methacrolein and, in the second stage, the methacrolein is oxidized to methacrylic acid .



$$CH_2{=}C(CH_3){-}CH_3 \xrightleftharpoons{O_2} CH_2{=}C(CH_3){-}CHO + H_2O \xrightleftharpoons{1/2\,O_2} CH_2{=}C(CH_3){-}COOH$$

The methacrylic acid is separated from the by products and is esterified with methanol to methylmethacrylate. For this route to be attractive compared with the ACH process, heterogeneous catalysts for both stages must be selective and have a long life, and isobutene must be available.

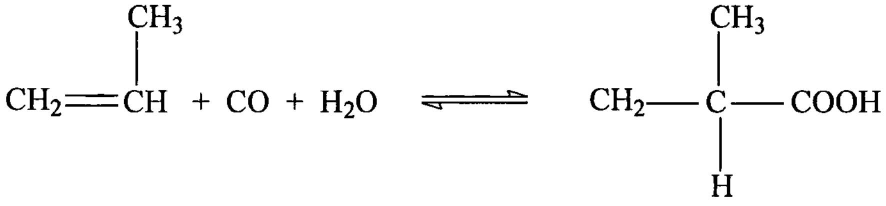
In a typical procedure, a mixture of 5% isobutene 30% steam and 65% air are passed over the first stage catalyst at about 350°C. Isobutene conversion is ca. 98% and selectivity to methacrolein plus methacrylic acid is 80-85%. In the preferred process configuration, the effluent from the first reactor, with or without additional air or diluent added to the interstage, is fed directly to the second stage reactor. Conversion in the second stage is kept low in order to ensure good catalyst selectivity and increase catalyst life. Unreacted methacrolein from the second stage reactor effluent is separated and recycled. the overall yield of methacrylic acid from isobutylene is about 65-70%. Typical catalysts for the first stage are multicomponent metal oxides containing bismuth, molybdenum and several other metals to promote activity and modify selectivity. Second stage catalysts are based on phosphomolybdic acid but they usually contain an alkali metal to control the acidity. Other elements such as copper and vanadium may also be present.

Plants based on the C4 route were introduced in Japan by Nippon Shokuboi in 1982 and by Mitsubishi Rayon in 1983. a joint venture plant operated by Simitomo and Nippon Shokuboi came on stream in 1984. Exploitation of C4 oxidation has only occurred in the far East due to feedstock availability and economics.

C_3 ROUTE:

Acid-catalysed carbonylation of propene to iso-butanoic acid, followed by oxidative dehydrogenation, presents still another route to methacrylic acid. This is the most extensively explored of the several proposed routes based on propene as the basic raw material. In this case, the starting material is propene itself rather than the oxidized derivative acetone, as used in the acetone cyanohydrin route. Although the propene - isobutanoic acid - methacrylic acid route is not currently in commercial use, several major methyl methacrylate manufacturers have research efforts aimed at its commercialisation. (1)

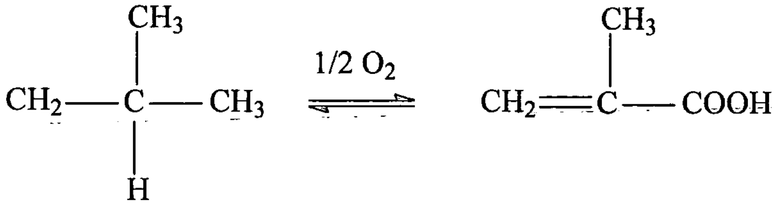
In the first stage of the process, propene, carbon monoxide and water are reacted in the presence of a strong acid catalyst to produce isobutanoic acid. Sulphuric acid, hydrogen fluoride and boron fluoride have all been reported to be effective catalysts.



$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}H} + CO + H_2O \rightleftharpoons CH_2{-}\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}COOH}$$

Hydrogen fluoride (which acts as both solvent and catalyst), carbon monoxide and propene are reacted in the presence of a slight stoichometric deffciency of water relative to propene to generate isobutanoic acid. The overall selectivity of this step with respect to propene is reported to be 95 - 97%. The plant design to accomplish this step incorporates features to prevent fluoride emissions and enable recycle of both hydrogen fluoride and carbon monoxide.

In the second stage of the process, isobutanoic acid, steam and air are passed over a fixed bed catalyst in a multitubular reactor, causing oxidative dehydrogenation to methacrylic acid.

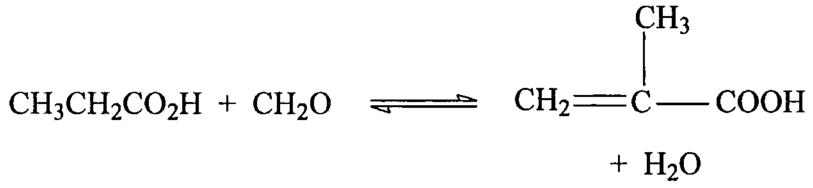


$$\mathrm{CH_2{-}\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_3 \xrightleftharpoons{1/2\ O_2} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}COOH}$$

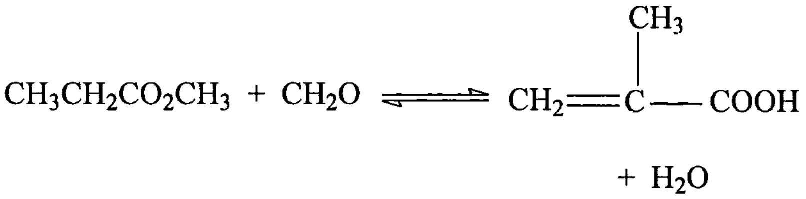
Catalysts for the oxidative dehydrogenation of isobutanoic acid to methacrylic acid are of two general types: The first series is similar in composition to those used in the oxidation of methacrolein, often referred to as Mo-P-V mixed oxide catalysts. Most are phosphomolybdic acid derivatives, usually with some replacement of molybdenum by vanadium or tungsten. The better catalysts frequently contain some copper, and they are partially neutralized by cesium, rubidium or potassium. Some catalysts are reported to achieve conversions of 99.8% with selectivites above 74%. The second series consists of iron phosphate-type materials and give selectivites of about 85% at conversions in the 85 - 95% range. Such catalysts are used at about 400°c, in contrast to 300°c for first series catalysts. Iron phosphate catalysts require high levels of steam in the reactor feed for optimum selectivity and life.

C_2 - ROUTE

The proposed ethene based route involves the reaction of either propanoic acid or methylpropanoate with methanal to form methacrylic acid or methylmethacrylate (MMA). The first step is preparation of propanoic acid by the carbonylation of ethene or by the hydroformylation of ethylene to propanal follwed by oxidation of the aldehyde to propanoic acid. The second step involves the vapour phase catalytic condensation of propanoic acid or methyl propanoate with methanal to form methacrylic acid or methyl methacrylate. The catalyst must provide high selectivity at high conversions.



$$CH_3CH_2CO_2H + CH_2O \rightleftharpoons CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH + H_2O$$



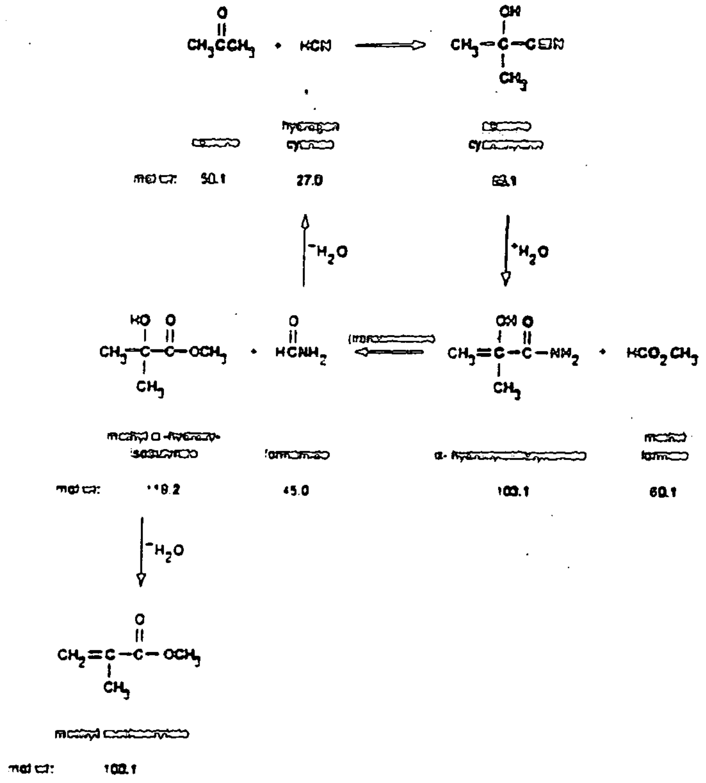
$$CH_3CH_2CO_2CH_3 + CH_2O \rightleftharpoons CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH + H_2O$$

Effective catalysts include alkali metal or alkaline earth metal aluminosilicates, potasium hydroxide or cesium hydroxide treated pyrogenic silica, alumina and lanthanum oxide. Results vary over a range of conversions and selectivites. The best reported results are at conversions of 50% where selectivites are >80%. This data was obtained over a short run time and it appears that additional catalyst development is required for this concept to be attractive. Improved results have occurred with the use of dimethoxymethane in place of methanal in the condensation reaction.

BASF Aktiengescellschaft have commercialised a variation of the above process. Ethene is hydroformylated to propanal then reacted with methanal to give methacrolein, which is subsequently oxidised to methacrylic acid and esterified to methyl methacrylate. The commercial viability of this process relies on the availability of low cost ethene and methanal.

MITSUBISHI GAS CHEMICALS ROUTE

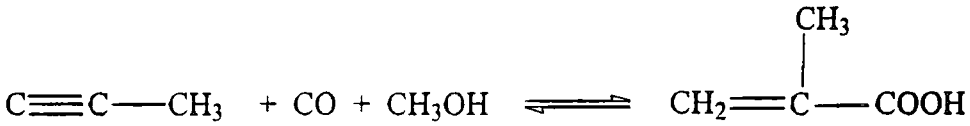
In May 1989, Mitsubishi Gas Chemical Co. Inc. announced a new process for manufacturing MMA from acetone cyanohydrin. This process is unusual because it does not use sulphuric acid or produce ammonium hydrogensulphate, which are major problems with the current method for producing MMA. The reaction sequence is as shown below in Figure 5.9.



The key to the successful operation of this process is with the catalysts used. The reaction sequence itself has been known since the 1940's; however, poor yields and side products have thwarted commercial development in the past. Details of catalysts and the conditions used have not been released.

SHELL METHYL ACETYLENE ROUTE:

The most recent technology to be developed has been that developed by Shell around methyl acetylene as a C_3 feedstock . Very little is known about this system. Shell have announced development to pilot plant scale.



$$\mathrm{C{\equiv}C{-}CH_3 + CO + CH_3OH \rightleftharpoons CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH}$$

The catalysts are homogenious palladium phosphine systems. Selectivites of >99% are reported. The barrier to development of this technology is the availability of methylacetylene feedstock.

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CHAPTER SIX

Synthesis of Nickel Phosphine and Nickel-Amine Complexes Derived from Methacrylic and Crotonic acids

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Synthesis of Nickel Phosphine and Nickel-Amine Complexes Derived from Methacrylic and Crotonic acids

INTRODUCTION

The objective of the experimental work has been to investigate the potential of a proposed catalysis cycle generating methacrylic acid from the oxidative coupling of propylene and carbon dioxide. The proposed catalysis has been mentioned earlier (see fig 1.0) and is considered possible given the right ligand and experimental conditions.

The approach adopted has been:-

1. To utilise the chemistry developed by Yamamoto et al(31-38 Chapter 5) and reviewed in chapter 5, to attempt the synthesis of perceived intermediates in the catalysis cycle. Yamamoto et al synthesized a range of compounds of the type:-

   I $\mathrm{L\ \overline{NiCH_2CH(CH_3)CONH}}$ $\mathrm{L = PEt_3}$
   $\mathrm{L = PCy_3}$

   II $\mathrm{L_2\ \overline{NiCH_2CH(CH_3)CONH}}$ L = DPPE

   III $\mathrm{L\ \overline{NiCH_2CH(CH_3)COO}}$ $\mathrm{L = PEt_3, PCy_3}$

   IV $\mathrm{L_2\overline{NiCH_2CH(CH_3)COO}}$ L = DPPE

   which involve the oxidative addition of methacrylamide (I and II) and methacrylic acid (III and IV) to a nickel(0) complex. An attempt has been made to utilise and extend this chemistry. Firstly the work to synthesize III and IV was repeated, and secondly the work was extended to the synthesis of a range of compounds of type III/IV, where L = a highly electron donating ligand. Highly electron donating ligands were identified from two sources as having potential in the proposed catalysis. 1) A study of the activation of CO_2 by transition metals revealed electron rich metal centres are required for the bonding/activation of CO_2 in many cases. 2) Where oxidative coupling of alkynes/alkenes and CO_2 has been demonstrated by Hoberg et al and others, it has only been shown to be sucessful in the prescence of electron donating ligands. The ligands identified from the work of Hoberg et al were DCPE, DCPP, DCPy, BIPY, Phen and TMEDA. The synthesis of

   $\mathrm{\overline{L_2NiCH_2CH(CH_3)COO}}$ has been attempted where L_2 = DCPE, DCPP, DCPy, BIPY, Phen and TMEDA. Also attempted were the syntheses of the crotonic acid derivatives $[L_2\overline{Ni\{CH(CH_3)CH_2COO}\}]$ where L_2 = DPPE, DCPE. These complexes result from coupling of the CO_2 with the terminal carbon of propene, a possible competing reaction in oxidative coupling. One of the purposes of synthesizing intermediates is to enable their identification in mixtures in which catalysis had been attempted.

Characterisation by a range of techniques was used, both to obtain confirmation of the synthetic product, and also to gain structural information about the compounds. The compounds are stable intermediates in a catalytic cycle and clues to their decomposition are sought to facilitate the catalysis. The results of these studies are presented in Chapter 6 are discussed in Chapter 7.

2. The second approach tried was a study of reaction chemistry of the intermediates synthesized as outlined above. The use of additives and/or high temperature and pressure conditions to attempt to liberate methacrylic acid from the complex

   $[DCPE\text{-}\overline{Ni\{CH_2CH(CH_3)COO}\}]$ and regenerate a nickel(0) complex was investigated. Attempts to induce β-hydride migration were made. From the proposed catalytic cycle (see Figure 1.0) it can be seen that β-hydride migration and reductive elimination are key steps. There are examples in the work of Yamammoto et al that indicate these steps may be possible:- 1) the metallacycle

   $[(DPPE)\overline{Ni\{CH_2CH(CH_3)CONH}\}]$ eliminates the unsaturated methacrylamide when heated to 210°C. This has almost certainly been formed as a result of β-hydride migration followed by reductive elimination. 2) The metallacycle

   $[(BIPY)\overline{Ni\{CH_2CH_2CH_2COO}\}]$ liberates 3-butenoic acid (100%) in the presence of maleic anhydride. The maleic anhydride has a promotional effect. Formation of 3-butenoic acid is again almost certainly a result of β-hydride migration followed by reductive elimination. The results of this investigation are presented in Chapter 6 and discussed in Chapter 8

3. Finally, the catalysis itself involving propene and CO_2 was investigated with the ligands outlined above. The products of reaction were characterised and rationalised. Evidence was sought for the intermediate resulting from oxidative coupling of propene and CO_2. Where synthesis of complexes was achieved also via the oxidative addition of methacrylic acid to phosphine liganded nickel(0), it is possible to directly compare spectroscopic data and demonstrate unequivocally the presence or otherwise of the intermediates in the process. The reaction solutions following coupling of propene and CO_2 were analysed for the evidence of catalysis, direct evidence being the presence of methacrylic and/or crotonic acids in the reaction solutions before hydrolysis. Further information was obtained by acid hydrolysis of the nickel containing solids. The metallacyclic structures present following reaction can be inferred from the structures of the organic acids and other compounds present after acid

hydrolysis(see chapter four this thesis). The results of this work are presented in Chapter 6 and discussed in Chapter 9.

EXPERIMENTAL ASPECTS

INTRODUCTION

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere, using standard vacuum line techniques. The solvents, tetrahydrofuran, toluene and diethyl ether were sodium dried and freshly distilled before use. The phosphine, 1,2-bis(dicyclohexylphosphino)ethane was supplied by Dr. Peter Edwards of Cardiff University and was used as supplied; dicyclohexylphosphine was purchased from Strem chemicals and used as supplied. All other reagents unless detailed were supplied by the Aldrich Chemical Company and used without further purification.

NMR spectra were recorded on JEOL GX400 series FT NMR spectrometers at ambient temperature (unless otherwise stated). Proton spectra were taken at 400MHz and chemical shifts [δ, (ppm)] are positive to high frequency of $SiMe_4$ unless stated. Carbon spectra were taken at 100MHz and chemical shifts were referenced by using the ^{13}C resonance of the solvent as an internal standard, but are reported with respect to $SiMe_4$. Phosphorus spectra were taken at 31MHz and chemical shifts are referenced by using the ^{31}P resonance of TMP as a calibration standard (chemical shift 140.00ppm).

Infa red spectra were recorded on a Nicolet 60SX FTIR instrument over the range 4000-400 cm^{-1} at a resolution of 2 cm^{-1}.

GC-MS were run under the following standard chromatography conditions (unless stated):-

25 metre CPSil 19 capillary column, 1.2 μm film thickness
Helium carrier gas 5psi
Injector temperature 250^{0}C
Oven programme 50^{o}C for 4 minutes rising to 200^{0}C at 20^{0}C/min and holding at 200^{0}C

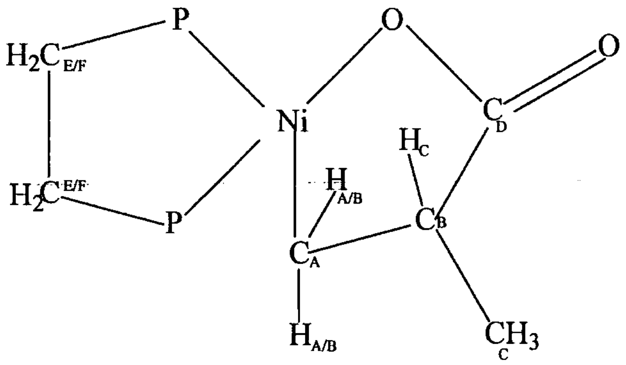
The mass spectra were obtained at 70eV on a VG Mass Lab TRIO 1 bench top quadrapole mass spectrometer.

All two sector mass spectrometry experiments were performed on a VG Analytical Ltd. ZAB-2SE mass spectrometer of reverse geometry. LSIMS (FAB +ve ion, FAB -ve ion) experiments were performed using the standard VG dedicated LSIMS ion source. A 35KV caesium ion gun, operating at 30KeV incident energy was used to bombard the sample. Matrices used were either m-nitrobenzyl alcohol(mNBA) or glycerol. Field Desorption experiments were carried out using 13μm emitters and manual increase of the emitter current to a maximum of 80mA. Tandem mass spectrometry data were acquired using a VG Analytical ZABT tandem mass spectrometer of BEBE geometry. Collision induced dissociation was carried out at 4KV collision energy. Argon was used as the collision gas. The MS-MS experiments carried out are known as daughter ion scans. In this experiment, the parent ion mass is fixed and the masses of all daughter ions formed from the parent ion are measured. The daughter ion scan is essentially the mass spectrum of an ion in the mass spectrum. The first stage of mass analysis selects ions of a particular m/z (the parent ion) from all ions initially formed (which taken together make up the normal mass spectrum). This mass selected parent ion when it passes into the reaction region generates daughter ions by collision-induced-dissociations between the parent ion and the collision gas. The translational energy of the selected ion is changed via collision with the inert gas molecules into vibrational energy which causes the ion (in most cases) to break into smaller fragments. Daughter ions formed from dissociations of the parent ion in the reaction region are then analysed by mass/charge. These daughter ions are generally characteristic of the structure of the parent ion and thus provide a means of determining that structure.

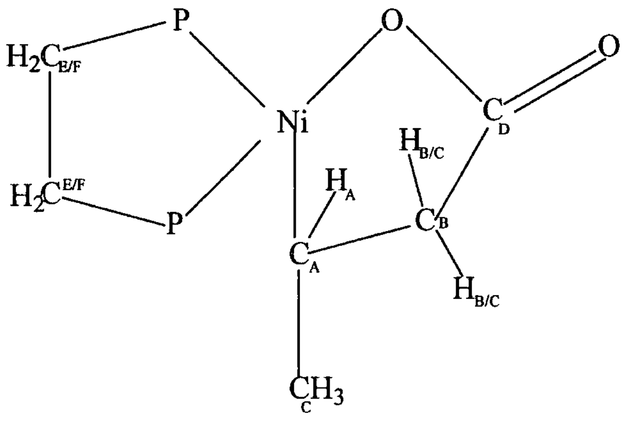
Microanalyses were obtained from the I.C.I microanalytical laboratory and from Durham University.

Yields are reported for the synthesis of oxa-nickella-cyclopentanones based on bis(cycloocta-1,5-diene)nickel.

Spectroscopic data for the synthesized oxa-nickela-cyclopentanones has been reported according to the following scheme. For the 4 methyl substituted oxa-nickela-cyclopentanones the atoms have been labelled as below.



For the 3-methyl substituted oxa-nickela-cyclopentanones, the atoms have been labelled as shown below.


H2CE/F
P
O
O
Ni
CD
HB/C
HA
H2CE/F
P
CB
CA
HB/C
CH3
C

SECTION 6.1.0 - SYNTHESIS OF STARTING COMPLEXES AND LIGANDS

6.1.1 Preparation of bis(cycloocta-1,5-diene) Nickel(0)

To a stirred solution of anhydrous nickel(II) acetylacetonate (20g, 78mmol) in toluene (300ml) was added dropwise cycloocta-1,5-diene (19.0ml, 156mmol). The solution was cooled by means of a dry ice/acetone cold bath to -78^{0}C, before 1,3-butadiene (1.5ml) was condensed into the reaction vessel which was equipped with a dry ice/acetone filled cold finger. A solution of triethylaluminium in toluene (82.0ml, 1.9M solution, 156mmol) was then added dropwise over a period of 30 minutes to the reaction. During this time the green solution darkened to a yellow/brown colour and after a further 30 minutes formation of a yellow precipitate was observed. The reaction mixture was allowed to stir overnight at -78^{0}C before being allowed to warm to room temperature. The mixture was then cooled to -30^{o}C for 2 hrs. before filtration. The yellow solid was collected and washed with cold toluene (-10^{0}C, 2x 50ml) and then cold ether (-10^{0}C, 2x 50ml), before drying *in vacuo*. The product bis(cycloocta-1,5-diene)nickel(0), a yellow microcrystalline powder (20.0g, 72.8mmol, 93.0%) was dried in vacuo, then stored in an inert argon atmosphere in the absence of light. The product was identified by NMR [^{1}H (d^8 toluene) : δ=2.35(s, 8H, CH$_2$), 4.55(s, 4H, CH); ^{13}C d^8 toluene: δ=31.0(s, CH$_2$), 89.0(s, CH) ppm ; literature data(1) ^{1}H (C$_6$D$_6$) 2.08(br, CH$_2$), 4.31(br, CH)] and used without further purification.

6.1.2 Synthesis 1,3-(dicyclohexylphoshino)propane

To a stirred solution of dicyclohexylphosphine (10g, 50.5mmol) in tetrahydrofuran (500ml) was added dropwise n-butyllithium as a 1.6M solution in hexane (34.4ml 50.5mmol). A yellow colour developed immediately. The reaction was allowed to stir for 18 hours at room temperature. To the mixture was added 1,3- dichloropropane (4.5g, 20.0mmol). The reaction solution was stirred for 2 hrs at room temperature before heating under reflux for 30 minutes when the colour lightened. The reaction was allowed to cool before ethanol (20ml) was added dropwise to destroy excess butyllithium. Further stirring for 30 minutes was followed by the addition of degassed water (200ml). The phosphine separated as an oil. The supernatant liquor was removed by syringe and the oil dissolved in diethyl ether. This was dried over magnesium sulphate, filtered and the solvent removed from the filtrate *in vacuo* to yield the product as a pale yellow viscous oil, (15g 34.4mmol) 86% yield (based on 1,3-dichloropropane), identified by ^{31}P NMR [-6.6ppm(s) (CDCl$_3$)](2).

6.1.3 Synthesis 2-chloroethylpyridine

To a stirred solution of 2-(2'pyridyl)ethanol (15g, 0.122mol) in carbon tetrachloride (100ml) was added triphenylphosphine (35.2g, 0.134mol) as a solution in carbon tetrachloride (100ml). The reaction was allowed to stir for 48 hours during which time a white precipitate of triphenylphosphine oxide formed. The reaction mixture was filtered and the filtrate concentrated in vacuo to 50ml volume. Pentane(100ml) was added to precipitate unreacted triphenylphosphine, and the solution filtered. Solvent was removed under vacuum, and the residue dissolved in diethylether(100ml). The diethyl ether solution was layered onto a column of chromatographic silica and the product eluted with diethylether(500ml). The diethylether fraction was dried over magnesium sulphate, filtered and the solvent removed to leave a clear liquid (13.75g, 80.3%), identified by ^{1}H NMR.

6.1.4 Synthesis 2-{2,-(dicyclohexylphosphino)ethyl}pyridine, referred to in the text as (cyclo-$C_6H_{11})_2PCH_2CH_2$-2-pyridine or DCPy ligand.

To a stirred solution of dicyclohexylphosphine (10.0g, 50.5mmol) in tetrahydrofuran (500ml) was added dropwise n-butyllithium as a 1.6M solution in hexane (34.4ml, 50.5mmol). After stirring for 24 hours 2-chloroethylpyridine (7.1g, 50.0mmol) was added dropwise. The reaction mixture was stirred for 2 hours at room temperature before heating under reflux for 30 minutes. A dark red colour formed on addition of 2-chloroethylpyridine, which changed to a straw coloured solution after stirring for 2 hours. Ethanol (50.0ml) was added to destroy unreacted n-butyllithium and stirring was continued for a further 30 minutes. Solvent was removed *in vacuo* and the residue was extracted with diethyl ether. The ether extract was dried over magnesium sulphate, filtered and concentrated at reduced pressure to yield 10.0g of a viscous oil. Purification by vacuum distillation gave pure product [b.p. 220°C at 2mm Hg, yield 2.5g (8.25mmol), 16.5% (based on 2-chloroethylpyridine); ^{31}P NMR-$^{-}$5.0ppm(s) (CDCl$_{3,}$)], characterised by reference to literature data(3).

SECTION 6.2.0- SYNTHESIS OF OXA-NICKELA-CYCLOPENTANONES VIA THE OXIDATIVE ADDITION OF α,β-UNSATURATED CARBOXYLIC ACIDS TO NICKEL(0) COMPLEXES.

6.2.1 Synthesis Tetra{1-oxa-2-(tricyclohexylphosphino)nickela-4-methyl cyclopentan-5-one, COMPOUND 1A

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran(20.0ml) at -10^{0}C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{0}C and 0^{0}C. The reaction solution became deep yellow/brown in colour. Solvent was removed *in vacuo*, and the remaining brown residue washed twice with cold ether(-10^{0}C) before drying. The product was a bright yellow powder, yield 0.5g , 64.8%. Found: C, 64.30; H, 8.88: $C_{88}H_{156}Ni_4O_8P_4$ requires C,62.26; H,9.2%.

I.R(KBR):cm^{-1}

ν=2925(s),2848(s),1569(vs),1446(m),

MASS SPECTRUM :(FAB +ve ion, m-nitrobenzylalcohol (mNBA) matrix):
M/z, 1721[(8%), (M+Na)$^+$], 593(4%), 460(7%), 367(7%), 297[(94%), (tricyclohexylphosphine oxide)], 281[(89%), (tricyclohexylphosphine)] 154[(100%), (matrix)]

^{1}H NMR (CD_2Cl_2): δ=0.82(d, 1H, J 7.32Hz, H_A/H_B), 0.91(d, 1H, J 6.84, H_A/H_B), 1.14(d, 3H, $^3J_{H-H}$ 6.83Hz, CH_3), 1.2-2.2(br, cyclohexyl CH_2), 2.34(s, 1H, H_C), 3.68(s), 5.32(s) ppm

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ=6.41(d, J 30.7Hz), 20.15(s), 20.4(s), 21.5(br), 26.45(br), 27.0-32.0(m, cyclohexyl CH_2), 32.19(d, J 12.2Hz), 32.76(m), 33.82(d, J 21.5Hz), 43.38(s), 43.24(s), 44.0(s), 44.82(s), 68.77ppm(s) .

$^{31}P\{^1H\}$ NMR (THF): δ=35.15(s), 34.52(s), 33.85(s), 33.72(s), 33.43(s), 33.23(s), 33.11(s), 32.99ppm(s).

$^{31}P\{^1H\}$ NMR (TOLUENE): δ=33.34(s), 33.15(s), 32.98(s), 32.26(s), 32.17(s), 31.99(s), 31.90(s), 31.75(s), 31.55ppm(s).

6.2.2 Synthesis 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-4-methyl cyclopentan-5-one. COMPOUND 1B

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10^{0}C, cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{0}C and 0^{0}C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing 1,2-bis(diphenylphosphino)ethane (0.72g,1.82mmol) was then added to the reaction mixture, which was then allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed, which was removed by filtration, washed with cold diethyl ether (-10^{o}C, 2x50ml) and dried. The product, the title complex, was isolated as a yellow powder (0.8g,81.6%). Found: C, 66.7; H, 5.90: $C_{30}H_{30}NiO_2P_2$ requires C,66.4; H,5.50%.

I.R(KBR):cm^{-1}

ν_{max}=2949(w), 2918(w), 1634(vs), 1435(s), 1329(m), 1102(m), 745(m), 712(m), 702(m), 692(m), 532(m), 522(m), 485(m)

MASS SPECTRUM(FAB +ve ion, mNBA matrix):
M/z 1165 (6%), 1086(6%), 998(17%), 940(8%), 854(7%), 622(26%), 543[(66%), (M+H)$^+$], 542[(40%), (M)$^+$], 541[(100%), (M-H)$^+$], 456[(69%), (M-86)$^+$], 428(85%).

Accurate mass measurement M/z 541=541.098290 daltons. Calculated mass for $C_{30}H_{29}Ni^{58}O_2P_2$ =541.099629 daltons.
Accurate mass measurement M/z 543=543.10625 daltons. Calculated mass for $C_{30}H_{31}Ni^{58}O_2P_2$ =543.115279 daltons.

^{1}H NMR (CD$_2$Cl$_2$): δ=0.526 (dddd, 1H, $^2J_{H-H}$9.8Hz, $^2J_{H-P\ TRANS}$ 9.8Hz, $^2J_{H-P\ CIS}$ 5.4Hz, $^3J_{H-H}$ 5.4Hz, H$_A$/H$_B$), 0.927(d, 3H, CH$_3$ $^3J_{H-H}$7.32Hz), 1.064(dddd, 1H, $^2J_{H-P\ TRANS}$ 13.2Hz, $^2J_{H-H}$10.2Hz, $^2J_{H-P\ CIS}$ 6.8Hz, $^3J_{H-H}$ 4.4Hz, H$_A$/H$_B$), 1.7-1.9(br, 2H, dppe CH$_2$), 2.1-2.3(br, 2H, dppe CH$_2$), 2.3-2.4(br, 1H, H$_C$), 7.3-7.9ppm(m, 20H, Ph protons).

^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ=21.52(s, C$_C$), 22.66(dd, $^2J_{P-C}$28.3Hz, $^2J_{P-C}$11.4Hz, C$_A$), 29.3(dd, $^1J_{P-C}$59.8Hz, $^2J_{P-C}$23.0Hz, dppe bridge CH$_2$), 30.02(dd, $^1J_{P-C}$29.2Hz, $^2J_{P-C}$21.5Hz, dppe bridge CH$_2$), 42.39(s, C$_B$), 129.06-134.09(m, Ph), 190.9ppm(s, C$_D$).

^{13}C NMR (CD$_2$Cl$_2$): δ=42.39ppm(d, $^1J_{C-H}$126.03Hz)

^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ=58.46(s), 34.31ppm(s)

6.2.3 Synthesis 1-oxa-2-{1,2-bis (dicyclohexylphosphino) ethyl} nickela-4-methyl cyclopentan-5-one. COMPOUND 1C.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10^{0}C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{0}C and 0^{0}C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) of 1,2-bis(dicyclohexylphosphino)ethane (0.77g, 1.82mmol) was then added to the reaction mixture, which was allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10^{o}C, 2x50ml), and dried. The product, isolated as a yellow powder (0.8g,77.6%), was identified as the title complex. Found: C, 63.4; H, 8.90: $C_{30}H_{54}NiO_2P_2$ requires C,63.6; H,9.54%.

I.R(KBR): cm^{-1}

v_{max}=2926(vs), 2850(s), 1631(s), 1447(m), 1328(m), 1004(w), 851(w)

MASS SPECTRUM.
(FAB +ve ion, mNBA matrix): M/z 567[(75), $(M+H)^+$], 566[(40), $(M)^+$], 565[(100), $(M-H)^+$], 480[(48), $(M-86)^+$].
Accurate mass measurement M/z 565=565.283719 daltons. Calculated mass for $C_{30}H_{53}O_2P_2Ni^{58}$ =565.287430 daltons.
Accurate mass measurement M/z 566=566.290205 daltons. Calculated mass for $C_{30}H_{54}O_2P_2Ni^{58}$ =566.295255 daltons

(FAB -ve ion, mNBA matrix): M/z 551, [(42%), $(M-CH_3)^-$], 165(100).
(FAB +ve ion, Glycerol matrix): M/z 658[(14%), $(M+glycerol)^+$] 590[(94), $(M+H+Na)^+$], 567[(70), $(M+H)^+$], 566[(40), $(M)^+$], 565[(98), $(M-H)^+$], 480[(45), $(M-86)^+$], 456(74), 368(100)

^{1}H NMR ($CDCl_3$): δ=0.57(dddd, $^2J_{H-H}$9.28Hz, $^2J_{H-P\ TRANS}$ 9.28Hz, $^2J_{H-P\ CIS}$ 4.9Hz, $^3J_{H-H}$ 4.9Hz, 1H, H_A/H_B), 1.07(dddd, $^2J_{H-P\ TRANS}$ 10.3Hz, $^2J_{H-H}$10.3Hz, $^2J_{H-P\ CIS}$ 4.8Hz, $^3J_{H-H}$ 4.3Hz, 1H, H_A/H_B), 1.18 (d,3H, CH_3 $^3J_{H-H}$6.83Hz) 1.2-2.2(br, ligand CH_2), 2.39ppm(br,1H, H_C)

^{13}C{^{1}H} NMR ($CDCl_3$): δ=17.65(dd, $^2J_{P-C}$22.25Hz, $^2J_{P-C}$9.95Hz, C_A), 22.25(s, C_C) 23.11(dd, $^1J_{P-C}$64.4Hz, $^2J_{P-C}$26.1Hz, dcpe bridge CH_2), 24.83(dd, $^1J_{P-C}$24.6Hz, $^2J_{P-C}$23.0Hz, dcpe bridge CH_2), 26.5-30.28(m, Cyclohexyl CH_2) 33.75(d, $^1J_{P-C}$13.8Hz Cyclohexyl CH), 33.90(d, $^1J_{P-C}$15.3Hz Cyclohexyl CH), 35.44(d, $^1J_{P-C}$16.8Hz Cyclohexyl CH) 35.69(d, $^1J_{P-C}$18.4Hz Cyclohexyl CH), 42.28(s, C_B), 192.0ppm(s, C_D).

^{13}C NMR (CD_2Cl_2): δ=42.28ppm(d, $^1J_{C-H}$122.37Hz)

^{31}P{^{1}H} NMR (CD_2Cl_2): δ=68.84(s), 60.66(s). (d^8 toluene) δ=:69.7(s), 62.6(s). (d^8 THF). δ=:70.1(s), 62.9ppm(s)

6.2.4 Synthesis 1-oxa-2-{1,3-bis(dicyclohexylphosphino)propyl}nickela-4-methyl cyclopentan-5-one. COMPOUND 1D.

To a flask containing bis(cycloocta-1,5-diene) nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10^{o}C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{o}C and 0^{o}C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) of 1,3-bis(dicyclohexylphosphino)propane (0.79g, 1.82mmol) was then added to the reaction mixture, which was then allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10^{0}C, 2x50ml), and dried. The product, isolated as a yellow powder (0.5g, 47.4%), was identified as the title complex. Found: C, 62.72; H, 9.87: $C_{31}H_{56}NiO_2P_2$ requires C,64.1; H,9.65%

I.R(KBR):cm^{-1}

ν_{max}=2927(vs), 2848(s), 1643(vs), 1445(m), 1328(m), 1253(m), 849(w), 641(w)

MASS SPECTRUM
(FAB +ve ion, mNBA matrix): M/z 581[(95%), (M+H)$^+$], 580[(60), (M)$^+$], 579[(100), (M-H)$^+$], 494[(90), (M-86)$^+$].

^{1}H NMR (CDCl$_3$): δ=0.55(dddd, $^2J_{H-H}$9.28Hz, $^2J_{H-P\ TRANS}$ 9.28Hz, $^2J_{H-P\ CIS}$ 4.88Hz, $^2J_{H-H}$ 4.88Hz, 1H, H_A/H_B), 0.93(dddd, $^2J_{H-P\ TRANS}$ 10.49Hz, $^2J_{H-H}$10.49Hz, $^2J_{H-P\ CIS}$ 4.15Hz, $^3J_{H-H}$ 4.15Hz, 1H, H_A/H_B), 1.16(d, 3H, CH_3 $^3J_{H-H}$6.84Hz) 1.2-2.2(br, ligand CH_2), 2.48ppm(br, 1H, H_C)

$^{13}C\{^1H\}$ NMR (CDCl$_3$): δ=18.19(dd, $^2J_{P-C}$22.53Hz, $^2J_{P-C}$11.59Hz, C_A), 21.89(s, C_C) 24.01(d, $^1J_{P-C}$31.46Hz, dcpp bridge CH_2), 24.59(d, $^1J_{P-C}$27.6Hz, dcpp bridge CH_2), 26.5-32.0(m, Cyclohexyl CH_2) 33.33(d, $^1J_{P-C}$16.8Hz Cyclohexyl CH), 33.86(d, $^1J_{P-C}$18.4Hz Cyclohexyl CH), 36.57(d, $^1J_{P-C}$27.6Hz Cyclohexyl CH) 36.90(d, $^1J_{P-C}$27.6Hz Cyclohexyl CH), 42.47(s, C_B), 191.05ppm(d, $^4J_{P-C}$13.8Hz, C_D).

$^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ=31.62(d, $^3J_{P-P}$31.88Hz), 8.31ppm(d, $^3J_{P-P}$31.88Hz))

6.2.5 Synthesis 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-3-methyl cyclopentan-5-one. COMPOUND 1E.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10^{0}C cooled by means of a salt/ice bath. Crotonic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{0}C and 0^{0}C. The reaction solution was deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) of 1,2-bis(diphenylphosphino)ethane was then added to the reaction mixture, which was then allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10^{0}C, 2x50ml) and dried. The product was isolated as a yellow powder (0.6g). Further purification proved impossible, the powder isolated is therefore not analytically pure. Found: C, 63.73; H, 5.17: $C_{30}H_{30}NiO_2P_2$ requires C,66.4; H, 5.50%

I.R(KBR):cm^{-1}

ν_{max}=2921(m), 2849(m), 1634(vs), 1584(m), 1434(s), 1338(m), 1278(m), 1103(m), 754(m), 700(s), 692(s), 535(m), 518(m), 491(m)

MASS SPECTRUM:

(FAB +ve ion, mNBA matrix): M/z 543[(18%), (M+H)$^+$], 542[(10), (M)$^+$], 541[(20), (M-H)$^+$], 456[(23), (M-86)$^+$], 431(88), 297[(100), (tricyclohexylphosphineoxide)]. Accurate mass measurement M/z 541=541.109000 daltons. Calculated mass for $C_{30}H_{29}O_2P_2Ni^{58}$ =541.099629daltons.

^{1}H NMR ($CDCl_3$): δ=0.53(t, 3H, $^3J_{H-H}$ 7.32Hz,CH_3), 1.42(m,1H, H_A), 1.64(ddd, 1H, $^2J_{H-H}$ 15.66Hz, $^4J_{H-P}$ 12.18Hz, $^3J_{H-H}$ 5.86Hz, 1H, H_B/H_C), 1.7-1.9(br,2H, dppe CH_2), 2.1-2.3(br, 2H, dppe CH_2), 3.06(dd, 1H, $^2J_{H-H}$ 16.6Hz, $^3J_{H-H}$ 6.35Hz H_B/H_C), 7.3-7.9ppm(m, 20H)

^{13}C{^{1}H} NMR ($CDCl_3$): δ=18.92(s,C_C), 21.58(dd $^2J_{P-C}$28.3Hz, $^2J_{P-C}$10.0Hz C_A) 28.64(dd, $^1J_{P-C}$30.6Hz, $^2J_{P-C}$20.0Hz dppe bridge CH_2), 30.0-31.5(br, dppe bridge CH_2), 46.05(s, C_B), 128-133(m, Ph), 189.24ppm(d, $^4J_{P-C}$13.8Hz, C_D).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ=56.68(d, $^3J_{P-P}$9.76Hz), 35.49ppm(d, $^3J_{P-P}$9.76Hz)

6.2.6 Synthesis 1-oxa-2- {1,2-bis (dicyclohexylphosphino) ethyl} nickela-3-methyl cyclopentan-5-one. COMPOUND 1F.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10^{o}C cooled by means of a salt/ice bath. Crotonic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10^{o}C and 0^{o}C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing 1,2-bis(dicyclohexylphosphino)ethane (0.77g,1.82mmol) was then added to the reaction mixture, which was then allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10^{o}C, 2x50ml) and dried *in vacuo*. The product was isolated as a yellow powder (0.5g). Further purification proved impossible, the powder isolated is therefore not analytically pure. Found: C, 61.56; H, 9.44: $C_{30}H_{54}NiO_2P_2$ requires C,63.60; H, 9.54%.

I.R(KBR):cm^{-1}

ν=2922(vs), 2848(s), 1623(vs), 1445(m), 1336(w), 1282(w), 1177(w), 1003(w), 887(w), 851(w).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 567[(85%), $(M+H)^+$], 566[(55), $(M)^+$], 565[(100), $(M-H)^+$], 480[(55), $(M-86)^+$], 455(36), 297(77), 281(62), 154(53), 136(40).

^{1}H NMR (CDCl$_3$): δ=1.036 (t, 3H,$^{3}J_{H-H}$ 7.1Hz, CH$_3$), 1.14-2.2(br), 2.80ppm(dd, 1H, $^{2}J_{H-H}$ 16.6Hz, $^{3}J_{H-H}$ 5.86Hz, H$_B$/H$_C$).

^{13}C{^{1}H} NMR (CDCl$_3$): δ=15.5(s, C$_C$), 20.5(br C$_A$), 26.0-37.0(m) 46.5ppm(s, C$_B$)

^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ=69.52(s), 63.09(d, $^{3}J_{P-P}$ 4.88Hz), 62.84(s), 61.49(d, $^{3}J_{P-P}$ 4.88Hz), 10.0ppm(s)

6.2.7 Synthesis 1-oxa-2-{2-[2-(dicyclohexylphosphino)ethyl]pyridyl}nickela-4-methyl cyclopentan-5-one. COMPOUND 1G.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10°C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10°C and 0°C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing 2-[2-(dicyclohexylphosphino)ethyl]pyridine, (0.55g, 1.82mmol) was then added to the reaction mixture, which was allowed to warm to room temperature with stirring for a further 2 hours. A yellow precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10°C, 2x50ml) and dried *in vacuo.* The product, isolated as a yellow powder (0.6g, 73.7%), was identified as the title complex. Found: C, 62.38; H, 8.92; N, 2.43: $C_{23}H_{36}NNiO_2P$ requires C,61.70; H, 8.05; N, 3.13%

I.R(KBR):cm^{-1}
ν=2929(vs), 2850(s), 1629(vs), 1604(s), 1445(m), 1339(m), 774(m).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 450(32%), 44[(87), $(M+H)^+$], 361(51), 279(47), 197(100), 106(85)

^{31}P{^{1}H} NMR TOLUENE δ= 44.33(s), 43.93(s), 37.31(s), 34.82(s), 33.24(s), 23.07ppm(s)

^{11}H NMR CDCl$_3$: δ=0.57(br, 1H, H$_A$/H$_B$), 0.79(br, 1H, H$_A$/H$_B$), 1.27(br, 3H, CH$_3$), 1.3-2.2(br, cyclohexyl CH$_2$), 2.54(s, 1H, H$_C$), 7.1-9.1ppm(m, 4H, pyridyl H).

$^{13}C\{^{1}H\}$ NMR $CDCl_3$: δ=12.26(br, C_A), 12.94(br, ethyl bridge CH_2), 21.67(s, C_C), 25.3-29.1(m, Cyclohexyl CH_2), 31.77(d, $^{1}J_{P\text{-}C}$27.6Hz Cyclohexyl CH), 32.17(d, $^{1}J_{P\text{-}C}$27.6Hz Cyclohexyl CH), 34.81(s, ethyl bridge CH_2), 43.13(s, C_B), 122.85(s, pyridyl CH), 123.83(s, pyridyl CH),138.15(s, pyridyl CH),151.61(s, pyridyl CH),160.21ppm(s, pyridyl CH)

6.2.8 Synthesis 1-oxa-2-(2,2-bipyridyl)nickela-4-methyl cyclopentan-5-one. COMPOUND 1H.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10°C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10°C and 0°C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing 2,2'-bipyridine (0.28g, 1.82mmol) was then added to the reaction mixture, which was allowed to warm to room temperature with stirring for a further 2 hours. A purple precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10°C, 2x50ml) and dried *in vacuo*. The product was isolated as a purple powder (0.4g). Further purification proved impossible, the powder isolated is therefore not analytically pure. Found: C, 51.30; H, 4.30; N, 8.3: $C_{14}H_{14}N_2NiO_2$ requires C, 56.0; H, 4.66; N, 9.30%.

I.R(KBR):cm^{-1}

v_{max}=2920(m), 2848(w), 1630(vs), 1606(m), 1600(m), 1568(m), 1472(m), 1443(m), 1330(w), 1310(w), 767(m), 727(w).

MASS SPECTRUM: (FAB +ve ion, mNBA matrix): M/z 372(15%), 370[(28%), $(Bipy)_2Ni)]$, 305(8%), 303(12%), 301[(22), $(M+H)^{+}$], 297(30), 295(21%), 233(8%), 231(18%), 216(44%), 214[(100), $(M-86)^{+}$], 185(15%), 93(18%).

^{1}H NMR ($CDCl_3$): δ=1.02 (d, 3H, $^{3}J_{H\text{-}H}$ 6.83Hz, CH_3), 1.11(d, 1H, $^{2}J_{H\text{-}H}$ 8.3Hz H_A/H_B), 1.43(t, 1H, $^{2}J_{H\text{-}H}$= $^{3}J_{H\text{-}H}$=8.3Hz H_A/H_B), 1.16(d, 2H cyclohexyl CH_2 impurity) 1.5-1.8(br, xH cyclohexyl CH_2 impurity), 2.21 (d,1H,$^{3}J_{H\text{-}H}$ 6.84Hz H_C), 7.2-8.7ppm(8H bipy H)

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=18.4 (s, C_A), 21.78 (s, C_C), 42.66 (s, C_B), 121.2, 121.88, 122.29, 127.55, 139.47, 139.97, 150.01, 150.81, 156.2 (Bipy carbon signals), 191.24ppm(s, C_D)

6.2.9 Synthesis 1-oxa-2-(1,10 phenanthroline)nickela-4-methyl cyclopentan-5-one. COMPOUND 1I.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10°C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10°C and 0°C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing 1,10 phenanthroline (0.33g, 1.82mmol) was then added to the reaction mixture, which was allowed to warm to room temperature with stirring for a further 2 hours. A purple precipitate was formed in the reaction which was removed by filtration, washed with cold diethyl ether (-10°C, 2x50ml) and dried in vacuo The product was isolated as a purple powder (0.4g). Further purification proved impossible, the powder isolated is therefore not analytically pure. Found: C, 59.0; H, 5.50; N, 6.60: $C_{16}H_{14}N_2NiO_2$ requires C, 56.0; H, 4.66; N, 9.30%

I.R(KBR):cm^{-1}

ν=2923(vs), 2849(m), 1625(vs), 1604(vs), 1578(vs), 1571(vs), 1514(m), 1449(m), 1425(s), 1411(m), 1362(m), 1342(m), 849(s), 728(s).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 391(42%), 325[(2), (M+H)$^+$], 307(24%), 297(48%), 281(74%), 240(8), 238(18), 154(100%), 136(84%).
(FAB +ve ion, Glycerol matrix): M/z 420(18%), 418[(40%), (M+H+ glcerol)$^+$], 325[(10%), (M+H)$^+$], 297(80%), 240(50%), 238[(100%), (M-86)$^+$], 181(10%), 133(84%).

^{1}H NMR (CDCl$_3$): δ=1.08 (br, 3H, CH$_3$), 1.2-2.1(br, cyclohexyl CH$_2$) 2.25 (br, 1H, H$_C$), 7.5-9.0ppm(m 8H, Phen H).

^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) : δ=17.33 (s, C$_A$), 21.38 (s, C$_C$), 125.9, 126.65, 126.98, 127.31, 129.29, 129.95, 137.36, 137.69, 144.62, 148.58, 149.85, 150.23 (Phen carbon signals), 191.32 ppm(s, C$_D$)

6.2.10 Synthesis 1-oxa-2-(tetramethylethylenediamino)nickela-4-methyl cyclopentan-5-one. COMPOUND 1J.

To a flask containing bis(cycloocta-1,5-diene)nickel(0) (0.5g, 1.82mmol) and tricyclohexylphosphine (0.51g, 1.82mmol) was added tetrahydrofuran (20.0ml) at -10°C cooled by means of a salt/ice bath. Methacrylic acid (0.16g ,1.86mmol) was added dropwise to the reaction mixture. The reaction was allowed to stir for 24 hours with the temperature maintained at between -10°C and 0°C. The reaction solution became deep yellow/brown in colour. A tetrahydrofuran solution (10.0ml) containing N,N,N',N' tetramethylethylenediamine (0.21g, 1.82mmol) was then added to the reaction mixture, which was allowed to warm to room temperature with stirring for a further 2 hours. Solvent was removed *in vacuo* and the residue washed with cold diethyl ether (-10°C, 2x50ml) and dried *in vacuo*. The product was isolated as a yellow/green powder (0.2g). Further purification proved impossible, the powder isolated is therefore not analytically pure. Found: C, 43.90; H, 7.30; N, 6.60: $C_{10}H_{22}N_2NiO_2$ requires C, 46.15; H, 8.46; N, 10.76%

I.R(KBR):cm^{-1} v=2924(m), 2852(m), 1652(m), 1624(vs), 1576(m), 1464(m), 1448(m), 1343(w), 807(w).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 342 (16%), 340(37%), 297(100%), 281(85%), 263(4), 261[(11), (M+H)$^+$], 154(27%), 136(24%), 117(33%).

SECTION 6.3.0 - FURTHER REACTIONS OF OXA-NICKELA-CYCLOPENTANONES

6.3.1 Reaction of 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-4-methyl cyclopentam-5-one(1C) with malaeic anhydride.

To an orange yellow solution of compound 1C (0.5g, 0.88mmol) in anhydrous dichloromethane(50ml) was added maleic anhydride (0.17g, 1.76mmol) dropwise as a solution in dichloromethane(20ml). Immediately after addition, a colour change occurred, the solution turning a deeper orange colour. The reaction mixture was allowed to stir for 1hour, but no further colour change occurred. The reaction was sampled by means of a syringe and analysed by GC-MS. The solvent was removed under vacuum from the remainder and the solid residue identified as predominantly [(dcpe)Ni{OOCCHCHCOO}] washed twice with cold diethyl ether(-10^{0}C) and dried. Found: C, 59.2; H, 6.70: $C_{30}H_{50}NiO_2P_2$ requires C, 60.6; H, 8.40%

I.R(KBR): v_{max}=2926(vs), 2852(s), 1781(w), 1644(s), 1601(vs), 1585(sh), 1447(m), 1367(s)

MASS SPECTRUM:

(FAB +ve ion, mNBA matrix): M/z 595[(95%), $(M+H)^+$], 565(25), 480(26), 154(34), 136(57), 73(80).

Accurate mass measurement M/z 595=595.2704 daltons. Calculated mass for $C_{30}H_{51}O_4P_2Ni^{58}$ =595.26161 daltons.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ=76.8(s), 68.96(s), 60.69(s), 24.58ppm(s)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ= 21.33 (d, $^2J_{P-C}$19.9Hz), 21.53 (d, $^2J_{P-C}$19.9Hz), 26.83 (s), 27.76 (d, $^2J_{P-C}$16.8Hz), 27.94(d, $^2J_{P-C}$6.1Hz), 29.46(s), 30.29(s), 34.79(d, $^1J_{P-C}$10.7Hz), 34.90(d, $^1J_{P-C}$ 10.8Hz) 133.97 (s), 171.38ppm(s).

H NMR (CD_2Cl_2):δ=1.2-2.4(br), 6.22ppm(br)

6.3.2 Thermal decomposition of 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-4-methylcyclopentan-5-one(1C) at atmospheric pressure.

A solution of compound 1C (100mg, 0.18mmol) in toluene(100ml) was introduced into a clean dry flask under a nitrogen atmosphere. A condenser was fitted to the flask which was heated with stirring to 110^{0}C for 1 hour, the solution darkened in colour from yellow to orange. The reaction solution was allowed to cool after which the solvent was removed *in vacuo* and the solid (A) remaining stored for analysis.

Analysis of isolated solid (A):

$^{31}P\{^{1}H\}$ NMR (toluene): δ= 69.8(s), 68.4(s), 63.66(s), 62.88(d, J 72.46Hz), 62.71(s), 60.05(s), 58.27(d, J 72.22Hz), 53.87(s), 47.10(s), 44.38(s), 33.74(s), 33.51(s), 33.33(s), 33.10(s), 29.39ppm(s).

^{1}H NMR: (d^{8}toluene) δ= -23.76(t, $^{2}J_{P\text{-}C}$77.4Hz, Ni-H), 0.25(s), 0.85(br), 1.2-2.1(br), 2.15ppm(s)

IR KBr cm^{-1} :ν_{max}=3085(w), 3025(w), 2924(vs), 2850(vs), 1894(m), 1772(w), 1632(s), 1446(s).

The solid sample (A) was redissolved in toluene 1 week later and reanalysed .

$^{31}P\{^{1}H\}$ NMR (toluene): δ=80.09(s), 69.49(s), 68.23(s), 62.47(s), 53.66(s), 46.77(s), 33.49(s), 33.27(s), 33.08(s), 32.85(s),28.94ppm(s).

^{1}H NMR: (d^{8}toluene) δ=0.27(s), 0.86(br), 1.2-2.0(br), 2.08ppm(s,toluene).

To the isolated solid sample (A), 50mg, was added deuterated chloroform(5ml). Immediately on addition of the chloroform a purple colour formed. An aliquot was taken by means of a syringe for NMR analysis. The solvent was removed *in vacuo* from the remaining solution, the product being isolated as a purple crystallline material (30mg).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ= 82.87(s), 73.06(s), 63.26(s), 39.81(s), 38.80(s), 24.76ppm(s)

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=20.276(s), 21.97(br), 24.82(s), 25.84(s), 26.07(s), 28.06(s), 28.92(s), 35.13(d, J 10.7), 35.24ppm(d, J 12.3).

IR KBr cm^{-1} :ν_{max}= 2924(vs), 2850(s), 2219(w), 2056(w), 1978(w), 1757(w), 1714(w), 1622(w), 1603(w), 1445(m), 1005(m), 850(w), 729(m), 535(w).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 517(5), 515(7), 437(42), 327(8), 281(15), 207(18), 147(39), 73(100).

6.3.3 Thermal decomposition of 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-4-methylcyclopentan-5-one(1C) when subjected to a pressure of propene/CO2.

A stirred solution of compound 1C (100mg, 0.18mmol) in toluene(100ml) was introduced into a previously evacuated and purged Bucchi glass autoclave at room temperature. A previously weighed stainless steel Whitey cylinder containing propylene was then connected to the unit before being opened to the vessel for 30 seconds. After the propene gas (8g, 180mmol) had been allowed to dissolve into the solution carbon dioxide gas (8 bar total pressure) was charged to the unit before the autoclave was isolated . The stirred reaction solution was heated to 110^{0}C by means of a silicone oil bath and held at this temperature for 1 hour . The reaction solution was allowed to cool, depressurised and an aliquot taken by means of a syringe for ^{31}P NMR analysis. The contents of the autoclave were transferred to a flask by means of a cannula, and the solvent was removed *in vacuo* to yield a yellow powder(100mg) .

^{31}P{^{1}H} NMR (toluene): δ=80.43(s), 69.68(s), 62.64(s), 47.23(s), 46.05(s), 9.99ppm(s)

IR (KBr) cm^{-1} :ν_{max}= 2925(vs), 2850(s), 1632(s), 1446(m)

^{13}C{^{1}H} NMR (CDCl$_3$): δ=17.13(dd, J 20.65Hz, 9.95Hz), 21.4(s), 22.24(s), 23.05(dd, J 61.4Hz, 26.1Hz), 24.6(dd, J 23.0Hz, 23.0Hz), 25.5-29.94(m, cyclohexyl CH$_2$), 33.44(d, J 15.4Hz), 33.28(d, J 16.9Hz), 35.12(d, J 6.1Hz), 35.38(d, J 6.1Hz), 36.09(m), 36.84(s), 42.22(s), 192.03ppm(d, J 12.3Hz).

SECTION 6.4.0 AUTOCLAVE REACTIONS

Synthesis of Oxa nickela Cyclopentanones from Carbon Dioxide and Propene.

Section 6.4.1 Synthesis of 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-4-methylcyclopentan-5-one and 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl} nickela-3-methylcyclopentan-5-one from bis(cycloocta-1,5-diene)nickel(0), 1,2-bis (dicyclohexylphosphino)ethane, propene and carbon dioxide.

The glass autoclave assembly, containing magnetic follower was sealed before being evacuated and purged with dry nitrogen three times. To the vessel was added a solution of bis(cycloocta-1,5-diene)nickel(0) (2.0g, 7.3mmol) in tetrahydrofuran (50ml) at room temperature by means of a canula. The mixture was stirred and cooled to -50^{o}c before 1,2-bis(dicyclohexylphosphino)ethane (3.1g, 7.3mmol) was added dropwise as a solution in tetrahydrofuran at -50^{o}c by means of a syringe. A previously weighed stainless steel Whitey cylinder containing propene was then connected to the unit before being opened to the vessel for 30 seconds. After the propylene gas (8g, 190mmol) had been allowed to condense into the solution, the autoclave was sealed and allowed to stir at -50^{o}c for 1 hour. Carbon dioxide gas (7 bar) was then charged to the unit before the autoclave was isolated again and allowed to stir at -50^{o}C for 18 hours. The cold bath was then removed and the mixture allowed to warm slowly to room temperature. During this time, the yellow solution darkened to brown and the initially present yellow precipitate dissolved. After 24 hours, the remaining pressure in the autoclave was vented to the atmosphere, and the solution was allowed to degas under nitrogen. The contents were then transferred to a flask by means of a canula. An aliquot of solution (2ml) was retained for analysis, the remaining material being concentrated under reduced pressure until a precipitate was observed to form. The latter mixture was then cooled to -50^{o}c, filtered and the solid, a yellow powder, compound A(2.5g), was washed with diethyl ether (3 x 10ml) at -50^{o}c before drying in vacuo.

Data for Compound A.

I.R. (KBr)cm^{-1} v_{max}= 2926(vs), 2849(s), 1623(vs), 1447(m), 1335(m), 851(w), 533(w).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ= 80.5(s), 68.5(s), 62.8(s), 61.2(s), 60.4ppm(s)

$^{31}P\{^{1}H\}$ NMR (THF) δ=70.21(s), 64.49(s), 63.96(s), 62.96(s), 60.54ppm(s).

$^{31}P\{^{1}H\}$ NMR (Toluene) δ= 68.31(s), 62.58(s), 62.14(s), 62.10(s), 61.75(s), 61.16(s), 58.90ppm(s)

^{1}H NMR ($CDCl_3$): δ=0.57(dddd, J 9.28Hz, J 9.28Hz, J 4.9Hz, J 4.9Hz), 1.036 (t, J 7.1Hz) 1.19 (d, J 6.83Hz) 1.2-2.2(br, ligand CH_2 both isomers), 2.39(br), 2.80ppm(dd, J 16.6Hz, J 5.37Hz).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ=15.43(s), 16.09(d, J 7.6Hz), 17.63(dd, J 21.5, J 9.2), 17.98(d, J 9.2), 18.21(d, J 10.7), 22.25(s), 23.08(dd, J 61.3. J 24.5), 24.80(dd, J 23.0, J 23.0), 26.5-30.5(m, cyclohexyl CH_2), 31.36(s), 33.46(d, J 13.8), 33.60(d, J 13.8), 33.74(d, J 13.8), 33.88(d, J 15.4), 34.21(d, J 16.9), 35.08(d, J 23.0), 35.43(d, J 16.9), 35.69(d, J 16.9), 36.47(d, J 24.6), 36.65(d, J 35.3), 42.28(s), 46.77(s), 188.20(s), 191.03ppm(d, J 13.8Hz)

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 646(94), 567(60), 566(40), 565(100), 480(42).

The supernatant liquor and ether washings were concentrated *in vacuo* to yield a yellow green powder, compound **B** (1.5g), which was washed with diethyl ether (3 x 50ml) before drying *in vacuo*.

Data for Compound **B**.
I.R. (KBr)cm^{-1} ν_{max}= 2925(vs), 2849(s), 1631(w), 1445(m), 1000(w), 850(w), 730(w), 649(w), 524(w), 455(w).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ=80.5(s), 68.5(s), 60.4ppm(s)

$^{31}P\{^{1}H\}$ NMR (THF) δ=70.19(s), 62.96(s), 60.5(s), 47.12(s), 46.18ppm(s).

$^{31}P\{^{1}H\}$ NMR (Toluene) δ=68.25(s), 62.49(s), 62.14(s), 62.10(s), 61.69(s), 61.18(s), 58.91ppm(s).

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 646(24), 567(5), 566(4), 565(6), 480(42).

The reaction mixture was analysed by GC-MS .

Hydrolysis of Reaction Products

6.4.2 Standard Reaction

The reaction was carried out as per section 6.4.1 with the following exception. No separation was performed at the end of the reaction, solvent being removed completely under vacuum to yield one fraction. To this fraction, in a round bottomed flask at room temperature was added aqueous sulphuric acid (2.0M, 200ml), and the resulting mixture was stirred for 2 hours. The reaction mixture was then extracted with diethylether (3x50ml) and the combined extracts washed with aqueous sodium hydroxide 1.0M (3x50ml). The basic liquor was acidified with sulphuric acid to pH < 4.0, before being extracted with diethylether (3x50ml) . The ether extracts were dried (magnesium sulphate), and the solvent removed at reduced pressure to yield an oil which was shown to be a mixture of normal and isobutanoic acid(0.60g, 6.76mmol, 62.0%, n:iso 1:2. The carboxylic acid sample was analysed by GC-MS .

Section 6.4.3 Effect of temperature

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene)nickel(0) (2.8g,10.2mmol), 1,2-bis(dicyclohexylphosphino)ethane (4.3g, 10.18mmol), propene(8.0g,190mmol) and carbon dioxide(7 bar) . After stirring at room temperature for 24 hours, the reaction was heated to 60^{0}C for 2 hours during which time no change in colour was observed. The reaction was hydrolysed as per section 6.4.2 to yield an oil which was shown to be a mixture of normal and iso-butanoic acid(0.39g, 4.43mmol, 43.4%, n:iso 1:1.45). The carboxylic acid sample was analysed by GC-MS .

Section 6.4.4 Effect of solvent

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene)nickel(0) (2.0g,7.3mmol), 1,2-bis(dicyclohexylphosphino)ethane(3.1g, 7.3mmol), propene(8.0g,190mmol) and carbon dioxide(7 bar) . The solvent used in this reaction was acetonitrile/tetrahydrofuran, 90/10. On addition of acetonitrile to Ni(COD)$_2$, a dark colour developed (almost black) and a green precipitate formed. Tetrahydrofuran was used as a solvent for the DCPE which is insoluble in small volumes of acetonitrile. The reaction temperature was -40^{0}C . After stirring overnight at -40^{0}C a grey precipitate developed. The supernatent solution was brown in colour. The reaction was hydrolysed as per section 6.4.2 to yield an oil, which was shown to be a mixture of normal and iso-butanoic acid(0.20g, 2.24mmol, 30.7%, n:iso 1:1.2). The carboxylic acid sample was analysed by GC-MS .

Data for solid before hydrolysis.

I.R, (KBr)cm^{-1} ν_{max}= 2923(vs), 2849(s), 1982(s), 1910(sh), 1903(s), 1654(s), 1630(vs), 1445(s), 1334(m), 1001(m), 850(m), 750(m),

MASS SPECTRUM
(FAB +ve ion, mNBA matrix): M/z 733(10), 648(47), 646(100), 618(10), 567(19), 566(14), 565(26), 510(11), 480(17), 136(18).

Section 6.4.5 Synthesis of 1-oxa-2-{2-[2-(dicyclohexylphosphino)ethyl]pyridyl}nickela-4-methylcyclopentan-5-one and 1-oxa-2-{2-[2-(dicyclohexylphosphino)ethyl]pyridyl}nickela-3-methylcyclopentan-5-one from bis(cycloocta-1,5-diene)nickel(0), 2-[2-(dicyclohexylphosphino)ethyl]pyridine, propene and carbon dioxide

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene) nickel(0) (1.1g, 4.0mmol), 2-[2-(dicyclohexylphosphino)ethyl]pyridine (1.23g, 4.1mmol), propene (8.0g,190mmol) and carbon dioxide (7 bar). At the end of the reaction the solvent was removed *in vacuo* and a yellow powder (1.7g) was isolated. Found: C, 59.8; H, 6.80; N, 3.10: $C_{23}H_{36}NNiO_P$ requires C, 61.7; H, 8.0; N, 3.10%

Data for Product.

I.R, (KBr)cm^{-1} ν_{max}= 2929(vs), 2850(s), 1629(vs), 1604(s), 1445(m), 1339(m), 774(m)

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 450(42), 449(32), 448(100), 363(40), 362(28), 361(94), 320(73), 197(27), 154(55), 136(39).

^{1}H NMR (CDCl$_3$): δ=0.5(br), 0.85(br), 1.1(br), 1.2-2.0(br, cyclohexyl CH$_2$), 2.05(br), 2.3(br), 7.1-8.9ppm (br, pyridyl protons).

^{13}C{^{1}H} NMR (CDCl$_3$): δ= 13.56(br), 13.76(br), 21.58(br), 25.87(br), 26.20-28.78(m, 10 signals), 32.50(d, J 27.7), 33.03(d, J 27.6), 35.22(s), 35.54(s), 122.85(s), 123.83(s), 138.15(s), 151.61(s), 160.21ppm(s).

^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ=38.28ppm(s), 34.22ppm(s)

6.4.6 Hydrolysis of reaction products.

The reaction was hydrolysed as per 6.4.2 to yield an oil which was shown to be a mixture of normal and iso-butanoic acid (0.28g, 3.2mmol, 80.0%, n:iso 1:3.2. The carboxylic acid sample was analysed by GC-MS .

Section 6.4.7 Synthesis 1-oxa-2-{1,2-bis(dicyclohexylphosphino)propyl}nickela-4-methylcyclopentan-5-one and 1-oxa-2-{1,2-bis(dicyclohexylphosphino)propyl} nickela-3-methylcyclopentan-5-one from bis(cycloocta-1,5-diene)nickel(0), 1,3-bis (dicyclohexylphosphino)propane, propene and carbon dioxide

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene) nickel(0) (1.1g,4.0mmol), 1,3-bis (dicyclohexylphosphino)propane (1.70g, 4.0mmol), propene (8.0g, 190mmol) and carbon dioxide (7 bar). At the end of the reaction the solvent was removed *in vacuo* and a yellow powder (1.9g) was isolated.

Data for Yellow Powder:

I.R, (KBr)cm^{-1} ν_{max}= 3035(w), 2929(vs), 2850(s), 1978(m), 1915(m), 1636(m), 1449(s)

MASS SPECTRUM:
(FAB +ve ion, mNBA matrix): M/z 632(40), 579(92), 494(86), 166(100).

^{1}H NMR (d$_8$ Toluene) δ= 0.269(br), 0.862(br), 1.1-2.2(m), 2.2(br), 4.25ppm(s).

$^{31}P\{^1H\}$ NMR (Toluene) δ=46.47(s), 31.45(d, J= 31.7Hz), 27.36(s), 23.93(d,J 32.21Hz), 22.91(d, J 32.20Hz), 19.72(s), 9.08ppm(d, J=31.7Hz)

Section 6.4.8 Reaction of bis(cycloocta-1,5-diene)nickel(0), 2,2-Bipyridine, Propene and Carbon Dioxide

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene) nickel(0) (1.1g, 4.0mmol), 2,2-bipyridine (0.62g, 4.0mmol), propene(8.0g,190mmol) and carbon dioxide(7 bar).

At the end of the reaction, the reaction solution was sampled (1ml) for analysis by GC-MS. The remainder of the solvent was removed under vacuum and a powder isolated (1.0g).

Data for Powder:

I.R, (KBr)cm^{-1} ν_{max}= 2043(w), 1973(m), 1880(m), 1799(w), 1638(br, m), 1605(m), 1599(m), 1516(s), 1492(s), 1473(s), 1449(s), 1344(m), 1310(m)

Above 3000cm^{-1} broad hump.

MASS SPECTRUM

(FAB +ve ion, mNBA matrix): M/z 536(12), 380(30), 370(20), 281(10), 231(10), 214(100), 147(20), 133(14), 73(68).

Section 6.4.9 Reaction of bis(cycloocta-1,5-diene)nickel(0), Tetramethylethylenediamine, Propene and Carbon Dioxide

The reaction was carried out as per section 6.4.1 using bis(cycloocta-1,5-diene) nickel(0) (1.1g, 4.0mmol), N,N,N,'N',-tetramethylenediamine(0.46g, 4.0mmol), propene(8.0g,190mmol) and carbon dioxide(7 bar).

At the end of the reaction, the reaction solution was sampled (1ml) for analysis by GC-MS. The remainder of the solvent was removed under vacuum and a powder isolated (0.5g).

Data for Product.

I.R, (KBr)cm^{-1} ν_{max}= 3009(m), 2979(m), 2955(m), 2888(m), 2842(m), 1652(m), 1635(m) 1520(br), 1464(s), 1389(br), 1449(s), 1344(m), 1310(m)

MASS SPECTRUM

(FAB +ve ion, mNBA matrix): M/z 574(10), 530(15), 457(10), 340(10), 174915), 115(50), 72(75), 58(100).

Section 6.4.10 Reaction of bis(cycloocta-1,5-diene) nickel(0), Tricyclohexylphosphine, Propene and Carbon Dioxide

The reaction was carried out as per section 6.4.1 using bis (cycloocta-1,5-diene) nickel(0) (1.1g,4.0mmol), tricyclohexylphosphine (1.0g, 6.6mmol), propene (8.0g,190mmol) and carbon dioxide (7 bar).

At the end of the reaction, the reaction solution was sampled (1ml) for analysis by GC-MS. The remainder of the solvent was removed under vacuum and a powder isolated (1.0g).

Data for Product:

I.R, (KBr)cm^{-1} ν_{max}= 3037(m), 3004(w), 2981(m), 2953(m), 2924(s), 2904(s), 2865(s), 2817(s), 1923(w), 1899(w), 1882(w), 1517(m), 1507(m), 1471(m), 1429(m), 1323(m), 1234(m), 1215(m), 856(m), 814(m), 750(m).

(FAB +ve ion, mNBA matrix): M/z 469(12), 391(35), 307((23), 297(37), 280(22), 154(100), 136(85).

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CHAPTER SEVEN

DISCUSSION OF RESULTS

Oxidative addition of methacrylic and crotonic acids to phosphine liganded Ni(0) and ligand exchange reactions . Synthesis of model compounds.

CHAPTER SEVEN

DISCUSSION OF RESULTS

Oxidative addition of methacrylic and crotonic acids to phosphine liganded Ni(0) and ligand exchange reactions . Synthesis of model compounds.

7.1.1 SYNTHESIS OF Tetra{1-oxa-2-(tricyclohexylphosphino)Nickela-4-methyl cyclopentan-5-one, COMPOUND 1A.

The reaction $Ni(COD)_2$ + tricyclohexylphosphine + methacrylic acid has been studied by other workers, usually in an attempt to prepare complexes of the type

$[L_2\overline{Ni\{CH_2CH(CH_3)COO\}}]$ where L = DPPE, DPPP, DPPB most commonly (1,2,3).

The primary interest of the present work has also been as a route to stable chelate phosphine and amine complexes of particular interest here because they may be intermediates in the proposed catalytic cycle involving oxidative coupling of propene and carbon dioxide. The nature of these complexes has been investigated in detail. The exact stoichiometry of the complexes formed using $Ni(COD)_2$ + tricyclohexylphosphine + methacrylic acid has not been reported previously. The closest analagous chemistry is that of the cyclic amides of the type $[(PR_3)_n$ $\overline{Ni\{CH_2CH(R^1)CONR^{11}\}}]$. Yamamoto et al (1,2) reported the synthesis of a complex proposed as $[(PCy_3)Ni\{\overline{CH_2CH(CH_3)CONH}\}]_{n1}$ (n_1, undetermined) from $Ni(COD)_2$ + tricyclohexylphosphine + methacrylamide. They performed a ligand exchange reaction using triethylphosphine and isolated a complex for which a crystal structure showed it to be $[(PEt_3)\overline{Ni\{CH_2CH(CH_3)CONH\}}_4]$. Previous to the crystal structure determination, the complex was thought to be a trimer on the basis of cryoscopic molecular weight determinations.

The exact 1:1 stoichiometry of the reactants was found in the present work to be important in the cyclization of the methacrylic acid. If greater than one equivalent of acid is present, there is a tendency to form π-complexes as has been reported by Yamamoto et al (1). The material isolated is a yellow powder, not uncommon for Ni-phosphine complexes, and is extremely air-sensitive. The material was recrystalised from hot hexane to yield yellow needle shaped crystals. Attempts to obtain a crystal structure proved impossible. Complete removal of the solvent resulted in collapse of the crystal structure and even when the crystals were kept in the presence of hexane and mounted in oil a structure could not be resolved. There appeared to be insufficient order in the crystals. They looked like well-formed crystals but, in fact, were not.

The evidence that the product of the cyclohexylphosphine complex is a tetramer is based on data from several spectroscopic techniques which is presented below.

Mass Spectra(see section 6.2.1)

Two sector FAB positive ion mass spectrometry of the product yielded an ion M/z 1721. Expansion of this area of the spectrum revealed a complex feature consisting of peaks ranging from M/z 1719 to M/z 1729 (see Figure 7.1), assigned to

$[(PCy_3)Ni\{\overline{CH_2CH(CH_3)COO}\}_4 + Na]^+$. The ion observed is the positively charged molecular ion + sodium. The presence of sodium containing derivatives is common using this technique(4). The complexity of the feature is fully accounted for by considering the isotopes of the component atoms and their relative natural abundances in nature.

Complementary evidence supporting the assignment comes from comparison of the raw data with a synthesized (instrument generated) isotope pattern (see Figure 7.1) for a compound having the elemental composition $C_{88}H_{156}O_8P_4Ni_4Na_1$, i.e. equivalent to

$[(PCy_3)Ni\overline{CH_2CH(CH_3)COO})_4$ + Na. Comparison of the relative peak ratios and absolute masses shows the two spectra to be identical.

Further supportive evidence comes from a tandem MS-MS experiment where the ion M/z 1721 was selected and bombarded in a collision chamber with Argon molecules of 4kV energy. The fragment ions generated were detected. Analysis of the fragment ions gives structural information on the nature of the 1721 ion as all fragment ions were generated from it. Several ions have been tentatively assigned and are consistent with the proposed tetrameric structure (see Table 7.1).

Table 7.1 Showing MS - MS Data M/z 1721

Ion generated	Ion
1722	$[M + Na]^+$
1699	$[M + H]^+$
1640	$[M$ - cyclohexyl$]^+$
935	$[(PCy_3)Ni\{\overline{CH_2CH(CH_3)COO}\}]^+_2$
617.9	$[Ni(PCy_3)_2]^+$
446	$[(PCy_3)Ni\{CH_2CH(CH_3)COO\} + Na]^+$
81	$[Cyclohexyl]^+$
44	$[CO_2]^+$

The major ion in the two sector FAB positive ion spectrum corresponds to the matrix material m-nitrobenzyl alcohol at (M/z 154 (100%) - $[M + H]^+$), but also predominate are ions corresponding to the ligand tricyclohexylphosphine (M/z 281, 89%) and its oxide (M/z 297, 94%). The presence of tricyclohexylphosphine oxide and tricyclohexylphosphine may be a consequence of the extreme air sensitivity of this complex. The sample was exposed to air for a brief period to enable mixing with the matrix and loading onto the probe before insertion into the spectrometer and subsequent evacuation. This is the likely explanation because the four sector tandem mass spectra of the tetramer ions at M/z 1721 and 1723 do not show daughter ions of mass 281 and/or 297. An alternative explanation is that the solvent associated with the crystals of the tetramer contained some PCy_3 which partially oxidised on sample preparation.

Other ions generated in the two sector FABpositive ion spectrum have been tentatively assigned as cluster ions, a phenomenon common to FAB MS. The ion M/z 593 has been assigned as to a cluster of two tricyclohexylphosphine oxide molecules. It is non nickel containing as judged by the abscence of a nickel isotope pattern.

Infra Red (see section 6.2.1).

The IR spectrum of the isolated solid contains a very strong absorbance at $1569cm^{-1}$. This is about $100cm^{-1}$ lower than the carbonyl stretches reported for nickel π-alkene coordinated acrylate complexes, such as $[(PCy_3)Ni(ema)]$ (ema = ethylmethacrylate) (1). This shift in $\nu(CO)$ cannot be accounted for by cyclization of the methacrylic acid moiety in the metallacycle. In the cyclic amide complexes studied by Yamamoto et al, a shift in $\nu(CO)$ of about $50\ cm^{-1}$ is associated with cyclization of the amide (2). The downfield shift observed here is associated with direct, end on type interaction of the carbonyl oxygen with a metal. It is envisaged that the tetrameric structure is similar to

that published for the complex $[(PEt_3)\overline{Ni\{CH_2CH(CH_3)CONH\}}_4]$. Each metallacycle

unit $[(PCy_3)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ is coordinatively unsaturated with a total count of 16 electrons for nickel.

It is envisaged that each metallacycle unit forms in solution and bonds to a nickel atom in an adjacent metallacycle unit through the carbonyl oxygen. In this way, the nickel is coordinatively saturated and has a total count of 18 electrons. Four metallacycle units form together in this way to give a more stable compound. The $\nu(CO)$ shift to lower frequencies is a result of a change in electron density in the carbonyl bond resulting from interaction with the nickel.

Other predominant bonds in the IR spectrum of 1A are associated with the cyclohexyl groups of the ligand. $2925cm^{-1}/2848cm^{-1}$ [CH stretching], $1446cm^{-1}$ [CH bending].

Proton NMR (see section 6.2.1).

Proton NMR spectra, taken in CD_2Cl_2 at room temperature, had as a main feature a broad multiple signal between 1.2-2.2ppm, assigned to the CH_2 protons of the cyclohexyl groups of the phosphine ligand. Other features are consistent with the cyclization of the methacrylic acid into the metallacycle shown in Fig. 7.1.

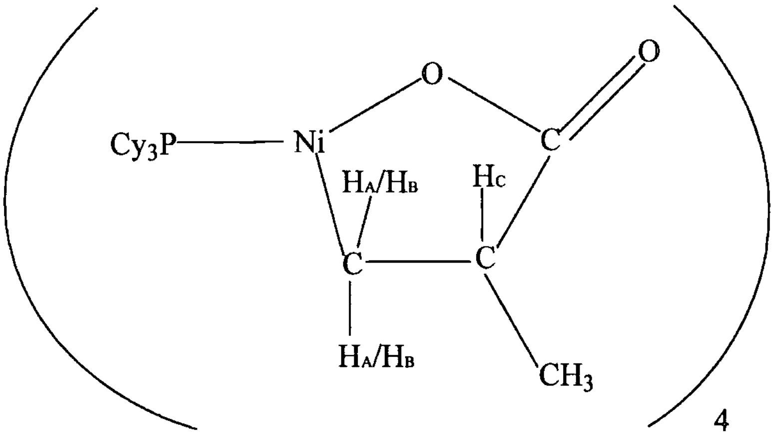


Fig 7.1

The two protons of the carbon atom α to the nickel appear as quite distinct doublets to lower chemical shift than expected for protons of a normal CH_2 group (8) as a result of their proximity to nickel. In general, proton spectra reveal that protons on hydrocarbon ligands which are in close proximity to nickel exhibit lower frequency shifts relative to chemical shifts of the corresponding protons in the parent hydrocarbons. Miller & Stauffer attribute this to antishielding believed to be caused by paramagnetic anisotropy of the nickel (8). The appearance of each proton at a different chemical shift demonstrates their magnetic inequivalence.

Each of the α carbon protons ($H_{A/B}$) appears as a doublet in the spectrum. An inspection of the proposed structure leads to an expected doublet of doublets of doublets i.e. a $^2J(H\text{-}H)$ geminal coupling $^3J(H\text{-}H)$ vicinal coupling and a $^3J(H\text{-}P)$ coupling for each proton. It is suggested that the latter $^3J(H\text{-}H)$ vicinal coupling and $^3J(H\text{-}P)$ coupling are unresolved.

The methine proton Hc on the carbon atom β to the nickel also appears at lower chemical shift due to its proximity to the metal. It appears as a broad singlet. There is no resolved coupling i.e. $^3J(H\text{-}H)$ vicinal coupling and/or $^4J(H\text{-}P)$ coupling. The methyl group protons, however, appear as a sharp doublet due to coupling with Hc, i.e. $^3J(H\text{-}H)$. The value of the coupling 6.83Hz is consistent with $^3J(H\text{-}H)$ coupling constants for related nickel metallacycles. The chemical shift of the methyl group protons is usual a lower frequency shift due to nickel not being experienced.

Carbon NMR Spectra (see section 6.2.1).

Evidence for the proposed tetrameric structure in the carbon NMR spectrum is less clear. Unfortunately changes to the colour of samples changed during overnight accumulation of data. This could be for one of two reasons:-

a) The spectra were recorded in CD_2Cl_2 which can oxidatively add to coordinatively unsaturated Ni if present. If the tetramer is quite labile in solution, as seems likely, it may decompose to monomeric coordinatively unsaturated units which can interact with solvent.

b) The complex is extremely air sensitive and a tiny ingress of air into the NMR tube would cause decomposition, but this explanation is less likely.

The signals in the ^{13}C NMR spectrum cannot be easily assigned. An inspection of the proposed tetrameric structure proposed reveals four chiral carbon atoms as opposed to one in a monomeric structure. This will broaden and complicate the carbon spectrum if in the optical isomers the carbon atoms have slightly different chemical shifts (different magnetic environment) which seems likely. The presence of the isomers in different concentrations will have an effect on the relative intensities of the signals and further complicate interpretation of the spectrum.

$[(Cy_3P)\overline{NiCH_2{}^*CH(CH_3)COO})_4$ * Chiral carbon centre

Six optically active isomers are suggested to be possible

RRRR RRRS RRSS RSRS RSSS SSSS

A doublet δ 6.41ppm has been assigned as the α carbon. The coupling constant 30.7Hz ($^2J(P\text{-}C)$) is consistent with this assignment (1). It is similar to the α carbon signal ($\delta = 10.4\text{-}9.6$ppm) assignment for the complex

$[(Et_3P)\overline{Ni\{CH_2CH(CH_3)CONH\}}]_4$ (6).

The remainder of the spectrum is too complex to assign with any certainty. This is thought to be due to the presence of diasterioisomers. Some insight can be gained from further work reported in this thesis (see Table 7.14). This shows that changing the phosphine ligand has almost no effect on the ^{13}C signal of the methyl carbon (C_C) and

the methine carbon (C_B) in the complexes $[L_2\overline{Ni\{CH_2CH(CH_3)COO\}}]$, where L_2 = DPPE (1B), DCPE (1C), DCPy (1G), DCCP (1D), Bipy (1H), Phen (1I).

Analysis of the ^{13}C spectrum of compound 1A shows the presence of signals in the region where it might be expected that the methyl and methine would resonate based on the above evidence. Signals at δ 20.4, 20.15, and 21.5(br) ppm may be due to the Methyl carbon (C_C) in the different isomers and signals at δ = 43.38, 43.24, 44.0, 44.8ppm may also be due to the methine carbon (C_B) in the different isomers.

No carbonyl carbon C_D is observed, and is perhaps not surprising given the long relaxation times of carbonyls together with the effective dilution of the signal by the presence of isomers.

The evidence from the carbon spectra, whilst not diagnostic, is supportive of the proposed tetrameric structure.

Phosphorous NMR Spectrum (see section 6.2.1).

The evidence from the phosphorous NMR spectrum is supportive of a non-monomeric structure. The spectrum in THF contains 8 signals and that in toluene 9 signals. In both cases, the signals are spread over an approximately 4ppm range. The result can be explained by assuming a multi nuclear structure (tetramer) in which the presence of several magnetically non-equivalent ^{31}P nuclei are possible due to the chirality in each monomer unit. Previous work (2) has shown that $[(Cy_3P)\overline{Ni\{CH_2CH(CH_3)CONH}\}]_4$ has 7 signals in benzene and $[(Et_3P)\overline{Ni\{CH_2CH(CH_3)CONH}\}]_4$ has 9 signals in benzene, at least one of which, it is suggested, is a triplet. It has not proved possible in the case of compound 1A to define any multiplicity in the ^{31}P NMR feature.

7.1.2 SYNTHESIS OF 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-4-methyl cyclopentan-5-one. COMPOUND 1B

This compound was isolated as a yellow powder which was recrystalized from THF. Crystals were grown but attempts to obtain a crystal structure proved unsuccessful. The material has been characterised by a range of techniques and the evidence for the structure of [(DPPE)Ni$\overline{\{CH_2CH(CH_3)COO\}}$] is presented. Also, since this compound has been reported previously(5,6,7), the two sets of data are compared and discussed.

This complex, unlike compound 1A, was moderately air stable, which facilitated its characterisation by a range of techniques. This is not surprising since, the nickel in this compound is coordinatively saturated in the +2 oxidation state and has a total count of 18 electrons. The elemental analysis (see Table 7.9) is in good agreement with that calculated for a compound of composition $C_{30}H_{30}NiO_2P_2$.

The compound is synthesised by the addition of DPPE to compound 1A in THF at -10°C. A ligand exchange reaction takes place. The driving force for this reaction is the increased stability of the chelate phosphine-nickel complex. Only one equivalent of DPPE is added to give 1B in high yields.

Infra Red Spectra (see section 6.2.2).

The presence of a very strong absorbance at $1634cm^{-1}$ is diagnostic of the carbonyl group in the metallacyclic structure. This is in full agreement with previously published data(1). The carbonyl band is some $50cm^{-1}$ lower than in π-alkene coordinated complexes (1), and is diagnostic of a metallacyclic structure.

Mass Spectrum (see Table 7.13 and section 6.2.2).

The major ions generated in the FAB positive ion mass spectrum are shown in Table 7.13 along with assignments. The most intense positive ion in the spectrum corresponds to $[M-H]^+$. This is not common for FAB positive ion mass spectroscopy where ionisation is thought to occur by addition of a proton (9a,9b) to generate an $[M+H]^+$ species.

It is possible the presence of the $[M-H]^+$ ion could be a feature of the ionisation technique known as "in-beam reduction". The process occurring is $[M+H]^+ - H_2$ fragmentation generating M/z 541 pseudo molecular ions. MS - MS of ions M/z 545, 543 and 541 provide evidence for this "in-beam reduction" hypothesis. Ions M/z 545 and 543 show a loss of 2 amu from the parent ions. These two ions have been assigned as $[M+H]^+$ ions containing Ni^{60} and Ni^{58} respectively. The ion M/z 541 does not show the 2 amu loss from the parent ion in the MS-MS experiment. Other structural information deduced from MS-MS experiments is as follows.

(i) All of the above pseudo-molecular ions show evidence of decarboxylation, a loss of 44 amu assigned as CO_2.

(ii) All of the above pseudo-molecular ions generate the following fragment ions:

M/z 456 by a loss of 86 amu, assigned as methacrylic acid

M/z 428 by a loss of 114 amu assigned as methacrylic acid + C_2H_4 (from ethyl bridge DPPE ligand)

The above fragmentation is complementary evidence that the ions generated in the two sector FAB positive ion experiment and fragmented by collision with argon molecules in the MS-MS experiment have the proposed metallacyclic structure. The MS-MS also demonstrates unequivocally the relationship of the fragment to the parent.

Accurate mass experiments were performed to obtain an elemental composition of M/z 541 and 543. The measured mass of M/z 541 was 541.098290 Daltons. This gave an elemental composition within 2.5ppm accuracy of $C_{30}H_{29}Ni^{58}O_2P_2$. An analysis of the instrument generated compositions compatible with the measured mass showed this to be the first sensible composition which tied in with the known characteristics of the ion. The elemental composition for M/z 543 of $C_{30}H_{31}Ni^{58}O_2P_2$ at a measured mass of 543.106250 Daltons, however, gave an accuracy of 16.6ppm which is outside the expected experimental error. Other compositions for this accurate mass were not readily rationalised. However, if it is assumed that the assignment for M/z 541 is correct, then it can be argued that M/z 543 is due to 2 peaks overlapping whose origin is $C_{30}H_{29}Ni^{60}O_2P_2$ (Ni^{60} isotope $[M-H]^+$) and $C_{30}H_{31}Ni^{58}O_2P_2$ (Ni^{58} isotope $[M+H]^+$). Simulation of the spectrum of these two species with all isotopes shows there are indeed two peaks separated by ~0.02 Daltons at nominal mass M/z543. Examination of the raw accurate mass data shows M/z543.10625 has a wider line width than M/z541 and also a shoulder on the peak shape. The M/z541 peak shape is symmetrical with no shoulder. These simulated and experimental observations can account for the 16.6ppm error in the accurate mass measurement (see diag 7.2).

Other ions present in the two sector FAB positive ion mass spectrum are those expected for the complex and the matrix, i.e. clustering and matrix adduct ions. Overall, the mass spectral experiments conducted confirm the presence of the compound 1B and provide insight into its structure and composition. No previous mass spectral information has been published concerning this compound.

Proton NMR Spectrum (see Figure 7.3, Table 7.2 and section 6.2.2)

Table 7.2 shows the ^1H NMR data obtained for compound 1B and the previously published literature (4). The essential difference is in the detail. In this study the multiplicities have been resolved and the values of the coupling constants calculated.

Comparison Of Proton NMR Data For 1-oxa-2-{1,2-bis(diphenylphosphino) ethyl} nickela-4-methyl cyclopentan-5-one. COMPOUND 1B.

ASSIGNMENT	This Thesis CHEMICAL SHIFT (ppm)	Previous Work CHEMICAL SHIFT (ppm)
Ha/Hb	O.53 (dddd, 1H, $^{2}J_{H\text{-}H}$9.8Hz, $^{2}J_{H\text{-}P\ TRANS}$ 9.8Hz, $^{2}J_{H\text{-}P\ CIS}$ 5.4Hz, $^{3}J_{H\text{-}H}$5.4Hz)	0.4 - 0.9 (m, 1H)
CH3	0.93(d, 3H, $^{3}J_{H\text{-}H}$6.8Hz)	1.0(d, 3H, J6.8Hz)
Ha/Hb	1.06(dddd, 1H, $^{2}J_{H\text{-}P\ TRANS}$ 13.2Hz, $^{2}J_{H\text{-}H}$10.2Hz, $^{2}J_{H\text{-}P\ CIS}$ 6.8Hz, $^{3}J_{H\text{-}H}$ 4.4Hz)	2.0-2.6(m, 1H)
Hc	2.3-2.4(m, 1H)	2.3-2.6(m, 1H)
Ligand CH2	1.7-1.9(m, 2H)	No data
Ligand CH2	2.1-2.3(m, 2H)	No data
Phenyl protons	7.3-7.9(m, 20H)	7.2-7.6(m, 20H)

Table No 7.2

The proton NMR spectrum shows quite clearly the magnetic inequivalence of the α CH_2 protons (H_A/H_B). Due to the planarity of the nickel containing five membered ring, one of these protons appears as a sharp multiplet centred at 0.53ppm. The feature is a doublet of doublets of doublets of doublets where two sets of coupling constants are equal and hence the peaks overlap and increase in intensity. The feature has been modelled to demonstrate this. The two largest couplings of equal magnitude are the geminal two bond proton-proton coupling and three bond proton-phosphorous trans coupling. The two smaller couplings of equal magnitude are the three bond proton-proton vicinal coupling to the proton on C_B and the three bond proton-phosphorous cis-coupling. Cis-couplings are generally smaller than trans-couplings.

The other α-CH_2 proton appears as a complex multiplet centred at 1.06ppm. Here, the magnitude of the couplings differ ie. $^{2}J_{H\text{-}P\ TRANS}$ 13.2Hz, and $^{2}J_{H\text{-}H}$10.2Hz versus $^{2}J_{H\text{-}P\ TRANS}$ 9.8Hz and $^{2}J_{H\text{-}H}$9.8Hz in the multiplet centred at 0.53ppm and hence the multiplet appears more complex, it remains though, a doublet of doublets of doublets of doublets in principle.

The assignment of one of the α-CH_2 protons as a broad multiple δ 2.0-2.6ppm in previously published work is, by the evidence presented here, incorrect. The region 2.0-2.6ppm is a normal area for CH_2 resonances in proton NMR. This assignment does not reflect the proximity to nickel, which pushes the signal to low frequencies. In the spectrum published here, there are complex features in the region 2.0-2.5ppm but 2-dimensional NMR experiments show these to be the methine proton (Hc) and the DPPE ligand bridge CH_2 proton signals which are sufficently separated from the nickel so as not to experience large low frequency shifts in the proton NMR.

The magnitudes of the various couplings not calculated previously, provide structural information. The vicinal couplings are of the magnitude (between 0-16Hz, most generally between 5-8Hz) (10) expected and have similar values. As an approximation, then, the dihedral angle between each α CH_2 proton and the methine proton will be similar (Karplus Rule)(10). A more detailed calculation based on Karplus Rule would be necessary to verify this.

The chemical shifts of the other protons in the metallacyclic ring are in good agreement with previously published data and are reasonable for the metallacyclic structure shown.

Carbon NMR Spectrum (see Figure 7.4, Table 7.3 and section 6.2.2).

Table 7.3 shows the carbon NMR data obtained for compound 1B and previously published data for comparison (4). The chemical shift data for the carbon atoms C_B, C_C, C_D and one of the ligand bridge carbons and the phenyl carbon atoms are in good agreement. The assignment of the α-CH_2 (C_A) and one of the ligand bridge carbons differ. The assignments previously published are made by comparing the two

complexes $[(DPPE)\overline{Ni\{CH_2CH_2COO\}}]$ and $[(d^4\text{-}DPPE)\overline{Ni\{CH_2CH_2COO\}}]$. Thus it should be possible to unequivocally assign DPPE ligand CH_2 carbons in the above acrylic acid complex. The other carbon atoms are assigned on the basis of chemical shift and magnitude of carbon-phosphorus coupling constants. This approach can be open to error. In the present study the proton-carbon atom connectivities in this compound and compound 1C have been established via 2-dimensional NMR experiments.

The α-CH_2 (C_A) is assigned as a doublet of doublets at δ 22.66ppm. The carbon is coupled through the metal to each of the phosphorus atoms of the ligand. The magnitude of the coupling is different as would be expected, two bond trans coupling being generally larger than two bond cis coupling. The magnitudes of the coupling constants are not unreasonable for the metallacyclic structure proposed. Previous work assigns the α-CH_2(C_A) as a doublet at δ 29.3ppm. This doublet is present in the carbon spectra of compound 1B, but 2D NMR experiments suggest that it is due to a ligand CH_2 group. The magnitude of one of the coupling constants (59.6Hz) seems more likely to be a one bond carbon-phosphorus coupling which would be expected for the bridge CH_2 group. It magnitude is twice as big as any other coupling constant observed in the molecule.

The two ligand CH_2 groups (C_E and C_F) are assigned as doublets of doublets experiencing coupling to both phosphorus atoms. One at δ 30.02ppm is in agreement with previous work(1,2,5). The other in the same work has been assigned at δ 25.1ppm as a doublet of doublets. No feature at this shift appears in the spectrum of the same compound published here.

The carbon spectra was also obtained under conditions which allowed the proton carbon couplings to be observed. Of interest is the value of the C-H coupling between the β-carbon (C_B) and the hydrogen directly bonded to it (Hc). The value $^1J_{C\text{-}H}$ obtained is typical of an sp^3 hybridized carbon atom. It was thought that the hydrogen (Hc) may be agostic. Literature evidence (11) gives C-H couplings of around 100Hz for agostic hydrogens. Clearly the β hydrogen in this complex is not agostic. There is no evidence in the carbon NMR to suggest an interaction between the methine hydrogen (Hc) and the nickel in complex 1B.

Comparison of Carbon NMR Data for 1-oxa-2-{1,2-bis (diphenylphosphino) ethyl} nickela-4-methyl cyclopentan-5-one. COMPOUND 1B.

ASSIGNMENT	**This Thesis (PPM)**	**Previous Work (PPM)**
C_A	22.66 (dd, $^2J_{p\text{-}c}$28.3Hz, $^2J_{p\text{-}c}$ 11.4Hz)	29.3(dd, $^2J_{p\text{-}c}$58.6Hz, $^2J_{p\text{-}c}$21.98Hz)
C_B	42.39(s)	42.5(s)
C_C	21.52(s)	21.7(dd, $^4J_{p\text{-}c}$10.3Hz, $^4J_{p\text{-}c}$2.9Hz)
C_D	190.9(s)	191.2(s)
Ligand ethyl CH2	29.3(dd, $^1J_{p\text{-}c}$59.8Hz, $^2J_{p\text{-}c}$23.0Hz)	25.1(dd, $^2J_{p\text{-}c}$29.3Hz, $^2J_{p\text{-}c}$11.7Hz)
Ligand ethyl CH2	30.02(dd, $^1J_{p\text{-}c}$29.2Hz, $^2J_{p\text{-}c}$21.5Hz)	30.0(dd, $^2J_{p\text{-}c}$29.3Hz, $^2J_{p\text{-}c}$20.5Hz)
Phenyl carbons	129.06-134.09	129.0-133.0

Table No 7.3

Phosphorous NMR Spectrum (See table 7.4 and section 6.2.2)

The $^{31}P\{H^1\}$NMR spectrum shows two signals with the same peak areas as would be expected for the proposed structure. The sharpness of the signals indicates that the phosphine is tightly bonded to the nickel on an NMR time scale. The reported chemical shifts from previous work are different to those found here. The difference Δ between the two signals in both spectra are virtually identical (24.15ppm vs

24.2ppm) suggesting the different result may be due to the solvent used. It is thought that the literature data was obtained for the complex in CD_2Cl_2 but this is not clearly stated The difference may also be due to a different reference compound having been used but this is also not stated.

Comparison Of Phosphorous NMR Data Compound 1B

ASSIGNMENT	**This Thesis (ppm)**	**Previous Work (ppm)**
DPPE Phosphorus	58.46(s)	65.1(d, J 1.95Hz)
DPPE Phosphorus	34.31(s)	40.9(d, J 1.95Hz)

Table No 7.4

7.1.3 SYNTHESIS OF 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-4-methyl cyclopentan-5-one. COMPOUND 1C.

The compound was isolated as a yellow powder by the addition of the chelating phosphine DCPE to compound 1A in THF at -10°C. A favourable ligand exchange takes place and 1C is isolated in high yield. The compound is soluble in THF and dichloromethane and crystals were grown from THF. As with compound 1B, attempts to obtain a crystal structure proved unsuccessful.

Elemental analysis measured for the compound agree well with that expected for the proposed structure (see table 7.9).

This complex has been fully characterised by a range of techniques; the results are discussed here. The complex is a key compound in this study. Hoberg et al have demonstrated that the oxidative coupling of propene and carbon dioxide occurs at DCPE-liganded nickel(O) to yield mixtures of normal and isobutanoic acid after acid hydrolysis. The presence of compound 1C is postulated as the intermediate nickel containing compound formed from oxidative coupling. Full characterisation of this material, synthesized by this route, should enable its identification if present in autoclave reaction mixtures, allowing clear identification of the nickel containing intermediates. No spectral characterisation of this compound has been published to date.

Infra Red Spectrum (see section 6.2.3)

There is a strong absorbance at 1631cm^{-1} diagnostic of the carbonyl in the proposed metallacyclic structure. Other bands at 2926cm^{-1} and 2850cm^{-1} are associated with CH_2 stretching in the cyclohexyl groups of the ligand. The remainder of the spectrum has not been assigned.

Mass Spectrum (see Table 7.13 and section 6.2.3)

The major ions generated in the FAB positive ion mass spectrum are shown in Table 7.13 along with the assignments. The most intense ions correspond to M/z 565 $[M-H]^+$. As with 1B, it is suggested that the reduced molecular ion may be formed as a feature of the ionisation technique. The process occurring is $[M+H]^+-H_2$ to give $[M-H]^+$. Complementary evidence comes from the FAB-ve ion spectra where the only nickel containing ion seen corresponds to loss of a methyl group. No $[M-H]^+$ ion is apparent, and suggests that loss of a proton to give $[M-H]^-$ is not occurring.

The interest in this decay process relates to the proposed catalysis by β-hydride extraction/migration first mentioned in Chapter 1 of this thesis. It was first thought that $[M-H]^+$ may be formed by loss of the β-hydrogen (H_C) and that, if this process was occurring in the mass spectrometer, it might be possible to induce it in other ways.

The MS-MS data, as with complex 1B provides complementary evidence for the "in beam reduction" process. MS-MS of ions M/z 567 shows a loss of 2 amu from the parent ion. The ion M/z 567 has been assigned as $[M+H]^+$ arising from Ni^{58}. All the pseudo-molecular ions studied by MS-MS show evidence of CO_2 loss, i.e. 44amu loss from the parent ion. The ions studied are M/z 565 $[M-H]^+$, 566 $[M]^+$ and 567 $[M+H]^+$. Also in common with compound 1B, the fragment ions [M-86] are observed, assigned to loss of the methacrylic acid moiety. It should be remembered that these fragmentation processes occur in gas phase and are highly energetic, so it is difficult to draw conclusions about mechanisms.

Accurate mass measurements performed to obtain an elemental composition gives for the ion M/z 565 an elemental composition of $C_{30}H_{53}Ni^{58}O_2P_2$ to an accuracy of 6.6ppm. An analysis of the instrument generated compositions compatible with the measured mass showed this to be the first sensible composition which tied in with the known characteristics of the ion. The ion M/z 566 gave an elemental composition of $C_{30}H_{54}Ni^{58}O_2P_2$ to an accuracy of 8.9ppm. This was also the first sensible composition calculated.

Two sector FAB positive ion spectra run using glycerol instead of MNBA as the matrix material produced almost identical ions to those observed in the MNBA matrix FAB positive ion spectra. The only feature not seen before was an ion M/z 590 assigned as $[M+H+Na]^+$.

Finally, for the mass spectra of this compound, it should not be ruled out that loss of 1 amu from the molecular ion may produce $[M-H]^+$. The discussion of "in beam reduction" is only presented as a hypothesis at present.

Proton NMR Spectrum (see Table 7.12 and section 6.2.3)

Table 7.12 shows the ^1H NMR data for the compound 1C. Analysis of this data shows that the chemical shifts and magnitudes of the coupling constants do not differ significantly from those in compound 1B. This is surprising given the very different nature of the phosphines.

As with compound 1B, the proton-carbon connectivites have been established by 2-D NMR experiments. The α-CH_2 protons (H_A/H_B) are quite clearly magnetically inequivalent. Each one is coupled to the other as well as to each phosphorus of the ligand and to the methine hydrogen (H_C). This coupling pattern is consistent with the proposed metallacyclic structure.

Carbon NMR Spectrum (see Table 7.14 and section 6.2.3)

Table 7.14 shows the carbon NMR data for the compound 1C. The chemical shift of the α-CH_2 (C_A) has moved approximately 5ppm downfield as a result of the change of ligand from DPPE TO DCPE. Of the carbon atoms of the metallacyclic ring, this is the only one whose chemical shift has been significantly shifted in changing ligand substituent groups.

The remaining carbon atoms of the metallacyclic ring have remained at approximately the same chemical shift. The ligand bridge CH_2's are different as would be expected.

It also proved possible to assign the cyclohexyl CH carbons in the ligand (ie. carbon atom bonded directly to phosphorus). They are all chemically inequivalent and appear as four doublets, each carbon being coupled to the adjacent phosphorus atom. This suggests there is no free rotation about the phosphorous carbon bonds in the metallacyclic structure. In the free ligand, you would expect the cyclohexyl CH carbons to be equivalent with no barrier of the ring to rotation and hence observe only 1 doublet. The chemical shifts and coupling constants are shown below:-

δ ppm	**$^1J_{P-C}$ Hz**
33.75	13.8
33.90	15.3
35.44	16.8
35.69	18.4

TABLE 7.5
Cyclohexyl CH Carbon NMR Parameters for Compound 1C

The carbon spectra was also obtained under conditions which allowed the proton carbon couplings to be observed. As with compound 1B, of interest was the value of the C-H coupling between the β carbon (C_B) and the hydrogen directly bonded to it (Hc). The value J_{C-H} obtained is typical of an sp^3 hybridized carbon atom. Clearly the β-hydrogen in this complex is again not agostic. There is no evidence in the carbon NMR to suggest an interaction between the methine hydrogen (Hc) and the nickel in complex 1C.

Phosphorus NMR Spectrum (see Table 7.10 and section 6.2.3)

The $^{31}P\{H\}$ NMR shows two signals with the same peak area as would be expected for a compound of the proposed structure (see Table 7.11). A solvent effect is noticeable, which is not uncommon in phosphorus NMR.

As with compound 1B, the sharpness of the signals indicates that the phosphine is tightly bound to the nickel on the NMR time scale.

The full range of characterisation techniques applied to this compound support the proposed structure and provide a comprehensive library of information, previously unavailable.

7.1.4 SYNTHESIS OF 1-oxa-2-{1,3-bis(dicyclohexylphosphino)propyl}nickela-4-methylcyclopentan-5-one. COMPOUND 1D.

The compound was isolated as a yellow powder in the same manner as 1C.

The yield is low relative to compound 1C. This may be related to the relative thermodynamics of the reaction

$$[(Cy_3P)Ni\{CH_2(CH_3)COO\}] + L_2 \rightleftharpoons [L_2Ni\{CH_2(CH_3)COO\}]$$

where L_2= DCPE or DCPP. The equilibrium lies further over to the right hand side of the equation when L_2= DCPE.

T. Kohara et al (12) working with the $[(PEt_3)_2NiMe_2]$ complexes found the following series for coordinating ability for complexes of the type L_2NiMe_2, prepared according to the following equation.

$$L_2Ni(CH_3)_2 + L'_2 \rightleftharpoons L'_2Ni(CH_3)_2$$

L'_2= DPPE > DPPP >> PEt_3> BIPY L= PEt_3

The reaction mechanism is proposed as an Sn_2 process and involves (i) initial coordination and (ii) chelation of the coordinated ligand / dissociation of the exchanged ligand. The difference in the metallacycle formation reaction between DCPE and DCPP can be seen as the difference in the thermodynamics of the chelation/dissociation step (see fig 7.2).

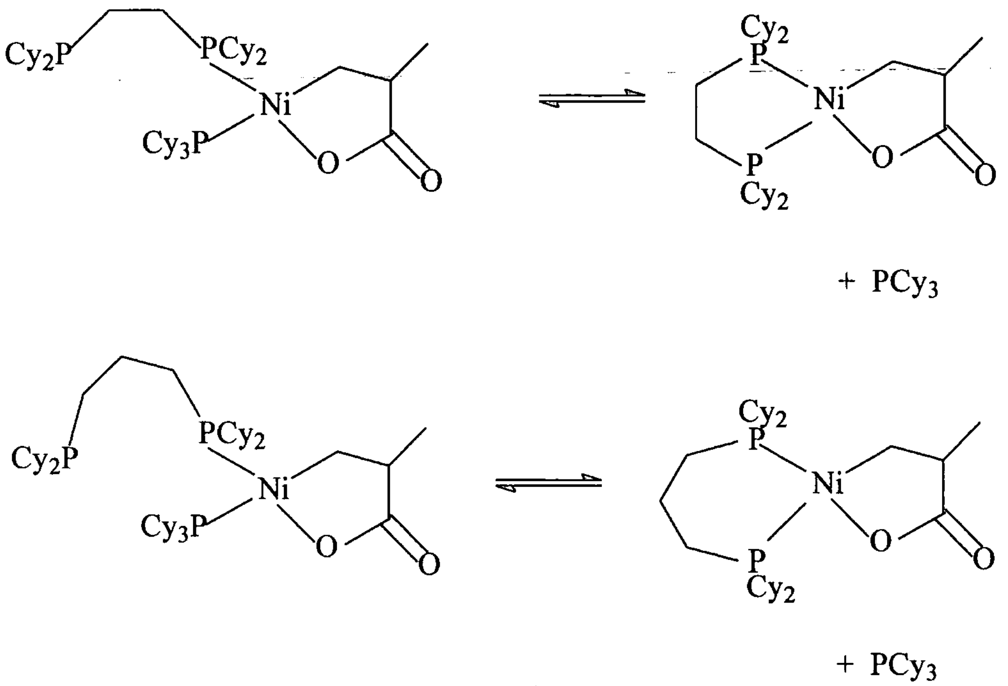


Fig 7.2

Formation of a five membered chelate ring is energetically more favoured over the formation of the six membered ring ie. $\Delta H_1 > \Delta H_2$.

In the work of T. Kohara et al the reaction described by the equation below

$$\underset{\mathbf{B}}{\mathrm{DPPPNi(CH_3)_2}} + \mathrm{DPPE} \rightleftharpoons \underset{\mathbf{A}}{\mathrm{DPPENi(CH_3)_2}} + \mathrm{DPPP}$$

results in a ratio A:B of 10:1 indicating compound A with the five membered chelate ring is the thermodynamically favoured product. Also found in this work is the first order rate dependence of the reaction on the chelate ligand. In this case the coordinating ability of the phosphorus of DCPE and DCPP should be similar.

The complex 1D has been fully characterised to enable its identification in autoclave mixtures. Also no published data for this complex has been published to date.

Infra Red Specta (See section 6.2.4)

There is a strong absorbance at 1643cm^{-1} diagnostic of the carbonyl in the proposed metallacycle structure. The shift of 12cm^{-1} from that of 1C is not believed to be significant. The other dominant bands in the spectrum are associated with ligand CH_2 stretching in the cyclohexyl groups (2927, 2848cm^{-1}).

Mass Spectrum (See table 7.13 and section 6.2.4)

The major ions generated in the FAB positive ion mass spectrum are shown in Table 7.13 along with assignments. In common with other compounds in this series, the most intense ions correspond to the pseudo-molecular ions $[M-H]^+$ M/z 579, $[M+H]^+$ M/z 581, M^+ M/z 580, $[M-86]^+$ M/z 494. The two sector mass spectroscopy experiment shows the compound to behave similarly to compound 1C. Four sector MS-MS however reveals structural differences in the way the pseudo-molecular ions fragment when bombarded by neutral argon molecules. Whilst the MS-MS experiment may be artificial(high energy gas phase processes), it is interesting to note differences in the ways ions interact under a given set of conditions. With the pseudo-molecular ions M/z 579, 580, 581, 582, no loss of CO_2 (44amu) is observed. The 44 amu loss, which has been attributed as the CO_2 fragment has been observed in the corresponding pseudo-molecular ions for compounds 1B and 1C. The other feature worth noting is that the ion M/z 581 assigned as $[M+H]^+$ shows a 2 amu loss associated with "in beam reduction".

The conclusion of the MS-MS experiment is that changing the length of the ligand bridge has a significant effect on the ions formed in the MS/MS experiment.

Differences in reactivity brought about by altering the ligand bridge from two carbons to three carbons have been observed before (12). The two complexes $[NiMe_2(Ph_2P(CH_2)_2PPh_2)]$ and $[NiMe_2(Ph_2P(CH_2)_3PPh_2)]$ have been studied. The latter complex is found to reductively eliminate C_2H_6 46 times faster at 64.3°C than the former complex at the same temperature. The analysis of crystal structures of two related platinum complexes $[PtCl_2(^tBu_2P(CH_2)_nP^tBu_2)]$ (n=2, 3) suggests that, on moving from n=2 to n=3, the structure reveals a distortion of geometry from square planar toward tetrahedral. A similar effect may be responsible for the observations in the dimethylnickeldiphosphine complexes where previously energetically disallowed or unfavoured orbital overlap can occur in the pseudo-tetrahedral complex.

An alternative explanation for differences in reactivity relates to the stabilities of the five and six membered ring complexes. It is suggested that less stable six membered ring complexes can form partially disassociated three coordinate species which again allows previously unfavoured orbital overlap or reaction with other species.

Proton NMR Spectrum (See Table 7.12 and section 6.2.4)

The proton NMR parameters for the compound 1D are recorded in Table 7.12. An inspection of the data shows that it is very similar to compound 1C, i.e. changing the ligand has had no effect on the magnetic environment of the protons of the metallacycle ring. This is not surprising given the close structural relationship between DCPE and DCPP.

Carbon NMR Spectrum (See section 6.2.4)

The carbon NMR parameters for the compound 1D are recorded in Table 7.14. It is similar to the data generated for compound 1C with some notable differences. Signals for the two carbon bridge atoms of the ligand appear as doublets each experiencing one-bond coupling to the adjacent phosphorus. No three-bond-coupling is observed. The central carbon of the ligand bridge has not been assigned; it is most likely hidden under the cyclohexyl CH_2 signals.

The carbonyl carbon appears as a doublet with a coupling constant of 13.8Hz. Similar values have been observed for related cyclic amide complexes (6). The coupling is best described as either three bond coupling through oxygen or four bond direct phosphorus carbon coupling.

The other feature of note is the change in magnitude of the P-C couplings of the cyclohexyl CH carbon atoms, which must be a result of confirmational changes in the molecule necessary to accommodate the extra CH_2 of DCPP (see table 7.6).

δ ppm	**$^1J_{p-c}$ Hz**
33.33	16.8
33.86	18.4
36.57	27.6
36.90	27.6

TABLE 7.6

Cyclohexyl CH Carbon NMR Parameters for Compound 1D

Phosphorus NMR Spectrum (See section 6.2.4)

The ^{31}P NMR shows two signals which is what we would expect for a compound of the proposed structure. Interesting to note is the fairly large coupling (31.88Hz) between the phosphorous atoms, not seen for the compound 1C. The sharpness of the signals indicates the tight bonding of the phosphine to the nickel on the NMR time scale.

7.1.5 SYNTHESIS OF 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-3-methyl cyclopentan-5-one. COMPOUND 1E.

The material was isolated as a yellow powder which was moderately air sensitive. Recrystallisation of the compound proved impossible and it was characterised after washing with ether to remove unreacted ligand. The elemental analysis is in quite good agreement with that calculated for the proposed structure, though the carbon percentage is slightly low.

This compound has been synthesised previously and some characterisation data presented. This will be reviewed and compared to the data obtained in this study. The purpose of synthesising the 3-methylnickelacyclopentanones is to enable identification of the crotonic isomer produced by the theoretical oxidative coupling of carbon dioxide with the terminal carbon of propene. Although DPPE was not tested as a ligand for the oxidative coupling of propylene/CO_2, the synthesis of 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-3-methylcyclopentan-5-one complex 1E greatly assisted the characterisation of compound 1F (see later).

Infra Red Spectra (See section 6.2.5)

The presence of a strong absorbance at 1634cm^{-1} is indicative of the proposed metallacycle structure. The presence of medium-weak absorbances at 2921cm^{-1} and 2849cm^{-1} indicate the compound is not entirely pure. These bonds are associated with CH_2 stretching in the cyclohexyl groups of tricyclohexyl phosphine, the ligand displaced in the preparation. The fact that they are not washed out by repeated ether washing suggests that the tricyclohexyl phosphine is complexed with nickel in some manner. The presence of an absorbance at 1584cm^{-1} close to that present in compound 1A (1569cm^{-1}) suggests the tricyclohexyl phosphine may be coordinated to nickel in a complex similar to 1A or a derivative of 1A. Attempts to isolate the crotonic acid analogue of 1A proved unsuccessful.

Mass Spectrum (See table 7.13 and section 6.2.5)

Table 7.13 records the major ions generated in the FAB positive ion mass spectrum of compound 1E along with assignments. The most intense ion in the spectrum corresponds to tricyclohexylphosphine oxide. Strong signals are, present though, corresponding to $[M-H]^+$ M/z 541, $[M+H]^+$ M/z 543 and M^+ M/z 542, as are found for the 4-methylnickelacyclopentanone compound 1B.

MS-MS studies of the ions M/z 541, 543 corresponding to $[M-H]^+$ and $[M+H]^+$ produce very similar data to the MS-MS data of similar ions of the same mass generated from compound 1B. This suggests there are no differences in the fragments generated, and the fragmentation mechanisms between the two isomers are the same. The MS-MS of the above two ions confirm the relationship of $[M-86]^+$ to the parent ion ie the parent ion loses a fragment of 86amu assigned as methacrylic acid providing complementary evidence for the proposed structure of complex 1E. The ion M/z 456 can also be expressed as a DPPENi fragment and might arise from a number of different compounds as a fragment ion. MS-MS is a valuable tool to demonstrate that this ion is arising from fragmentation of the proposed molecular ions. Also demonstrated by MS-MS are 44 amu loss assigned as CO_2 loss from the psuedo-molecular ions M/z 541 and 543 again this provides complementary information supporting the structure proposed for compound 1E. The ion M/z 543 shows 2 amu loss assigned as "in beam reduction" whereas M/z 541 does not show this fragmentation. This is in line with findings for other compounds in this series.

Proton NMR Spectrum (See table 7.7 and section 6.2.5)

The proton NMR parameters for the compound 1E are recorded in Table 7.7. The positioning of the methyl group at the 3-position of the nickellacyclopentanone completely alters the NMR data as would be expected. The α-carbon proton resonates at 1.42ppm, which is lower frequency shifted compared with methine protons in organic compounds due to proximity to the nickel. The couplings to each of the phosphorus atoms of the ligand and the β-carbon protons are not resolved. The two β-carbon protons are shown to be magnetically inequivalent. The magnitudes of the couplings have been calculated and are consistent with the proposed structure and in agreement with previously reported work(5). The methyl group protons also experience a large low frequency shift as a result of the proximity to nickel, resonating at 0.53ppm, and they are coupled to the α-carbon proton. The magnitude of the coupling is consistent with other three bond proton-proton couplings observed in this work. It has also proved possible to assign the ligand bridge CH_2 protons, these resonate over the identical ranges as the ligand ethyl CH_2 protons in the 4-methyl substituted oxa-nickela-cyclopentanone (compound 1B).

Comparison of Proton NMR Data For 3 Methyl Substituted Oxa-nickela-Cyclopentanones

ASSIGNMENT	**This Work 1E (ppm)**	**Previous Work[(5)] 1E (ppm)**	**This Work 1F (ppm)**
H_A	1.42(br, m,1H)	1.4(m, 1H)	
CH_3	0.53(t, 3H, $^3J_{H-H}$ 7.32Hz)	0.52(t, 3H, $^3J_{H-H}$ 7.0Hz)	1.036(t, 3H, $^3J_{H-H}$ 7.1Hz)
H_B/H_C	1.64(ddd, 1H, $^2J_{H-H}$ 15.66Hz, $^4J_{H-P}$ 12.18Hz, $^3J_{H-H}$ 5.86Hz)	1.70(ddd, 1H, $^2J_{H-H}$ 16.0Hz, $^4J_{H-P}$ 13.0Hz, $^3J_{H-H}$ 6.0Hz)	
H_B/H_C	3.06(dd, 1H, $^2J_{H-H}$ 16.6Hz, $^3J_{H-H}$ 6.35Hz)	2.9(dd, 1H $^2J_{H-H}$ 16.0Hz, $^3J_{H-H}$ 6.0Hz)	2.80(dd, 1H $^2J_{H-H}$ 16.6Hz, $^3J_{H-H}$ 5.86Hz)
Ligand bridge CH_2	1.7-1.9(br, 2H)	No Data	
Ligand bridge CH_2	2.1-2.3(br 2H)	No Data	
Phenyl Protons	7.3-7.9(m, 20H)	7.2-7.6(m, 20H)	n/a

Table 7.7

Carbon NMR Spectrum (See table 7.8 and section 6.2.5)

Table 7.8 records the carbon NMR data for compound 1E and compares it to previously published data. Assignments have been made on the basis of chemical shift and the magnitudes of coupling constants.

The carbon spectra also contained signals attributable to $(cyclohexyl)_3P$ which could not be removed. These signals occur in the region δ 26.0-28.0ppm and may be obscuring signals from the compound 1E.

Comparison Of Carbon NMR Data For 3 Methyl Substituted Oxa-nickela-Cyclopentanones

ASSIGNMENT	This Work 1E (ppm)	Previous Work(5)1E (ppm)	This Work 1F (ppm)
C_A	21.58(dd, $^2J_{P-C}$28.3Hz, $^2J_{P-C}$10.0Hz)	27.4(dd, $^2J_{P-C}$56.4Hz, $^2J_{P-C}$18.7Hz)	20.5(br)
C_B	46.05(s)	46.5(d, $^3J_{P-C}$2.3Hz)	46.5(s)
C_C	18.92(s)	19.3(d, $^3J_{P-C}$3.5Hz)	15.5(s)
C_D	189.24(d, $^4J_{P-C}$ 13.8Hz)	201.0(d, $^4J_{P-C}$5.0Hz)	
Ligand CH_2	28.64(dd, $^1J_{P-C}$30.6Hz, $^2J_{P-C}$20.0Hz)	22.3(dd, $^1J_{P-C}$27.8Hz, $^2J_{P-C}$4.7Hz)	
Ligand CH_2	30.0-31.5(br)	34.2(dd, $^1J_{P-C}$27.6Hz, $^2J_{P-C}$17.3Hz)	
Phenyl carbons	128.0-133.0	127.6-131.2	n/a

Table 7.8

Phosphorus NMR Spectrum (See table 7.10 and section 6.2.5)

The $^{31}P\{H\}$ NMR showed two signals, each of which is a doublet, due to coupling with the other phosphorus in the molecule. Two signals are expected for the proposed structure.

7.1.6 SYNTHESIS OF 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-3-methyl cyclopentan-5-one. COMPOUND 1F.

This material was synthesised by the same route as 1E. A yellow powder was isolated which, like 1E, was not amenable to recrystallisation. The product was washed with ether to remove impurities. The product appeared to be moderately air sensitive as judged by discoloration of THF solutions exposed to the air. The compound is the proposed intermediate resulting from oxidative coupling of propene and carbon dioxide when coupling occurs at the terminal carbon atom of the propene molecule. For the purposes of catalysis to generate methacrylic acid, it represents coupling at the wrong carbon atom of the propene molecule. It is, however, important in any study to be able to identify by products, and hence this compound has been fully characterised to enable its identification in autoclave mixtures to assist the screening of ligands in the oxidative coupling reactions.

The elemental analysis does not agree as well with the required composition for 1-oxa-2-{1,2-bis(dicyclohexylphosphino)ethyl}nickela-3-methylcyclopentan-5-one as some of the other compounds synthesised in this series. The low carbon figure is indicative of a small amount of impurity which based on other analyses is thought to be tricyclohexylphosphine containing.

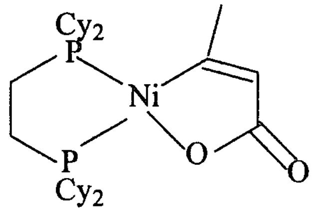
Infra Red Spectra (See section 6.2.6)

The presence of the strong absorbance at 1623cm^{-1} indicates the presence of the carbonyl group in the proposed metallacycle.

Mass Spectrum (See Table 7.13 and section 6.2.6)

Table 7.13 records the major ions generated in the FAB positive ion mass spectrum of compound 1F. The most intense peaks in the spectrum correspond to $[M-H]^+$ and $[M+H]^+$ as we have seen previously. Ions of M/z 281 and 297 amu are also present; these indicate the presence of tricyclohexylphosphine and its oxide and therefore suggest 1F is contaminated by the ligand displaced in the preparation.

MS-MS studies of ions M/z 565, 566, 567, 568 provide interesting additional information. In the MS-MS spectra of the above ions, methyl loss is suggested $[P- 15]^+$ in all except M/z 565,which is the ion suggested to be formed by "in-beam reduction" $[[M+H]^+ - H_2.]$ One possible explanation is that the in-beam reduction is probably occuring to give species such as that indicated below. This observation is useful for differentiating between the isomers. The two ions of the same relative molecular mass but have different structures and fragment differently. Each isomer can, therefore, be identified in the MS-MS experiment. Another interesting feature of the MS-MS studies is that the CO_2 loss appears to be more significant for the 3-methyl isomer than for the 4-methyl isomer. This is another clear differentiation of the isomers.



Proton NMR Spectrum (See table 7.7 and section 6.2.6)

Table.7.7 records the proton NMR data for compound 1F. A number of the protons of the metallacyclic ring are lost amongst the signals from the cyclohexyl protons. The methyl group and one of the protons on the β–carbon have been assigned. The chemical shifts and magnitudes of the coupling constants are consistent with similar compounds synthesised in this study (1E) and by other workers(4) (Table.7.7).

Carbon NMR Spectrum (See Table 7.8 and section 6.2.6)

The compound was not amenable to long periods of data collection necessary for good carbon NMR spectra as decomposition occurred in the NMR tube over a period of 2-4 hours in CD_2Cl_2. Other solvents were not tried. The signals have been assigned (see Table 7.8) and are consistent with similar compounds synthesised in this study and by other workers(5).

Phosphorus NMR Spectrum (See Table 7.10 and section 6.2.6)

The $^{31}P\{H\}$ NMR shows two signals each of which is a doublet due to phosphorus-phosphorus coupling. However, for the structure proposed for this compound two ^{31}P signals are expected.

7.1.7 Synthesis of 1-oxa-2-{2-[2-(dicyclohexylphosphino)ethyl]pyridine}nickela-4-methyl cyclopentan-5-one. COMPOUND 1G.

The compound was isolated as a yellow powder which proved impossible to recrystallise. It was thus purified by washing with ether. However a low nitrogen percentage in the elemental analyses (Table 7.9) was found.

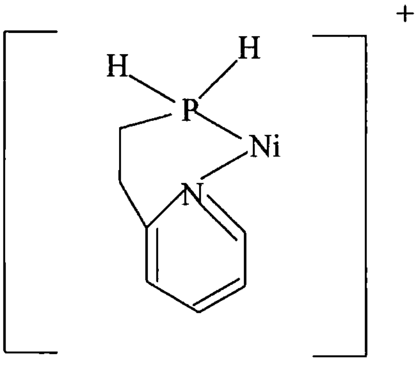
Infra Red Spectra (See section 6.2.7)

There is a strong absorbance at 1629cm^{-1} diagnostic of the carbonyl in the proposed metallacycle. Also present are bands at 2929cm^{-1} and 2850cm^{-1} associated with the cyclohexyl groups ν(C-H) stretching vibration and bands above 3000cm^{-1} associated with pyridine aromatic ν(C-H) vibrations.

Mass Spectrum (See Table 7.13 and section 6.2.7)

Table.7.13 records the major ions generated in the FAB positive ion mass spectrum of this compound. Signals corresponding to $[M+H]^+$ are abundant in the spectrum. Interestingly, no peaks corresponding to $[M-H]^+$ appear. This is clearly a ligand effect although it is not well understood. MS-MS studies of M/z 448 $[M+H]^+$ confirm the absence of any in-beam reduction process. No 2amu loss is seen. Also the MS-MS shows no 44amu loss attributed to CO_2 and no 15amu loss attributed to loss of a methyl group. It does, though, establish the relationship of M/z 361 $[M-86]^+$ to the parent ion, ie. the parent ion decays, when induced to do so by collision with argon molecules in the collision cell of a mass spectrometer, by loss of an 86 amu fragment assigned as a methacrylic acid moiety.

The major ion in the MS-MS spectrum of M/z 448 is M/z 197. This has been assigned as the fragment show below:-



Changing the ligand from DCPE to DCPy quite clearly alters the fragmentation behaviour. The different steric and electronic properties of the ligand may be influencing the fragmentation of compound 1G compared with 1C. The MS-MS spectrum is not as revealing in this case. Fragmentation to yield an $[M-44]^+$ ion (CO_2 loss) does not occur the predominant loss of 86 as stated earlier attributable to loss of methacrylic acid.

Proton NMR Spectrum (See Table 7.12 and section 6.2.7)

Table 7.12 records the proton NMR of compound 1G. The peaks are broad and it was not possible to extract any phosphorus-proton coupling information from the spectra. The data is consistent with the similar compounds in the series synthesised in this study.

Carbon NMR Spectrum (See Table 7.14 and section 6.2.7)

Table 7.14 records the carbon NMR of compound 1G. The α-CH_2 signal has shifted downfield approximately 6ppm from compound 1D, which also forms a 6 membered ring incorporating the ligand and nickel atom. The signals for the carbons in the ring have remained constant (carbonyl carbon signal is not observed). This is expected. The α-carbon chemical shift reflects the electronic changes in the ligand, i.e. more electron donating/electron withdrawing. The ligand ethane bridge carbons have different chemical shifts to those corresponding bridge carbons in compound 1D as would be expected for a ligand of this type.

Phosphorus NMR Spectrum (See Table 7.10 and section 6.2.7)

The $^{31}P\{H\}$ NMR spectrum shows contains four signals, one of which is the major peak in the spectrum and has been assigned as the ^{31}P signal from the proposed compound. It is consistent with other compounds published in this series and elsewhere (13). The nature of the three remaining signals is not clear.

7.1.8 Synthesis 1-oxa-2-(2,2-bipyridyl)nickela-4-methyl cyclopentan-5-one. COMPOUND 1H.

A deep purple solid was isolated from the reaction of 1A with one molar equivalent of 2,2' bipyridine. Elemental analyses are not in good agreement with that calculated for the target compound. The material proved impossible to recrystallise and decomposed in solution quite quickly in the presence of air. It seems likely that, in the equimolar equivalence used here, bipyridine is unable to completely exchange the tricyclohexyl phosphine of compound 1A. This is in line with the work of T. Kohara et al (12) discussed earlier with reference to the coordinating ability of DCPP. The isolated material could then contain some of complex 1A or similar type material being very air sensitive. The equilibria discussed with reference to compound 1D and illustrated diagramatically probably exist, with equation 1 lying over to the right hand side and equation 2 lying over to the left hand side resulting in the formation of some of the desired product but incomplete reaction under the conditions used here.

Infra Red Spectrum (See section 6.2.8)

The IR spectrum contains one very strong absorbance at 1630cm^{-1}, which is most likely the carbonyl stretch in the metallacycle shown above. Also present are three other medium intensity bands in the region of the spectrum associated with carbonyl stretches. One of these at 1568cm^{-1} is almost certainly from complex 1A (i.e. tetrameric). Complementary evidence for this are the bands at 2920 and 2848cm^{-1} previously assigned as ν(C-H) stretching modes of cyclohexyl groups.

The two medium strength bands at 1606cm^{-1} and 1600cm^{-1} are associated with bipyridine the spectrum of free bipyridine contains similar absorbance bands. The IR spectrum suggests that the synthesis has produced primarily compound 1H but it is impure with probably more than one other compound. This is in line with the work of T.Kohara discussed earlier. The study looked primarily at the coordinating ability of ligands to dimethylnickel (II) and found that the coordinating ability decreased in the order DPPE>, DPPP>>, PEt$_3$ > Bipy. This is in line with the findings of this study. The ligands DPPE and DPPP will exchange PCy$_3$ effectively to yield pure exchanged product. Bipy on the other hand has a coordinating ability probably similar to PCy$_3$ and the addition of one equivalent is not sufficient to fully exchange it even given the chelate effect.

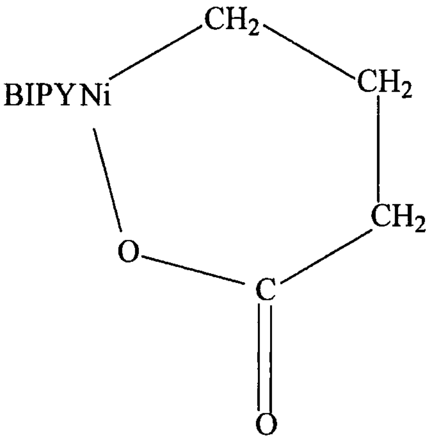
Mass Spectrum (See Table 7.13 and section 6.2.8)

Ions corresponding to [M+H]$^+$ of the proposed compound are evident in the mass spectrum (FAB positive ion) of compound 1H (see Table 7.13). The main ion present has been assigned as the [M-86]$^+$ moiety. There is also evidence for tricyclohexylphosphine oxide M/z 297 in the spectrum. There is no evidence of complex 1A, the mass spectroscopy experiment was not carried out over a high enough mass range to pick up M/z 1721 if present.

One ion present in this spectrum not seen before has been assigned as $[(BIPY)_2Ni]^+$. This extremely stable bis chelate complex ion was not observed for any of the phosphine ligands used in this study and suggests that using > 1 equivalent of BIPY will not increase the yield of 1H .

Proton NMR Spectrum (See Table 7.12 and section 6.2.8)

Table 7.12 records the proton NMR data assigned for the proposed Bipy-nickel metallacycle. The α-CH2 protons still show magnetic inequivalence but the 2,2' bipyridine ligand has a large effect on the chemical shift of the two protons. The spectra show multiple signals in the range 1.2-1.4 and 1.5-1.8ppm attributable to cyclohexyl CH_2 in PCy_3 type impurities (as detected before). The presence of these signals makes assignment more difficult. A complex of proposed structure (6) shown below,



would have signals attributable to the α-CH_2 protons at ~0.8ppm signals attributable to β-CH_2 protons at ~1.3ppm and signals attributable to the γ- CH_2 protons at 2.2 ppm.

The complexity of the proton NMR is again suggestive of incomplete ligand exchange or formation of intermediates.

Carbon NMR Spectrum (See Table 7.14 and section 6.2.8)

Table 7.14 records the carbon NMR data for the compound 1H. The carbon spectra was relatively simple to interpret compared to the proton spectra.

The trends observed for the diphosphine complexes appear to hold for Bipy complexes. The methyl, methine and carbonyl are all relatively constant and appear as sharp singlets. The α-CH_2 was then assigned by inspection.

7.1.9 Synthesis of 1-oxa-2-(1,10 phenanthroline)nickela-4-methylcyclopentan-5-one. COMPOUND 1I.

Isolated as a purple solid, this material proved not to be amenable to recrystallisation and to be quite air sensitive. The elemental composition calculated for the proposed complex is in poor agreement with that found. This is likely to be for the same reasons discussed for compound 1H, i.e. the coordinating ability of the ligand versus tricyclohexylphosphine. The material isolated is most likely a mixture of the desired complex and tricyclohexylphosphine bound nickel complexes (1A or similar).

Infra Red Spectra (See section 6.2.9)

The IR spectrum contains a strong absorbance at 1630cm^{-1}, diagnostic of the carbonyl in the proposed metallacycle structure. Also present is a band 1578cm^{-1}, very strong in this material diagnostic of the tetramer (compound 1A). The bands associated with cyclohexyl ν(C-H) stretching 2923, 2849cm^{-1} are also very strong .

Proton NMR Spectrum (See section 6.2.9)

The proton NMR spectrum had very broad signals and was complicated, possibly due to the presence of some paramagnetic species present. It was only possible to assign based on previous trends the CH_3 resonance as a broad feature, no proton-proton coupling was observed.

Carbon NMR Spectrum (See section 6.2.9)

Table 7.14 records the carbon NMR spectrum for the material. The trends observed for the other compounds in this series are evident here also. The trends observed for the diphosphine ligands appear to hold for phenanthroline. The methyl and carbonyl carbon signals are relatively constant and appear as sharp singlets. The α-CH_2 can then be assigned by inspection. The methine carbon was not observed.

Mass Spectrum (See Table 7.13 and section 6.2.9)

Table 7.13 records the major ions generated in the FAB positive ion mass spectrum. The major ion corresponds to $[M-86]^+$ or $[(phen)Ni]^+$. Molecular ions corresponding to $[M+H]^+$ are present at low levels. This may be a function of ionisation potential in the matrix used. MS-MS studies would be required to confirm the relationship of M/z 238 to M/z 325 observed for the diphosphine complexes.

7.1.10 Synthesis of 1-oxa-2-(tetramethylethylenediamine)nickela-4-methylcyclopentan-5-one. COMPOUND 1J.

The material isolated was a yellow green powder which was not amenable to recrystallisation. The elemental composition calculated for the proposed complex was in poor agreement with that found. The material isolated is a mixture of complexes as found for compound 1H. The characterisation aims to identify features associated with the proposed structure of the complex thought to be the major component of the mixture.

Infra Red Spectra (See section 6.2.10)

The IR contains a strong absorbance at 1624cm^{-1} diagnostic of the carbonyl in the proposed metallacycle. Familiar impurity bands seen in the syntheses of compound 1H and 1I are also present (1576cm^{-1}, 2924, 2852cm^{-1}),associated with compound 1A and the tricyclohexylphosphine ligand displaced in the preparation of 1-oxa-2-(tetramethylethylenediamine)nickela-4-methylcyclopentan-5-one.

NMR Proton and Carbon Spectra.

It proved impossible to make any sensible assignments of the NMR data collected. Proton NMR spectra were broad and the presence of signals due to TMEDA (free) resonances in the carbon spectra made sensible assignment impossible.

Mass Spectrum (See Table 7.13 and section 6.2.10)

Table 7.13 records the main ions generated in the FAB positive ion mass spectrum. Ions corresponding to $[M+H]^+$ are pesent at low levels. The most intense peaks in the spectra are assigned to the impurity tricyclohexylphosphine oxide M/z 297. It should be noted that this technique is by no means quantitative. The low intensity of pseudo-molecular ion is probably a result of the low ionisation potential for the material in the MNBA matrix .

For a wider discussion of the complexes synthesised in this section refer to chapter ten.

TABLE 7.9

Analytical Data For 4-Methyl Substituted Oxa-nickela-cyclopentanones

Compound (Formula)	Yield (%)	M.p./°C (decomp)	Found (%) (Required) C	H	N	Colour	ν_{max}C=O (cm^{-1})
1A $C_{88}H_{156}Ni_4O_8P_4$:	64.8	130	64.3 (62.26)	8.88 (9.2)		Yellow	1569
1B $C_{30}H_{30}NiO_2P_2$:	81.6	220	66.7 (66.4)	5.9 (5.5)		Yellow	1634
1C $C_{30}H_{54}NiO_2P_2$:	77.6	182	63.4 (63.6)	8.9 (9.54)		Yellow	1631
1D $C_{30}H_{56}NiO_2P_2$:	47.4	180	62.72 (64.1)	9.87 (9.65)		Yellow	1643
1E $C_{30}H_{30}NiO_2P_2$	60.8		63.73 (66.4)	5.17 (5.5)		Yellow	1634
1F $C_{30}H_{54}NiO_2P_2$	48.5		61.56 (63.6)	9.44 (9.54)		Yellow	1623
1G $C_{23}H_{36}NO_2P_1Ni$:	73.7	90	62.38 (61.7)	8.92 (8.05)	2.43 (3.13)	Yellow	1629

TABLE 7.10

Phosphorus NMR Data For 3 and 4 Methyl Substituted Oxa-Nickela-Cyclopentanones[c]

ASSIGNMENT	COMPOUND					
	1B[a] (L=DPPE)	1C[a] (L=DCPE)	1D[a] (L=DCPP)	1E[a] (L=DPPE)	1F[a] (L=DCPE)	1G[b] (L=DC-Py)
P1	58.46(s)	68.84(s)	31.62(d, J31.88Hz)	56.68(d, J9.76Hz)	63.09(d, J4.88Hz)	37.31(s)
P2	34.31(s)	60.66(s)	8.31(d, J31.88Hz)	35.49(d, J9.76Hz)	61.49(d, J4.88Hz)	n/a

a) measured in CD_2Cl_2 b) measured in d-6 toluene
c) ppm relative to TMP.

TABLE 7.11

Solvent Variation Of Phosphorus NMR Data In Compound 1C(a).

	CD_2Cl_2	Toluene	THF
P1	68.84	69.7	70.1
P2	60.66	62.6	62.9

a) ppm relative to TMP.

TABLE 7.12

Proton NMR Data For 4 Methyl Substituted Oxa-Nickela-Cyclopentanones(a)

ASSIGNMENT	COMPOUND						
	1A(b)	1B(b)	1C(c)	1D(c)	1G(d)	1H(c)	1I(c)
Ha/Hb	0.82(d, $^2J_{H-H}$7.32Hz, $^3J_{H-P}$ 7.32Hz)	0.526(dddd, $^2J_{H-H}$9.8Hz, $^2J_{H-P\ TRANS}$ 9.8Hz, $^2J_{H-P\ CIS}$ 5.4Hz, $^3J_{H-H}$5.4Hz)	0.57(dddd, $^2J_{H-H}$9.28Hz, $^2J_{H-P\ TRANS}$ 9.28Hz, $^2J_{H-P\ CIS}$ 4.9Hz, $^2J_{H-H}$ 4.9Hz)	0.55(dddd, $^2J_{H-H}$9.28Hz, $^2J_{H-P\ TRANS}$ 9.28Hz, $^2J_{H-P\ CIS}$ 4.88Hz, $^2J_{H-H}$ 4.88Hz)	0.57(br)	1.11(br)	
Ha/Hb	0.91(d, $^2J_{H-H}$6.84Hz, $^3J_{H-P}$ 6.84Hz) $^2J_{H-H}$10.2Hz, $^3J_{H-H}$ 4.4Hz)	1.064(dddd $^2J_{H-P\ TRANS}$ 13.2Hz, $^2J_{H-H}$10.3Hz, $^2J_{H-P\ CIS}$ 6.8Hz, $^3J_{H-H}$ 4.3Hz)	1.07(dddd, $^2J_{H-P\ TRANS}$ 10.3Hz, $^2J_{H-H}$10.49Hz, $^2J_{H-P\ CIS}$ 4.8Hz, $^3J_{H-H}$ 4.15Hz)	0.93(dddd, $^2J_{H-P\ TRANS}$ 10.49Hz, $^2J_{H-P\ CIS}$ 4.15Hz,	0.79(br)	1.43(br)	
Hc	2.34(s)	2.34(br,m)	2.39	2.48	2.54	2.21	
CH_3	1.14(d, $^3J_{H-H}$ 6.83Hz)	0.927(d, $^3J_{H-H}$ 6.8Hz)	1.18(d, $^3J_{H-H}$ 6.83Hz)	1.16(d, $^3J_{H-H}$ 6.84Hz)	1.27(br)	1.02(d, $^3J_{H-H}$ 6.84Hz)	1.08

a) ppm relative to TMS. b) solvent (CD_2Cl_2). c) solvent ($CDCl_3$). d) solvent d^8 toluene.

TABLE 7.13

Two Sector FAB positive ion Mass Spectral For 3 and 4 Methyl Substituted Oxa-Nickela-Cyclopentanones

ASSIGNMENT	COMPOUND								
	1B	1C	1D	1E	1F	1G	1H	1I^{a}	1J
[L-Ni-L]$^{+ (b)}$							370(28)		
[M+MATRIX]$^{+}$	622(26)							418(40)	340(37)
[M+H]$^{+}$	543(66)	567(75)	581(95)	543(18)	567(85)	448(87)	301(22)	325(10)	261(11)
[M]$^{+}$	542(40)	566(40)	580(60)	542(10)	566(55)				
[M-H]$^{+}$	541(100)	565(100)	579(100)	541(20)	565(100)				
[M-86(MAA)]$^{+}$	456(69)	480(48)	494(90)	456(23)	480(55)	361(51)	214(100)	238(100)	174(10)
[PCy$_3$]$^{+}$					281(62)				281(85)
[O=PCy$_3$]$^{+}$				297(100)	297(77)		297(30)	297(80)	297(100)
[PCy$_2$]$^{+}$						197(100)			

Data presented as mass number(intensity %). Matrix is mNBA unless stated
a) Glycerol matrix. b) L= bidentate ligand

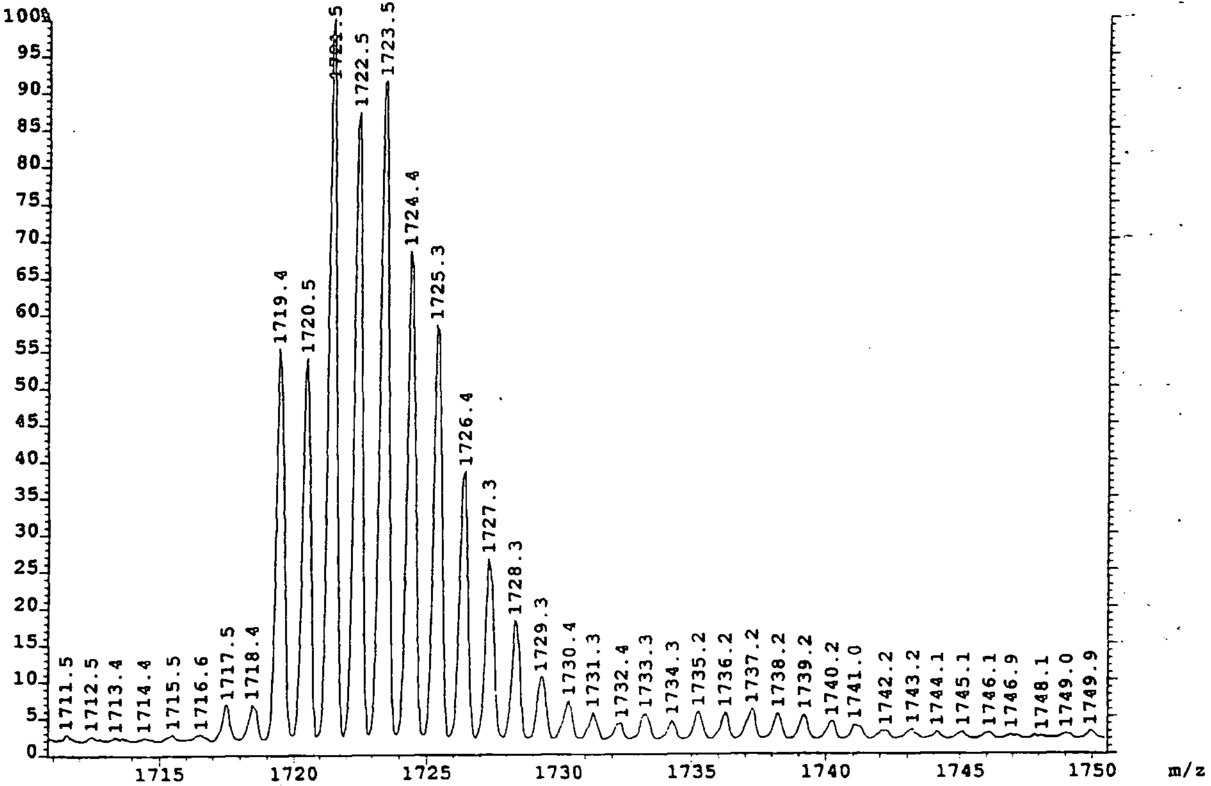
TABLE 7.14

Carbon NMR Data For 4 Methyl Substituted Oxa-Nickela-Cyclopentanones [d]

ASSIGNMENT	COMPOUND					
	1B[a]	1C[a]	1D[a]	1G[b]	1H[a]	1I[a]
C_A	22.66(dd, $^2J_{P\text{-}C}$28.3Hz, $^2J_{P\text{-}C}$ 11.4Hz,	17.65(dd, $^2J_{P\text{-}C}$22.25Hz, $^2J_{P\text{-}C}$9.95Hz,	18.19(dd, $^2J_{P\text{-}C}$22.53Hz $^2J_{P\text{-}C}$11.59Hz)	12.12(d, $^2J_{P\text{-}C}$29.2Hz)	18.4(s)	17.33(s)
C_B	42.39(s)	42.28(s)	42.47(s)	43.13(s)	42.66(s)	
C_C	21.52(s)	22.25(s)	21.89(s)	21.67(s)	21.78(s)	21.38(s)
C_D	190.9(s)	192.0(s)	191.05(d,	 $^4J_{P\text{-}C}$13.8Hz)	191.24(s)	191.3(s)
C_E[c]	29.3(dd, $^1J_{P\text{-}C}$59.8Hz, $^2J_{P\text{-}C}$23.0Hz)	23.11(dd, $^1J_{P\text{-}C}$64.4Hz, $^2J_{P\text{-}C}$26.1Hz)	24.01(d, $^1J_{P\text{-}C}$31.46Hz)	12.94(br)	n/a	n/a
C_F[c]	30.02(dd, $^1J_{P\text{-}C}$29.2Hz) $^2J_{P\text{-}C}$21.5Hz)	24.83(dd, $^1J_{P\text{-}C}$24.6Hz) $^2J_{P\text{-}C}$23.0Hz)	24.59(d, $^1J_{P\text{-}C}$27.6Hz)	34.81(s)	n/a	n/a

a) measured in CD_2Cl_2 b) measured in d-DMSO c) ethyl bridge carbons in chelate ligands
d) ppm relative to TMS

Mass Spectrum generated by Tetra{1-oxa-2-(tricyclohexylphosphino)nickela-4-methyl cyclopentan-5-one, COMPOUND 1A , composition $C_{88}H_{156}Ni_4O_8P_4$.



Instrument generated theoretical isotope pattern for a complex of composition $C_{88}H_{156}Ni_4O_8P_4$.

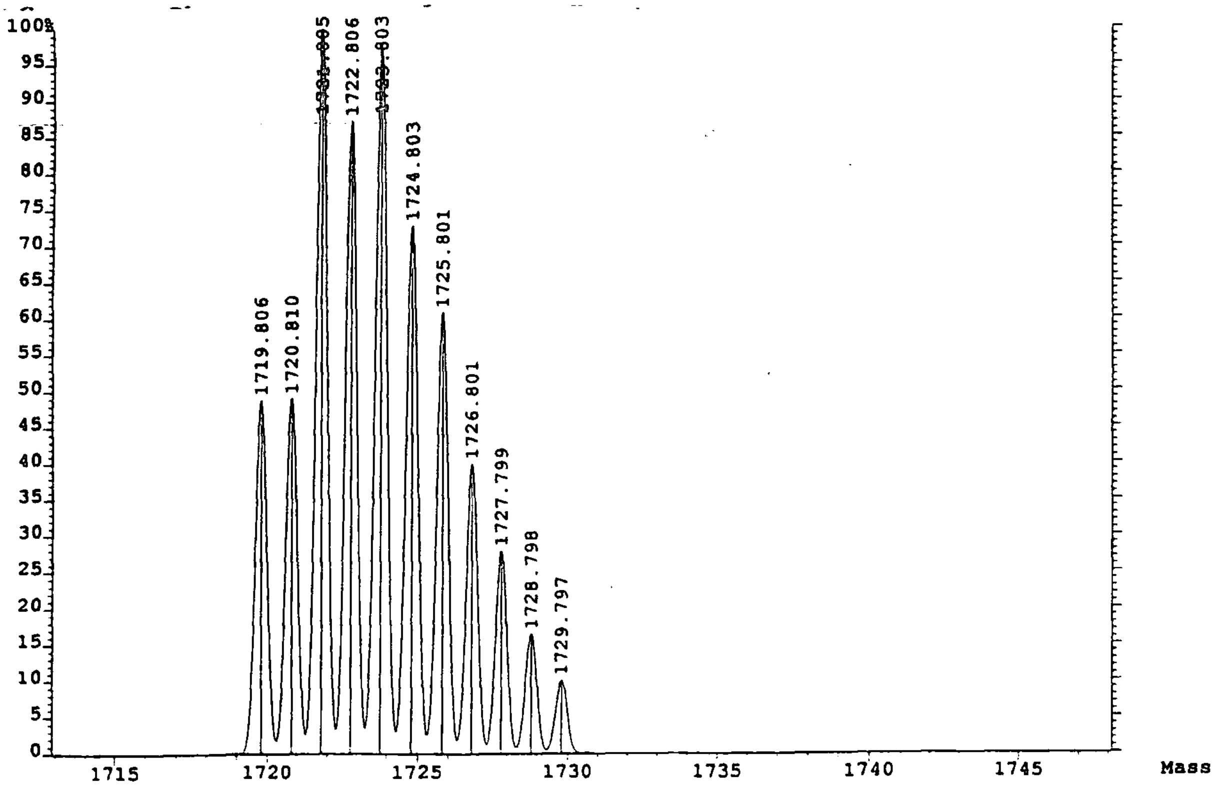
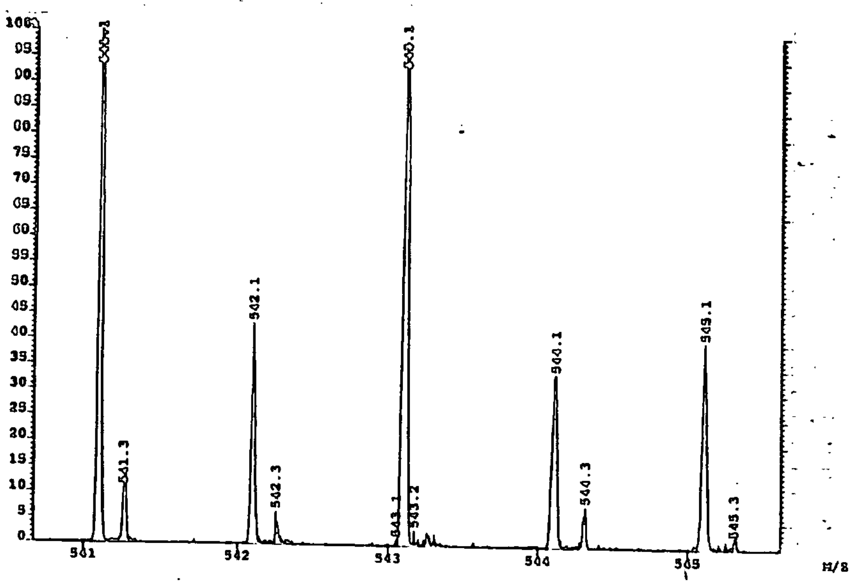
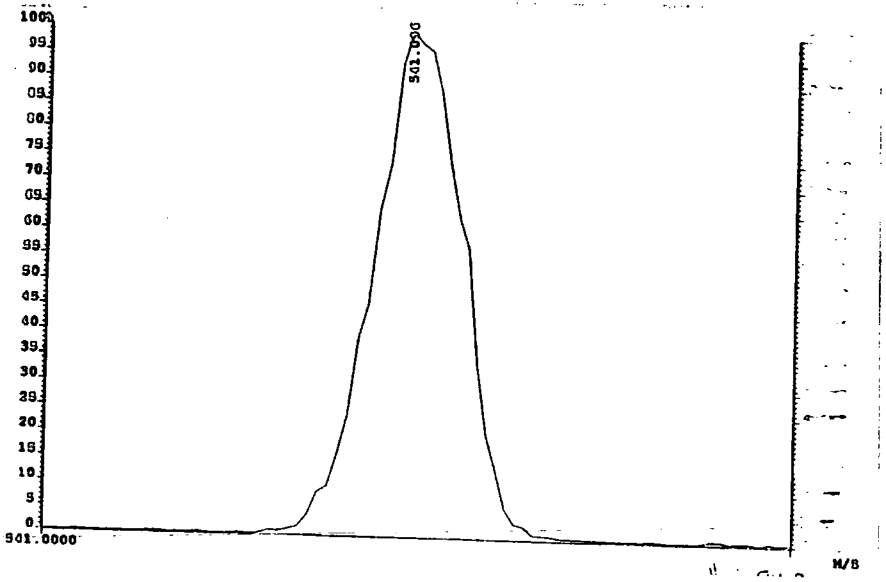


Diagram 7.1

Mass Spectrum generated by 1-oxa-2-{1,2-bis(diphenylphosphino)ethyl}nickela-4-methyl cyclopentan-5-one over the mass range 540-546amu.



High Resolution Mass Spectrum of M/z 541.



High Resolution Mass Spectrum of M/z 543.

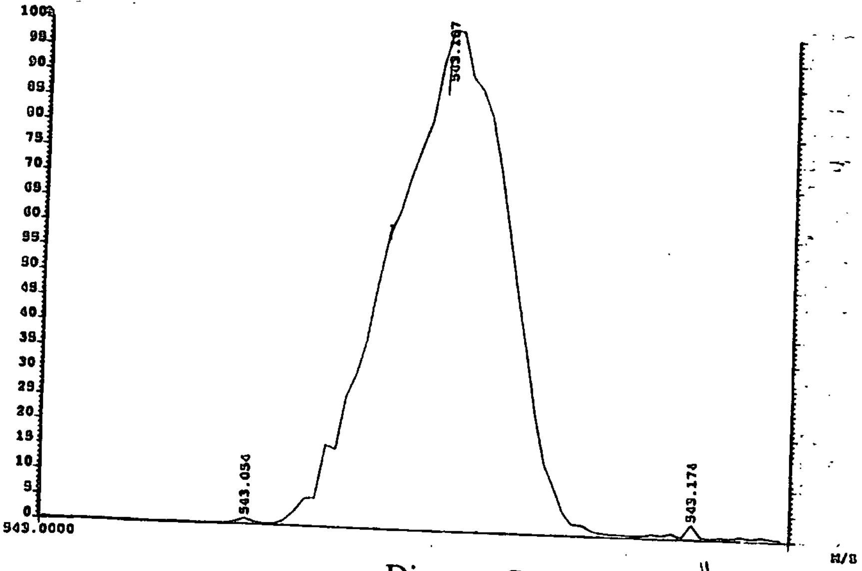
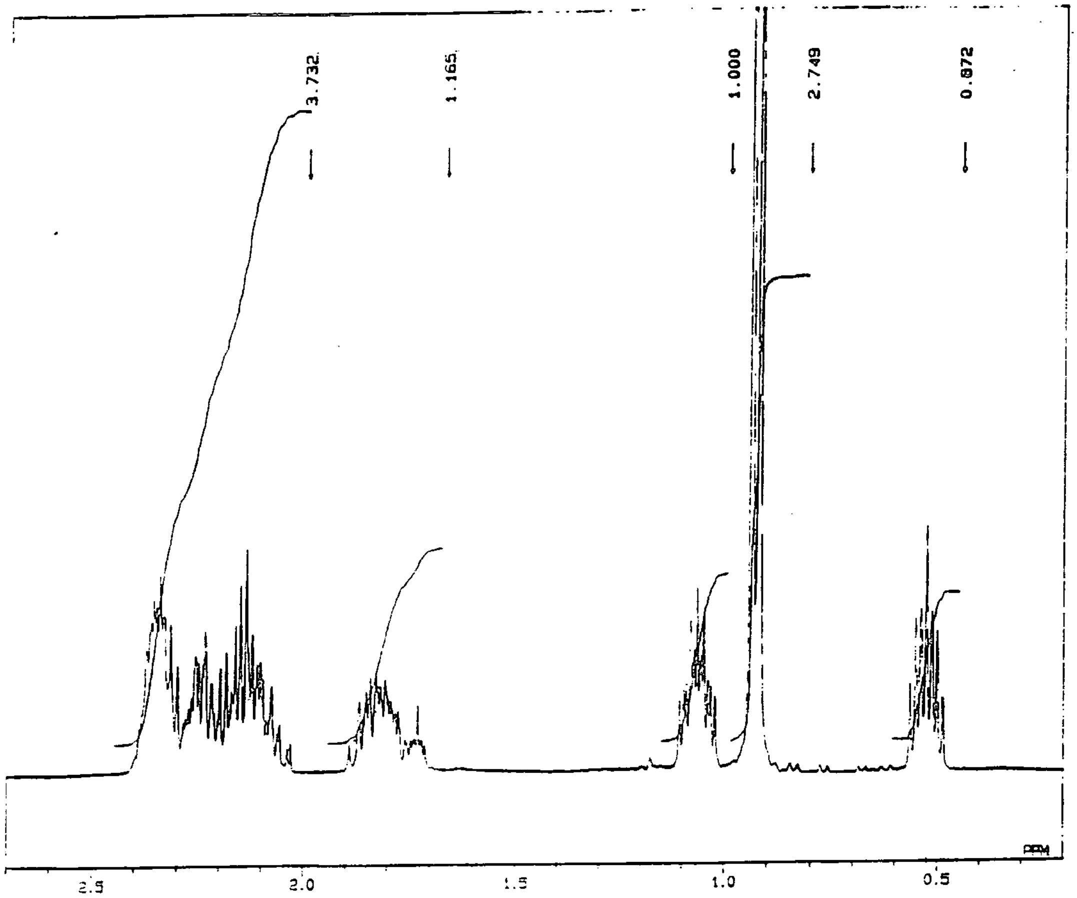


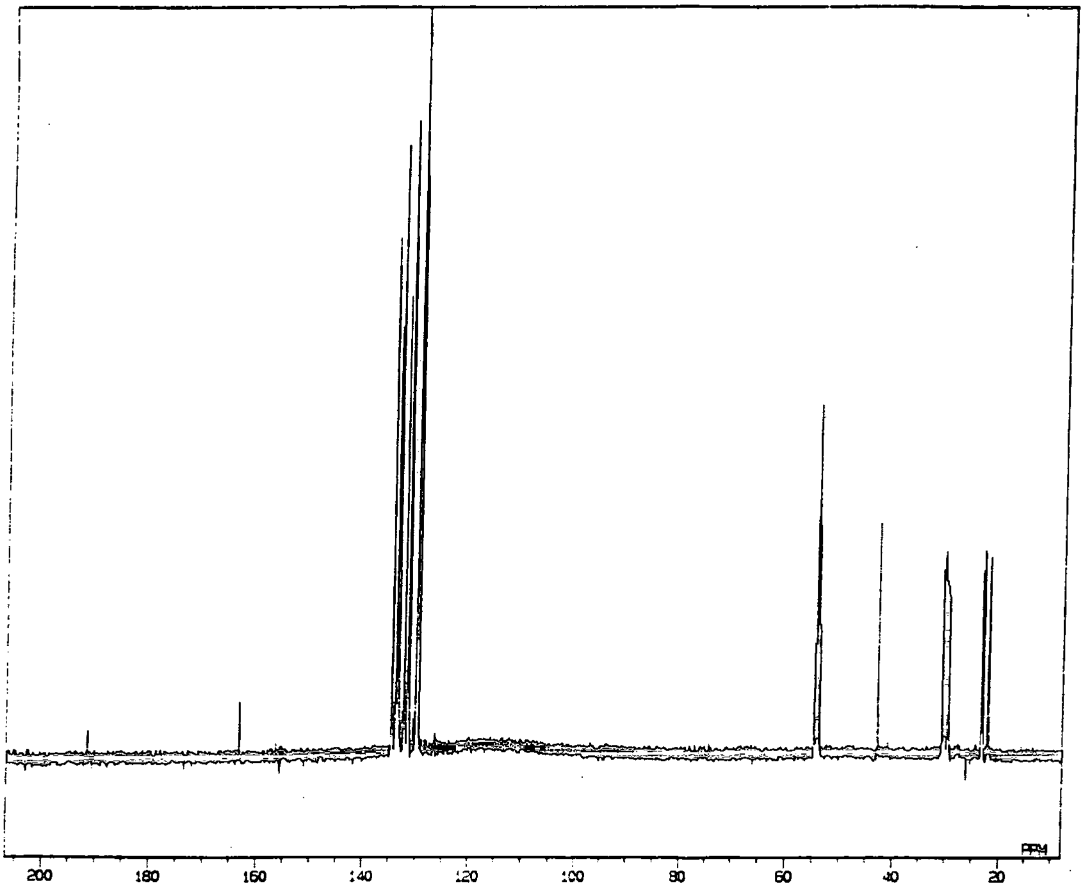
Diagram 7.2



^{1}H NMR Spectrum of [(DPPE)$\overline{\mathrm{NiCH_2CH(CH_3)COO}}$], (0-2.7ppm).

Diagram 7.3

^{13}C NMR Spectrum of [(DPPE)$\overline{\text{NiCH}_2\text{CH(CH}_3\text{)COO}}$], (O-210ppm).



^{13}C NMR Spectrum of [(DPPE)$\overline{\text{NiCH}_2\text{CH(CH}_3\text{)COO}}$], (16-36ppm).

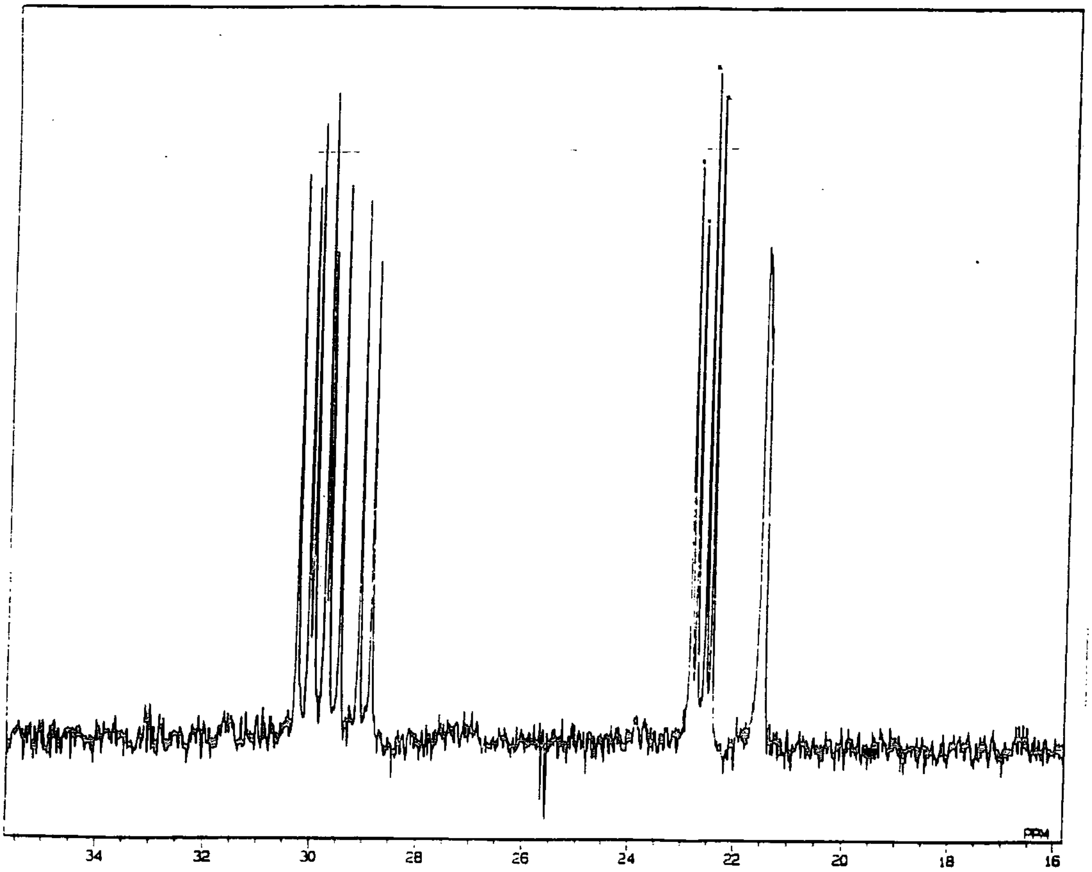


Diagram 7.4

^{13}C NMR Spectrum of [(DPPE)$\overline{\text{NiCH}_2\text{CH(CH}_3\text{)COO}}$], (122-144ppm).

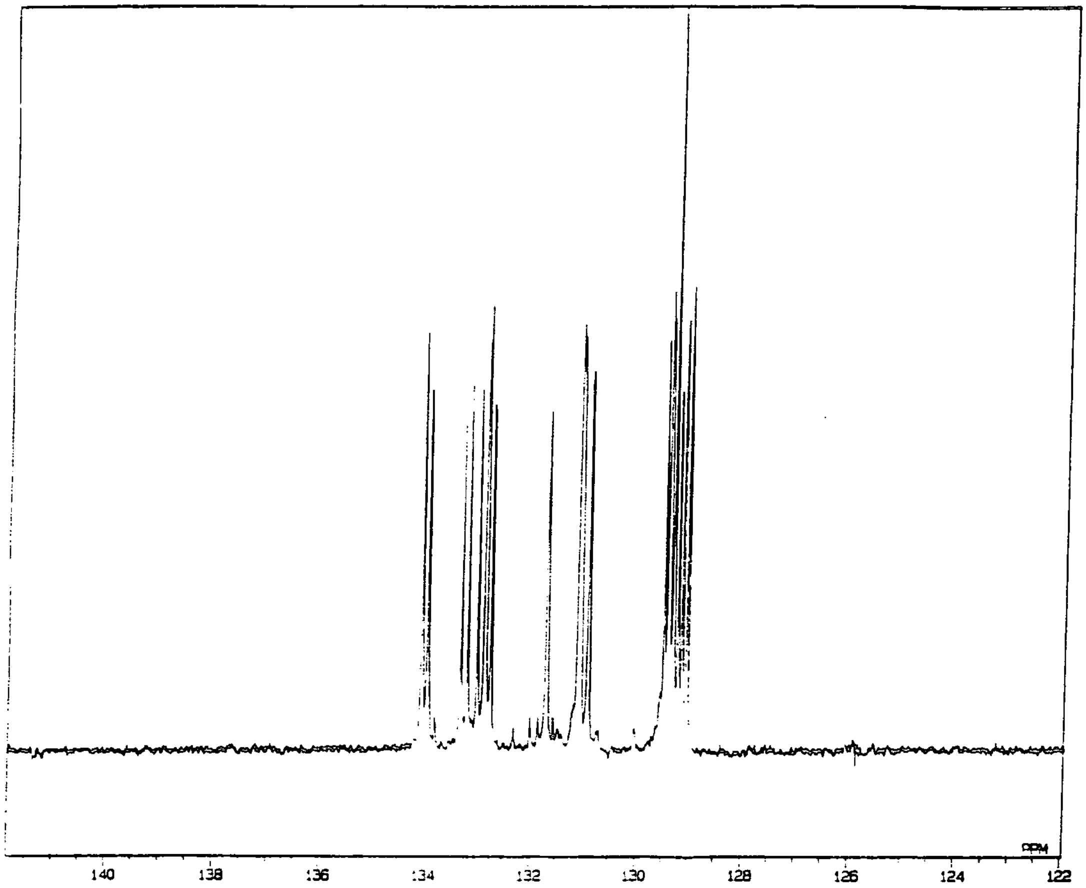


Diagram 7.4

CHAPTER EIGHT

DISCUSSION OF RESULTS

DECOMPOSITION REACTIONS OF 1-oxa-2-{1,2-bis(dicyclohexylphosphino) ethyl}nickela-4-methylcyclopentan-5-one. COMPOUND 1C.

CHAPTER EIGHT

DISCUSSION OF RESULTS

DECOMPOSITION REACTIONS OF 1-oxa-2-{1,2-bis(dicyclohexylphosphino) ethyl}nickela-4-methylcyclopentan-5-one. COMPOUND 1C.

8.1 REACTION OF 1C WITH MALEIC ANHYDRIDE

The purpose of this reaction is to utilise the π acid property of maleic anhydride to liberate methacrylic acid from 1C whilst retaining Ni(O) in the form of a bis-alkene complex according to the equation below:

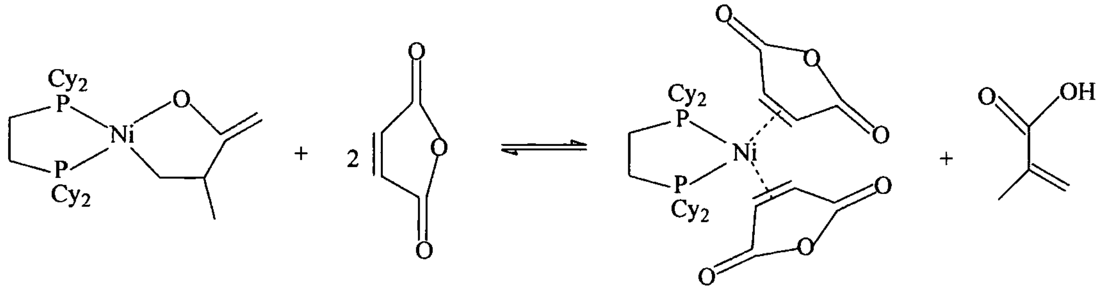
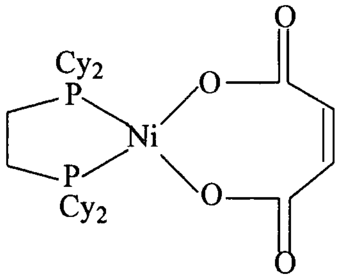


Fig 8.1

This type of reaction was reported for the Bipy complex $[(Bipy)NiCH_2CH_2CH_2COO]$ by Yamamoto et al (6) in 100% yield. The idea behind the experiment if it worked, was to attempt to use higher pressures of propene to effect the same process.

The reaction solution sampled by syringe and analysed by GC-MS was shown to contain saturated isobutyric acid as the major product, both acrylic acid and the expected methacrylic acid were also present, along with malaeic anhydride and a trace of succinic anhydride.

To help explain this result, the solid isolated by removal of the solvent was analysed. Infra red revealed a strong carbonyl at $1601cm^{-1}$ significantly shifted from the carbonyl in 1C ($1631cm^{-1}$). Clearly some reaction had taken place. A weak bond at $1781cm^{-1}$ was attributed to free malaeic anhydride and bands at 2926 and $2852cm^{-1}$ were attributed to ligand cyclohexyl ν(C-H) stretching frequencies. Mass spectra of the isolated solid contained a previously unseen peak at M/z 595 which dominated the spectrum. Accurate mass measurement revealed an elemental composition of $C_{30}H_{51}{}^{58}NiO_4P_2$. The structure which best fits this is shown below



Phosphorus NMR provides complementary evidence in favour of this compound. The spectrum contains a singlet at 76.8ppm not observed before. The remaining signals can be attributed to compound 1C. The presence of only one signal is in line with the above assignment. The right hand side of the molecule is symmetrical, therefore you might expect both phosphorus atoms to resonate at the same frequency.

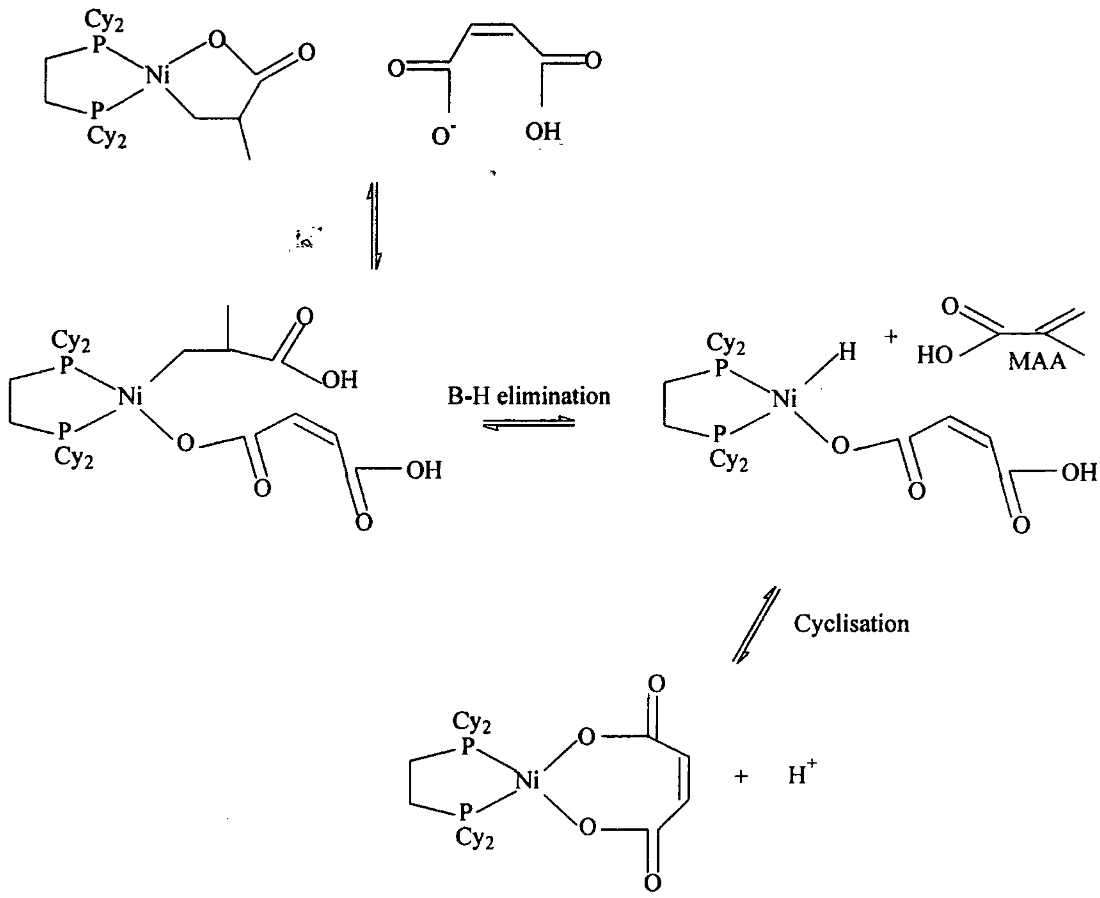
The proton NMR spectrum is very informative. A resonance at 6.22ppm assigned to the C-H protons of the double bond in the above structure, which integrates to equal 2 protons is consistent with the proposed structure. The other feature of the spectrum is a broad multiplet 1.2-2.4ppm equal to 44 protons and consistent with the cyclohexyl CH_2 protons of DCPE.

Carbon NMR also confirms the proposed structure. Because of the symmetry in the molecule, the spectrum is quite simple. There are 5 signals for the CH_2 groups of the ligand as each of the carbon atoms of the cyclohexyl groups is magnetically equivalent to its corresponding carbon atom in the other cyclohexyl groups. The cyclohexyl CH carbons appear as a doublet for the same reason; the magnitude of the $^1J_{P\text{-}C}$ coupling is 10.7Hz. The carbon atoms of the double bond appear as a singlet at 134.0ppm.

Four reaction schemes are postulated to account for the product spectrum observed.

Scheme 1, as reported in the literature for the complex $\{(Bipy)\overline{NiCH_2CH_2CH_2COO}]$ metallacycle (6), where the maleic anhydride acts as a π-acid and methacrylic acid is formed.

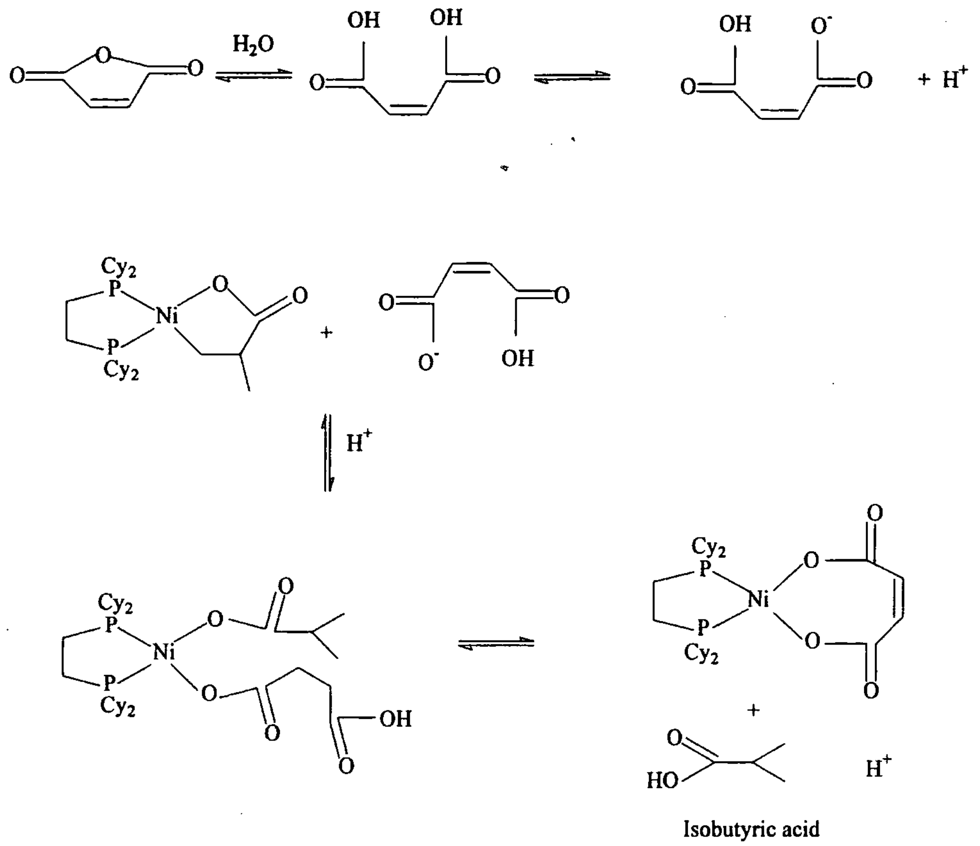
Scheme 2, where the enolate anion of maleic anhydride is postulated as being formed this reaction scheme assumes the presence of water in the reaction mixture to explain the result.



Protonation of the α oxygen of the metallacycle 1C followed by attack of the enolate anion. This is acid hydrolysis, β-H elimination can then occur to form methacrylic acid. In the last step the carboxylate moiety cyclises to give the observed nickel

metallacycle [(DCPE)$\overline{\text{NiOCOCHCHCOO}}$] and generate a nickel hydride. In this reaction scheme the nickel hydride postulated could also be responsible for the formation of iso-butanoic acid via hydrogenation of methacrylic acid.

Scheme 3 where the enolate anion of maleic anhydride is also postulated as being formed, requires protonation of the α-carbon of metallacycle 1C followed by attack of carboxylate anion producing a thermodynamically favourable nickel oxygen bond in place of a nickel carbon bond followed by ring closure to yield the observed product.



Scheme 4, oxidative addition of maleic anhydride to Ni(0) generated in scheme 1

followed by decarbonylation to give the metallacycle $[(DCPE)Ni\overline{CH_2CHCOO]}$, which can liberate acrylic acid via acid hydrolysis occuring in scheme 2. There is some precedent in the literature for this (6). The complex Ni(Bipy)(cod) reacts with glutaric anhydride to give $[(Bipy)\overline{NiCHCH_2CH_2COO}]$ + CO. There is also literature precedent for reaction of nickel(0) with other anhydrides via oxidative addition and ring contraction isomerisation induced by ligand exchange(3).

$[(Bipy)NiCH_2CH_2CH_2COO]$ + DPPE ———> $[(DPPE)NiCH(CH_3)CH_2COO]$

The reaction schemes put forward to explain this result require further work to provide evidence of which mechanisms are operating. The important observation, here, is that in this study, for various reasons, the addition of the malaeic anhydride to 1C did not result in liberation of methacrylic acid in 100% yield.

8.2 Thermal Decomposition Atmospheric :

The idea behind the heating experiments was to induce β-hydride migration in the metallacycle 1C and obtain spectroscopic evidence for the transformation. Variable temperature ^1H NMR experiments were undertaken with 1C dissolved in DMSO, then in TCE, in sealed NMR tubes (under nitrogen) at temperatures up to 120°C and the

the region 0 to 10ppm monitored looking for developing unsaturation resulting from hydride migration.

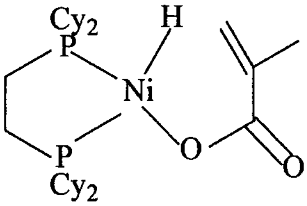
Breakdown of the metallacycle structure was observed above 90°C. The α-CH2 proton features at ~0.6ppm and 1.0ppm in TCE disappear at temperatures above 90°C and a feature at ~1.6ppm emerges.

The nickel carbon bond is possibly breaking at elevated temperature degrading the metallacycle.

When the thermal decomposition experiment was performed in toluene in a nitrogen atmosphere at atmospheric pressure, a nickel hydride resonance was observed when the solid isolated from the reaction was studied by ^1H NMR in d^8 toluene. The chemical shift δ - 23.76 and the magnitude of the coupling J77.4Hz are consistent with nickel hydrides observed in related compounds (14, 15, 16, 17), as given below.

$H\,Ni\,(PCy_3)_2\,Br$	δ -23.0	$J_{PH}77.9$
$H\,Ni\,(PCy_3)_2\,Cl$	δ -24.6	$J_{PH}73.5$

The suggested structure for the hydride containing compound is shown below.



This compound would be expected to show two signals in the ^{31}P NMR consistent with the unsymmetrical nature of the molecule. This is observed, two doublets at δ 62.88 and 58.27 being found. The magnitude of the coupling observed (J, 72.3Hz) is approximately equal and similar to the proton phosphorus coupling observed in the proton NMR. It is thought these two doublets are, in fact, the ^{31}P signals from the above hydride complex and the coupling is ^2J phosphorus-proton coupling. Slight differences in the values of coupling constants obtained from different spectra are not unusual (14-17).

Supportive evidence for the proposed hydride structure comes from three sources:-

(i) IR spectra of the solid isolated from the reaction contain an absorbance band at $1894cm^{-1}$ assigned as the ν(Ni-H) stretching frequency. This is consistent with literature data for nickel-hydride stretching frequencies (14-17).

Compound	ν_{max} (Ni-H)
$HNi(PCy_3)_2Cl$	1916cm^{-1}
$HNi(PCy_3)_2Br$	1917cm^{-1}
$HNi(PCy_3)_2OCOCH_3$	1920cm^{-1}
$HNi(PCy_3)_2CH_3$	1800cm^{-1}

Two other absorbance bands at 3085cm^{-1} and 3025cm^{-1} are consistent with the prescence of unsaturated species.

(ii) Phosphorous and proton NMR of the same sample analysed 1 week later (i.e. NMR tube stored for 1 week) did not show the hydride in the proton NMR or the two doublets in the phosphorus NMR. This is consistent with the known reactivity of metal hydrides suggesting the complex has decomposed/reacted in some way in solution in the NMR tube. A new signal appeared in the ^{31}P NMR not seen in the original analysis at δ 80.09. The presence of only one signal is indicative of a symmetrical molecule. ^{1}H NMR does not show the presence of methacrylic acid ruling out reductive elimination from the metallacycle as having occured.

(iii) When $CDCl_3$ was added to the reaction product containing the proposed hydride, an immediate reaction took place suggesting quite clearly that compound 1C had reacted prior to the addition of $CDCl_3$. Compound 1C dissolves in $CDCl_3$ and no reaction occurs. Two possibilites exist for the identity of the purple solid product resulting from the interaction with $CDCl_3$. These are a) [(DCPE)$NiCl_2$] and b) [(DCPE)NiCl]. The purple colour of the compound is suggestive of it being a nickel(I) complex, these are less well documented. The [(DCPE)$NiCl_2$] complex would most likely be yellow in colour. The ^{31}P NMR spectrum contains one signal at δ 82.87 consistent with a symmetrical DCPE liganded nickel complex. The product of the thermal decomposition reacted with $CDCl_3$ also yields an ion M/z 515 as the major nickel containing species in the FAB positive ion mass spectrum.

The complex [(DCPE)Ni(COD)] synthesised in this study by the addition of a molar equivalent of DCPE to $Ni(COD)_2$ in solution in tetrahydrofuran has a ^{31}P NMR chemical shift of 60.5ppm in toluene. If the spectrum is run in CD_2Cl_2 the ^{31}P NMR chemical shift moves to 80.5ppm. This shift is thought to be the result of the oxidative addition of the CD_2Cl_2 to [(DCPE)Ni(COD)]. Oxidative addition of alkyl halide to zero valent nickel is well documented(refs 18-21). The FAB positive ion mass spectrum of the above reaction product contains an ion M/z 515 which is the major nickel containing species generated, this corresponds to [(DCPE)NiCl]. The instrument generated isotope pattern for ($C_{26}H_{48}P_2ClNi$) assigned to [(DCPE)NiCl], taking into account the known isotopes in their known relative proportions compares well with the observed isotope pattern in the spectra. The complex [(DCPE)NiCl$_2$] may of course be the source of the ion M/z 515 by fragmentation loss of Chloride ligand. No parent ion corresponding to [(DCPE)NiCl$_2$] is observed in the mass spectrum.

This data suggests that the product resulting from the reaction of [(DCPE)Ni(COD)] and CD$_2$Cl$_2$ may be the same as that resulting from the reaction of the solid isolated in 6.3.2 with CDCl$_3$. The spectroscopic evidence suggests this is [(DCPE)NiCl], this is most likely present as the nickel(II) compound [(DCPE)NiCl]$_2$ dimeric in nature. The possibility of [(DCPE)NiCl$_2$] has not been eliminated.

The IR spectrum contains familiar strong absorbance bands associated with DCPE 2924cm^{-1}, 2850cm^{-1} and 1445cm^{-1}. Also present are a number of weak absorbences which can only be tentatively assigned. There are 3 weak bands at 2219cm^{-1}, 2056cm^{-1} and 1978cm^{-1} in that region of the spectrum normally associated with metal carbonyls absorbing indicating some decarbonylation may be occuring. There are also 4 weak bands at 1757cm^{-1}, 1714cm^{-1}, 1622cm^{-1} and 1603cm^{-1} in that region of the spectrum associated with CO stretching both in free organic compounds and metal bound complexes.

The complex [(DCPE)NiCl] is reported to be formed by the reaction of [(DCPE)NiH]$_2$ with [(DCPE)NiCl$_2$], with the liberation of hydrogen according to the equation shown below. No characterisation data is given for the Nickel (1) chloride (14).

$$[\text{DCPENi-H}]_2 + 2\,[(\text{DCPE})\text{NiCl}_2] \rightarrow 4[(\text{DCPE})\text{NiCl}] + \text{H}_2$$

The nickel (I) chloride is reported as stable reacting with lithium borohydride to reform the hydride [DCPENi-H]$_2$. The only references to stable nickel (1) chlorides found are when the chelating phosphine DCPE is used as a stabilising ligand (14, 22, 23).

The mechanism of formation of [(DCPE)NiCl] is not known but it is likely to have formed from the reaction of CDCl$_3$ with the nickel hydride identified from the heating experiments conducted with compound 1C. An alternative is the interaction of CDCl$_3$ with Ni(0) generated by some mechanism in the heating experiments. As mentioned above whilst literature references exist attesting to the stability of [(DCPE)NiCl] it is thought most likely to exist as a nickel(II) dimer. This could feasably generate the observed mass spectroscopic fragment M/z 515, as well as having a single phosphorus nmr resonance. The purple colour is also not unusual for dimers of this type, [(DCPE)NiH]$_2$ is reported to be red.

8.3 THERMAL DECOMPOSITION UNDER A PROPYLENE/CARBON DIOXIDE ATMOSPHERE

The thermal decomposition was studied under an atmosphere of propene/CO_2 at 8 bar pressure. The behaviour of compound 1C under these conditions was quite different to its behaviour at the same temperature under nitrogen. The yellow powder recovered from the autoclave was virtually unchanged as judged by ^{31}P NMR, IR and ^{13}C NMR. No nickel hydride species were detected and there were no nickel(O)/nickel(1) species indicated by the stability of the sample with

respect to $CDCl_3$. Also no isomerisation of the $[(DCPE)\overline{NiCH_2CH(CH_3)COO}]$ is

indicated to give $[(DCPE)\overline{NiCH(CH_3)CH_2COO}]$.

This suggests the propene/CO_2 overpressure is effecting the equilibria at the metal centre inhibiting hydride migration. For a wider discussion of the results of this section refer to chapter ten.

CHAPTER NINE

DISCUSSION OF RESULTS

ALKENE : CARBON DIOXIDE COUPLING REACTIONS

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DISCUSSION OF RESULTS

ALKENE: CARBON DIOXIDE COUPLING REACTIONS

Introduction

This section deals with autoclave reactions where the oxidative coupling of propene and carbon dioxide was attempted in the presence of liganded nickel(0), where the ligands are those identified from a study of the literature and $Ni(COD)_2$ is used as the source of Ni(0). The autoclave reactions have been analysed in three ways:-

(i) Characterisation of isolated solids. Evidence was sought for intermediates of the

type $[(ligand)\overline{Ni(CH_2CH(CH_3)COO)}]$ synthesised and characterised in this study(chapter 7).

(ii) GC-MS of reaction solutions for evidence of catalysis and/or other processes.

(iii) Where it was indicated that coupling may have taken place, hydrolysis of solid products with acid to release the product acids from the metal to enable identification.

Also of interest in this work is the n:iso ratio of acids formed. Clearly the coupling reaction can occur at one of two carbon atoms in the propene molecule as in the alkene/CO_2 coupling investigated by Hoberg et al and reviewed in chapter 5. Coupling at the central carbon would generate methacrylic acid derivative, whereas coupling at a terminal carbon would generate a crotonic acid derivative. The n:iso ratio is influenced by a number of factors such as choice of ligand, temperature and solvent. Acid hydrolysis enables accurate determination of the n:iso ratio for a given experiment. The carboxylic acids are extracted into diethyl ether and the ratio determined by proton NMR integration. Clearly we are interested in directing coupling to the central carbon to generate methacrylic acid derivatives. The exact mechanism of this oxidative coupling is not fully understood, though subject to speculation.

9.1 Use of 1,2-(dicyclohexylphoshino)ethane (DCPE) Ligand .

Table 9.1, 9.2 and 9.3 detail the spectroscopic characterisation of the yellow powder isolated as a precipitate from the autoclave reaction of $Ni(COD)_2$, DCPE, propene and CO_2 (section 6.4.1, solid A). The data is compared to that generated for compounds 1C and 1F, the methacrylic and crotonic derivatives synthesised characterised and discussed in chapter 7 of this study.

Firstly, phosphorus NMR spectra in CD_2Cl_2 of the isolated solid (see experimental section 6.4.1) contains five signals, two of which are in good agreement with the ^{31}P NMR of 1C under the same conditions and two of which are in good agreement with the ^{31}P NMR spectra of 1F under the same conditions. The fifth signal at 80.5ppm has been shown to be a derivative of unreacted [(DCPE)Ni(COD)], (an intermediate in the reaction) resulting from its interaction with CD_2Cl_2 by the following evidence:

One molar equivalent of DCPE added to $Ni(COD)_2$, dissolved in THF in an NMR tube, produces a ^{31}P NMR spectrum containing one signal at 60.5ppm. When CD_2Cl_2 is added to this under a nitrogen blanket and the sample reanalysed by ^{31}P NMR a spectrum containing one signal at 80.5ppm results. The suggestion that the chlorinated solvent is interacting with the Ni(0) species by an oxidative addition reaction is not unusual. Supporting evidence that this third component of the reaction $Ni(COD)_2$ + DCPE + propene + CO_2 is [(DCPE)Ni(COD)] comes from two sources:-

(i) The ^{31}P NMR of the solid A isolated in section 6.4.1 in THF where an oxidative addition reaction is not thought to occur, shows the absence of the signal at 80.5ppm and the prescence of a signal at 60.5ppm. This is consistent with the ^{31}P NMR of [(DCPE)Ni(COD)] in THF as measured above.

(ii) Mass spectrum (FABpositive ion) of a CD_2Cl_2 solution of solid A (section 6.4.1) yields an intense ion at M/Z 515 which has been assigned as [(DCPE)NiCl] on the basis of its isotope pattern. This ion is not present in the mass spectrum (FABpositive ion) of a THF solution of the same solid

The overall evidence of the phosphorus NMR is that oxidative coupling of propene and CO_2 to generate the two types of acid derivative has occurred, but that unreacted liganded Ni(0) remains.

Further supportive evidence for the presence of 1C and 1F type materials is the strong IR absorbance at 1623cm^{-1} indicative of the metallacycle structure. Also the FAB positive ion mass spectrum contains the pseudo-molecular ions seen in the study of 1C and 1F.

Finally, an examination of the proton and carbon NMR data (Tables 9.1 and 9.2) shows there are features in the spectra identical to those in compounds 1C and 1F synthesised earlier. The cumulative evidence is very strong in favour of the product A (section 6.4.1) from the autoclave being a mixture of 1C, 1F and [(DCPE)Ni(COD)].

This being the case, the evidence shows the linkage of both halves of the catalysis cycle described in Chapter 1 of this study (Figure 1.0). Going to the left, Ni(0) and methacrylic acid have been sucessfully reacted to yield intermediate II. Going to the right in the diagram, Ni(0), propene and carbon dioxide have been sucessfully reacted to yield the same intermediate II.

Compound B (section 6.4.1) isolated by removal of the solvent from the supernatant resulting from filtration of the reaction mixture to isolate compound A, appears to be unreacted DCPE-Ni-COD plus a small amount of the methacrylic acid derivative.

This conclusion is based on the ^{31}P NMR spectra in CD_2Cl_2, toluene and THF and comparison with data obtained for authentic samples.

The reaction mixture analysed by GC-MS showed the absence of any methacrylic or crotonic acids indicating the reaction was stoichiometric in nature. The main component in the GC-MS of the reaction mixture was cyclooctadiene and its isomers (see Table 9.4). The isomerization is occurring in the autoclave reaction as the starting material was derived from pure 1,5-cyclooctadiene. Nickel compounds are known isomerization catalysts (see chapter 4) so the presence of isomers of cyclooctadiene is not unexpected.

In the preparation of an ethene oligomerization catalyst, Keim et al (9 ch.4) formed cyclooctadiene isomers as follows

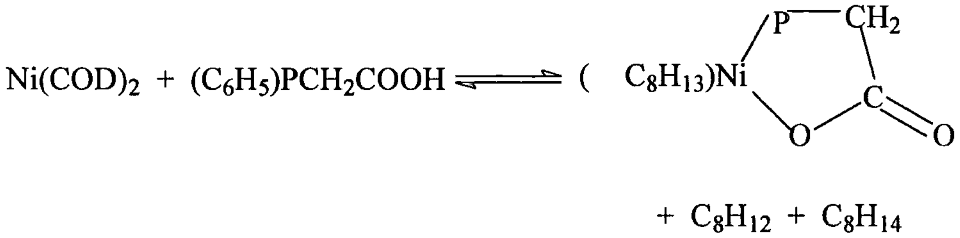
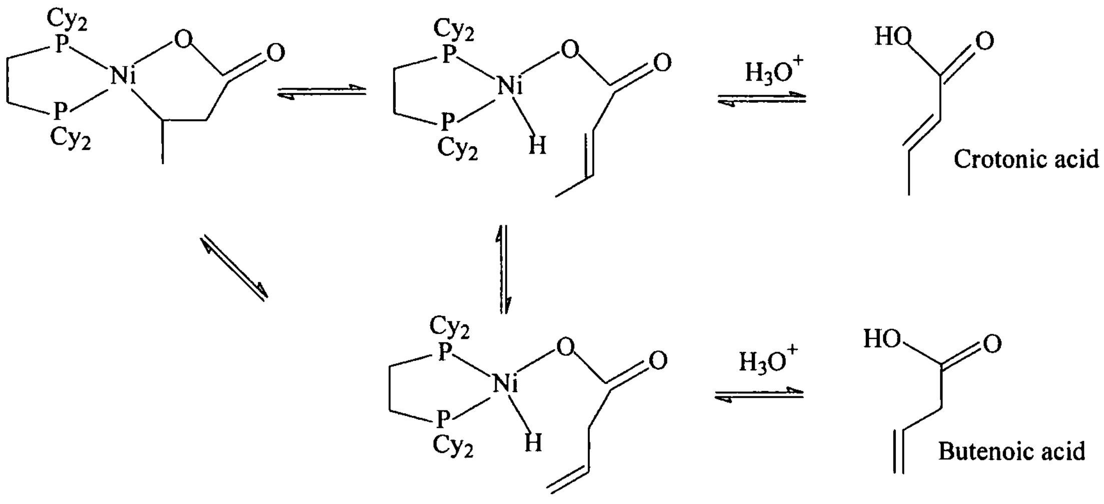


Fig. 9.1

Whilst this may not be exactly what is occurring in the present system, it shows that the propensity to form isomers of COD is not uncommon during the formation of active nickel catalysts.

When acid hydrolysis was carried out on the total solids isolated from a repeat autoclave experiment, the acids produced amounted to a yield of 62% with an n:iso ration of 1:2 (see Table 9.4). DCPE as ligand selectively directs coupling to the central carbon of the propene under the conditions employed. The interesting feature of the GC-MS analysis of the acid hydrolysis extract is the presence of small amounts of crotonic and linear butenoic acids. The suggested route to the formation of these materials is shown below:-



In the crotonic derivative β-hydride transfer followed by acid hydrolysis would lead to the generation of crotonic acid. There is some precedent for this in the oxidative coupling of styrene + CO_2 to generate the unsaturated cinnamic acid, which is proposed to occur by the same mechanism of β-hydride transfer although no spectroscopic data is presented. The presence of the phenyl group on the α-carbon may be influencing the geometry of the ring and hence the orbital overlap/interactions, thus making β-hydrogen transfer to the metal an allowed process or thermodynamically more favourable. The methyl group may be acting in a similar manner in this system. It is then more likely that isomerisation is the source of butenoic acid .

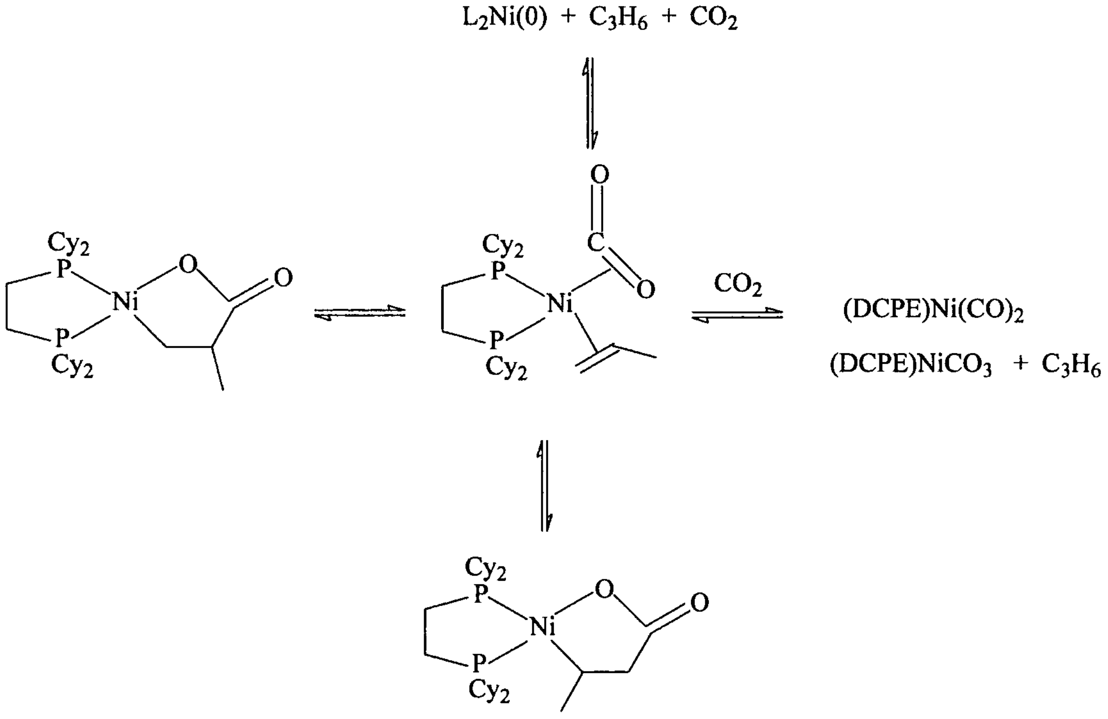
The total amount of crotonic acid and butenoic is estimated to be less than 5% of the total n and iso butyric acids formed. This is a rough estimate calculated from the total ion counts of each peak in the GC-MS spectrum and is in agreement with the proton nmr spectra.

The main conclusion from the acid hydrolysis is that it provides further evidence that oxidative coupling has indeed taken place and tells in what proportions the metallacycles 1C and 1E must have been present. Isobutyric acid can only have come from 1C and crotonic from 1E.

Temperature Dependence

The idea behind the investigation of the effect of temperature is the observation by Hoberg et al (5 ch.5) that the ratio of isomers formed, i.e. n:iso ratio, can be influenced by temperature. Hoberg reported that raising the temperature from 20°C to 60°C altered the n:iso ratio from 1:4 to 1:25 in the coupling reaction of hexene and CO_2 at DCPE liganded Ni(0), and postulated the reversibility of the coupling step as the reason for the change. Even subsequent heating of the complexes obtained at 20°C (i.e. 1:4 n:iso) resulted in the 1:25 ratio at 60°C.

We attempted to emulate this effect in this study by following the protocol outlined in chapter 6, section 4.12 and heating the autoclave to 60°C for 2 hrs in the presence of propene and CO_2. The result after hydrolysis was a reduced yield of carboxylic acids and a lower selectivity to oxidative coupling at the central carbon of the propene, as judged by the drop in n:iso ratio (see Table 9.4). This is the opposite effect to that published by Hoberg et al. Further work is required to establish the nature of the observed effect. There is a suggestion from the thermal decomposition experiments reported in chapter 6, section 3.0 that, the pressure of propene and/or CO_2 suppresses decomposition. Compound 1C heated to 110°c in the presence of 8 Bar propene/CO_2 mixed gas did not appear to decompose significantly whereas, when compound 1C was heated to 100°c under atmospheric pressure of nitrogen, significant changes occurred as judged by ^{31}P NMR. The propene/CO_2 pressure suggested by Hoberg to be necessary, for the regiochemical temperature effect may be influencing the complex set of equilibria shown .



The importance of a 1:1 stoichiometry (alkene:CO_2) has been stressed by other workers. Hoberg et al stress for the catalysis involving phenyl isocyanate (CO_2 analogue), that the isocyanate is added to the solution of nickel(0), ligand and alkene via a metering pump to maintain a stoichiometric amount or less. Simultaneous mixing gives rise to the catalytic product in lower yield. Secondary reactions similar to the reductive disproportionation of CO_2 occur (14 chapter 5). Because no solid was isolated in this reaction, it is only possible to speculate on the production of [(DCPE)Ni$(CO)_2$]. Infra red analysis of the solid would have been diagnostic in this case.

The much simpler argument is to accept the findings of this study and suggest that the literature report of Hoberg et al is incorrect. Based on the amount of analysis available concerning the effect of temperature, this is not prudent, more work is required to confirm this finding.

Solvent Effect

The reason behind the investigation of the effect of acetronitrile as a solvent on the n:iso ratio is based on literature evidence that alkyne:CO_2 cooligomerization is more selective when acetonitrile is used as a solvent. The attributed effects of acetronitrile are listed in chapter 5. Probability of greatest significance is the ability of acetonitrile to act as a ligand and be able to come on and off the metal ie. a coordinating solvent. The result in this study was a reduced yield of carboxylic acids and an n:iso ratio of 45:55. The effect on the n:iso ratio is the opposite to what was hoped. The presence of the competing ligand appears to be directing coupling at the terminal carbon of propene. Further work is necessary to fully characterise this effect.

Characterisation of the solid produced using acetonitrile as a solvent does lead to the assignment of two bands in the infra red at 1982cm^{-1} and 1910cm^{-1}, of approximately equal intensity, as metal carbonyl bands(see diag 9.1). These are consistent with previously published data for complexes of the type [$L_2Ni(CO)_2$], (24) and it is concluded that [(DCPE)$Ni(CO)_2$] has been formed.

Compound	I.R Absorbance
$(C_2H_5CN)_2\,Ni(CO)_2$	ν_{max} (CO) 2013cm^{-1}, 1968cm^{-1}
$(CO)_2$ Ni BIPY	ν_{max} (CO) 1983cm^{-1}, 1914cm^{-1}
$(CO)_2\,Ni[P(C_2H_5)_2\,C_2H_4P(C_2H_5)]_2$	ν_{max} (CO) 1978cm^{-1}, 1915cm^{-1}
$(CO)_2$ Ni [P(Cyclo - $C_6H_{11})_3]_2$	ν_{max} (CO) 1980cm^{-1}, 1912cm^{-1}

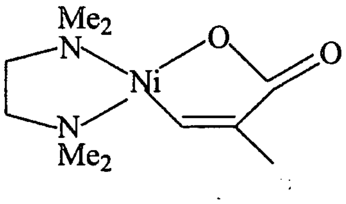
The reduction in yield can be accounted for in this case by the following reaction

$$3L_2Ni\,CO_2 + CO_2 \rightarrow L_2Ni(CO)_2 + 2L_2\,Ni\,CO_3$$

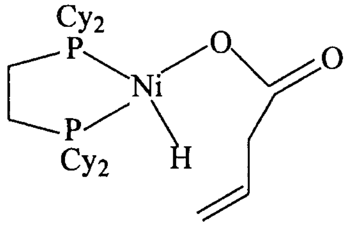
The mass spectrum (FAB positive ion) shows the presence of ions corresponding to the target metallacycles (3-and 4-methyl substituted oxanickellacyclopentanones). Also present though is an ion at M/z 509 which corresponds to [M+H]$^+$ of [(DCPE)Ni(CO)]. The most intense nickel containing ion corresponds to a matrix adduct common to many samples (see Diag 9.1).

The peak in the IR at 1903cm^{-1} has been tentatively assigned as [(DCPE)Ni(CO)L'] where L' = acetonitrile [literature values for [(CO)$Ni(PMe_3)_3$] ν_{max} (CO) 1923cm^{-1}](14), [(CO)Ni{$P(C_6H_5)_2(CH_2)_4\,P(C_6H_5)_2\}_2$] ν_{max} (CO) 1910cm^{-1} suggest the mono CO complex absorbs in the region observed. It is reasonable to assume an equilibrium exists between the two complexes, [$L_2Ni(CO)_2$] and [$L_2Ni(CO)L'$] in the presence of excess L' (acetonitrile).

One other possible explanation of the IR data is the assignment of one of the peaks 1903cm^{-1}, 1910cm^{-1}, 1982cm^{-1} as a nickel hydride absorbance. Supportive evidence that this might be the case comes from previous work done on the oxidative coupling of Alkene/CO_2 at TMEDA liganded Nickel(O) (ICI report). In this well-characterized compound having the structure shown below

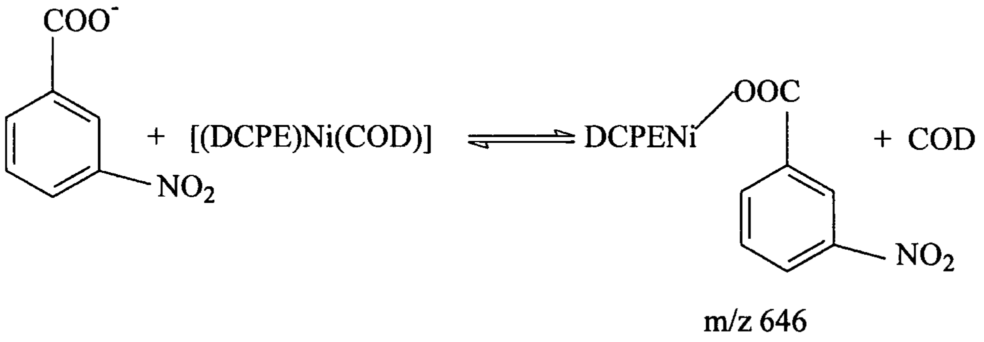


the ν(C=C) appears as a sharp band at 1651cm^{-1} on the side of the carbonyl absorbance 1635cm^{-1}. In the above reaction, the IR spectra of the solid isolated shows a strong band at 1654cm^{-1} is present, which may be the unsaturation in the complex as shown below.



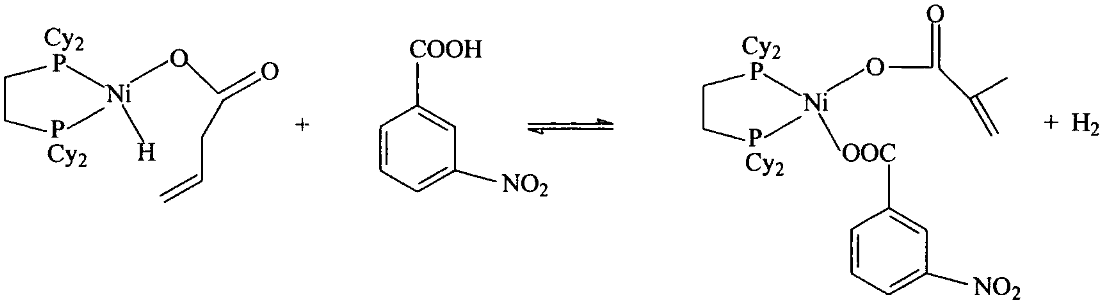
However such a complex would be expected not to be stable in chlorinated solvents, in which hydride would be replaced by the chloride ligand.

Further indirect evidence to support the presence of a reactive Nickel hydride comes from the mass spectrum of a different system. In the mass spectroscopic analysis of samples containing nickel(0), ie.[(DCPE)Ni(COD)], the major nickel containing ion is found to be M/z 646. This has been assigned as a matrix adduct ion resulting from the interaction of an acid form of the mNBA matrix with the sample.



This ion has been accurately mass measured and found to have the correct elemental composition for the above assignment. The above 646 ion is only observed in samples where Nickel(O) is thought to be present. As mentioned previously, in samples containing DCPENiCOD, a large ion M/z 646 is evident. The suggestion in this case is that this matrix ion forms when other reactive species are present in the sample. In the mass spectral analysis of Nickel II compounds such as 1B and 1C by FAB positive ion mass spectroscopy using mNBA as matrix, no ion M/z 646 is detected.

For the solid reaction product isolated from the oxidative coupling reaction of propene/CO_2 in the presence of acetonitrile, an ion M/z 733 is observed. This ion has not been seen before and it is suggested may be formed in an analogous way to the M/z 646 by interaction of the reactive hydride with the acid form of the matrix .



The mass of the proposed product is 732amu, therefore the ion we see is $[M+H\}^+$.

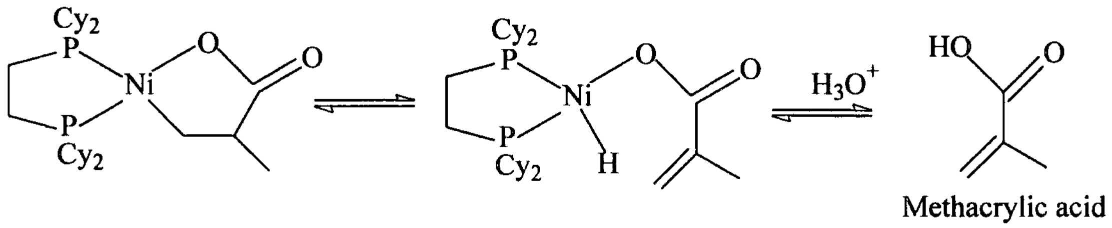
Given this hypothesis, this ion M/z 733 is expected to form from other autoclave products where unsaturated acids have been detected after acid hydrolysis and nickel hydrides are implicated. This is not the case. Interestingly in these latter cases IR analysis has failed to detect any Nickel hydride absorbances suggesting that they are either not present or decay rapidly.

Phosphorous NMR spectra were recorded several months after the reaction was initially performed and show the sample has changed somewhat even during storage in an argon atmosphere. Four signals are present two of which 69.5 and 62.5ppm are from the $[(DCPE)\overline{NiCH_2CH(CH_3)COO]}$ product, there are no signals present for the crotonic isomer $[(DCPE)\overline{NiCH(CH_3)CH_2COO]}$. These signals should be present given the 45:55 n:iso ratio determined from acid hydrolysis of the sample directly after the reaction.

The two remaining signals are at 53.69ppm and 80.16ppm. The signal at 80.16ppm is close to the signal observed to appear after the Nickel hydride reported in section 6.3.2 is left to stand for 1 week in d8 toluene and reanalysed (80.09). The origin of the peak at 53.69ppm is unknown.

In conclusion, the evidence of this study is that oxidative coupling of propene/CO_2 occurs in the presence of acetonitrile but there appears to be some loss of selectivity to the methacrylic isomer. The presence of carbonyl and hydride species can be argued from the spectroscopic data but more work is required to confirm these suggestions.

The interesting fact observed here and not seen previously is the presence of methacrylic acid, detected by GC-MS, following hydrolysis. Whilst there is only a trace (<1% based on total ion count analysis of mass spec peaks), it is still noteworthy. Methacrylic acid may have been formed according to the equation shown below.

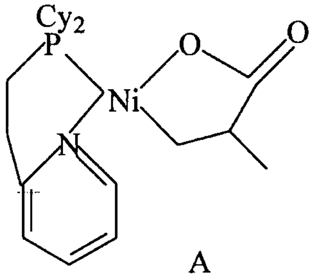


This equilibrium may be well over to the left hand side under the conditions employed. The role of the acetonitrile in promoting this proposed reaction is not known, but it is only in the presence of acetonitrile that this phenomenon has been observed.

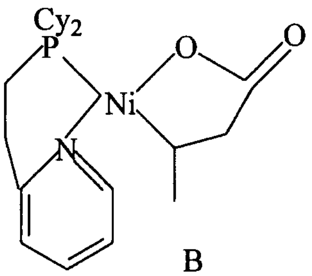
9.2 Use of 2-{2,-(dicyclohexylphosphino)ethyl}pyridine (DCPy) Ligand.

Tables 9.6, 9.7 and 9.8 detail the spectroscopic data for the solid isolated at the end of the reaction, and is compared to that obtained for compound 1G, the methacrylic derivative synthesised and discussed in chapter 7.0. Table 9.4 details the results of acid hydrolysis and the analysis of the reaction mixture.

High yields of normal and iso-butanoic acid result from the oxidative coupling of propene and carbon dioxide at DCPy liganded nickel(0) complexes(approximate 1:3 ratio after acid hydrolysis). The intermediate metallacycles are shown below:-



A



B

The phosphorus NMR confirms the presence of two phosphorus containing compounds. Allowing for a solvent effect not uncommon in ^{31}P NMR measurement and observed previously for compounds 1C and 1E, the signal at 38.28 of larger intensity has been assigned as the ^{31}P NMR signal of A above(compound A = compound 1G model compound synthesis). Based on the acid hydrolysis result and the presence of normal butanoic acid, the signal at 34.22 has been assigned as the ^{31}P NMR signal of B above.

The FAB positive ion mass spectrum shows ions consistent with the formation of compound A. The observation of the phenomenon of formation of $[M+H]^+$ ions M/Z 448 and 450 for Ni^{58} and Ni^{60} isotopes respectively and the absence of $[M-H]^+$ ions provides complimentary evidence for the presence of compound A in the isolated solid.

Infra red spectra confirm that the metallacyclic structure is present. The very strong absorbance band at $1629 cm^{-1}$ is diagnostic of a carbonyl in cyclic nickel containing metallacycles of the type $[(L_2)\overline{NiCH_2CH(CH_3)CO}O]$. Other bands in the spectra are associated with the DCPy ligand and have been observed previously.

Proton NMR confirms the presence of the methacrylic isomer. The spectra of the mixture generated in the autoclave reaction and the spectra of compound 1G have been taken in different solvents and hence the chemical shifts in some cases differ slightly. Taking this into consideration, the spectrum of the mixture shows all the signals observed in the spectrum of 1G and assigned to the methacrylic isomer. As in compound 1G, no couplings were observed/resolved. No signals definitely assigned as the crotonic isomer have been observed; it is likely that these signals having lower intensities are hidden underneath the cyclohexyl resonances, (based on the trends observed for 1E/1F). There is a feature in the proton NMR spectra of the autoclave product mixture at δ 0.26 which is consistent with the methyl group protons of the crotonic isomer(compound 1B above).

Signals to high frequency are not uncommon for methyl protons in close proximity to nickel(23). Complexes of the type $L_2Ni(CH_3)X$ can have -ve chemical shifts relative to TMS e.g.

$[P(isoC_3H_7)_3]\ Ni(CH_3)Cl$ $\delta = -0.8ppm$

$[P(CH_3)_3]_2\ Ni(CH_3)Br$ $\delta = -1.0ppm$

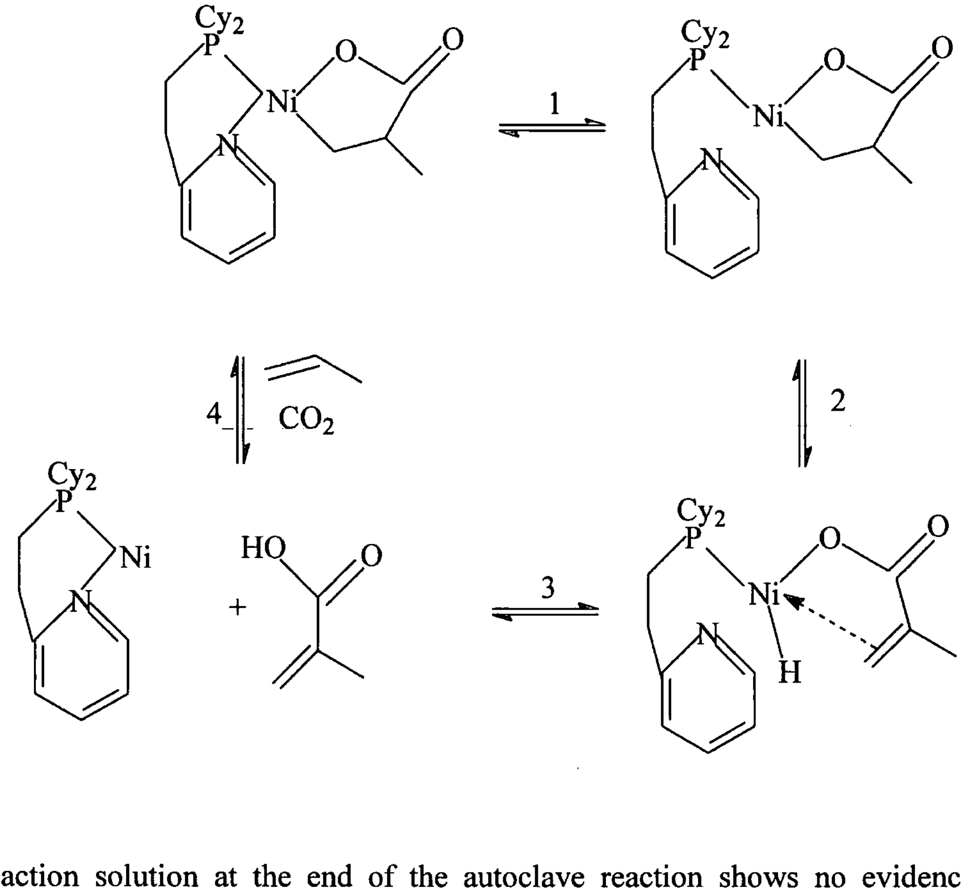
It is not unreasonable to suggest that the methyl group in the crotonic isomer which is one bond further shifted from the nickel than the methyl group in the above examples may have a chemical shift of ~ +0.20 in a DCPy liganded Ni complex.

The carbon spectra also confirms the presence of the methacrylic isomer. The spectra of the methacrylic isomer synthesised by the oxidative addition of methacrylic acid to Ni(0) and the spectra of the solid isolated from the oxidative coupling reaction of propene/CO_2 at DCPy liganded Ni(0) were recorded in different solvents. This it is suggested accounts for the minor chemical shift differences observed between features in the two spectra. The broadness associated with peaks at δ 13.76 and 35.54 may be due to contributions from the crotonic isomer. These signals have been assigned as the bridge methylenes which were observed not to shift significantly in the DCPE methacrylic and crotonic complexes.

Prolonged aquisition of ^{13}C spectra proved not feasible for the DCPy liganded complexes because of decomposition problems. One result of decomposition was that the carbonyl carbon resonance was not observed and, in the case of the autoclave mixtures neither was the methine carbon of the methacrylic isomer.

Overall characterisation of the solid and hydrolysis products leads to the conclusion that DCPy used as a ligand in the standard autoclave run to oxidatively couple propene and CO_2 results in high yields of the stable intermediates. Coupling is selectively directed at the central carbon to a greater extent than previously observed with other ligands. There is no evidence for the competing reductive disproportionation of CO_2 and also no evidence of unreacted DCPyNi(COD) according to ^{31}P NMR spectroscopy.

The reasoning behind the use of this ligand relates to its potential ability of one coordinating atom to flip off the metal and create an empty coordination site as illustrated in the following diagram. This might allow the β-hydride transfer to occur where it had previously been not possible. The electronic properties of the ligand are thought to be not too dissimilar to DCPE, i.e. electron donating enough to be active in the oxidative coupling reaction. The catalysis cycle according to equations 1-4 below is proposed. The four centre coplanar transition state thought to be required for β hydride migration (chapter 3) is thought to be more favourable under these circumstances.



The reaction solution at the end of the autoclave reaction shows no evidence of methacrylic acid which would result from the suggested catalysis. Only cyclooctadiene isomers, were detected. The acid hydrolysis also showed no evidence for methacrylic acid which would form from a hydride intermediate in the same way as crotonic acid. Crotonic acid was detected at a similar <5% level using DCPy as was found using other phosphines. There appears to be no evidence for the enhancement of β-hydride transfer using DCPy, though it does give increased selectivity to the 4 methyl substituted oxanickellacyclopentanone intermediate. Other workers (see chapter 5) have generated unsaturated and branched carboxylic acids after acid hydrolysis by using beryllium chloride and pyridine as additives in the reaction. The product spectrum has been explained in terms of β-hydride transfer being initiated or enhanced in some way. This is by interaction of the beryllium chloride with either the pyridine nitrogen of the ligand or the carboxylate moiety. Interaction in the first case is thought to favour equation 1 above where the pyridine portion of the ligand leaves the metal. No direct evidence for hydride migration is given only explanations based on the product spectrum.

9.3 Use Of 1,3-bis(dicyclohexylphosphino)propane (DCPP) Ligand

The spectroscopic data for this reaction is recorded in section 6.4.7. When DCPP was used as a ligand in the oxidative coupling reaction, a mixture of products was obtained. It appears some propene/CO_2 was oxidatively coupled to give metallacycle ID. The evidence for this is:-

(i) Absorbance 1636cm^{-1}. Since it is only of medium strength in the spectrum as opposed to the very strong band observed for the authentic complex ID, this suggests it is present in small amount.

(ii) Presence of ions in the FAB positive ion mass spectrum corresponding to $[M-H]^+$ ions previously observed by the same technique for complex 1D. It was observed that, if the sample was exposed to air for a few minutes, the nature of the spectrum changed rapidly. Ions at M/z 579 were not observed at the same relative intensity compared with the authentic material.

(iii) Peaks in the ^{31}P NMR having similar chemical shifts to those in compound 1D and similar coupling constants to 1D.

The evidence is that oxidative coupling has occurred but to a small degree. Other, more predominant reactions are indicated by the spectroscopic analysis. Infra red bands at 1978cm^{-1} and 1915cm^{-1} of approximately equal intensity are consistent with carbonyl stretches for the complex $[(DCPP)Ni(CO)_2]$. This suggests that reductive disproportionation of CO_2 is occurring. An absorbance at 1174cm^{-1} is consistent with P=O in phosphine oxide. A strong singlet in the ^{31}P NMR spectrum at δ46.47ppm is also consistent with the presence of phosphine oxide.

Further evidence for the cis dicarbonyl compound $[(DCPP)Ni(CO)_2]$ is the presence of a singlet in the ^{31}P NMR spectrum of the isolated solid at δ 27.36ppm. The chemical shift reported for the compound $[(DEPE)Ni(CO)_2]$ is a singlet at δ 48.6ppm (23).The above chemical shift for the DCPP complex is not unrealistic accounting for the different phosphine(DCPP vs DEPE) and also taking into account the difference in chelate ring size for the two complexes and the well documented shift to low frequency (five membered ring > six membered ring)observed for phosphorus chelate complexes compared to monodentate complexes of the same composition(25). Hence in the above case the complex $[(DCPP)Ni(CO)_2]$ might be anticipated to resonate at higher frequency than the complex $[(DEPE)Ni(CO)_2]$. Complimentary evidence for the presence of carbonyl species comes from the presence of an ion M/z 522 consistent with [(DCPP)Ni(CO)], the parent ion corresponding to the dicarbonyl not being observed.

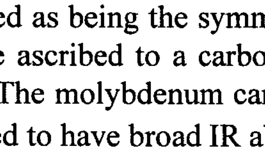
The remaining feature of the ^{31}P NMR spectra is the presence of two doublets at δ23.93 and 22.91ppm of equal coupling and intensity. This suggests a complex in which the phosphorous atoms are magnetically inequivalent as is the situation in compound 1D. The magnitude of the coupling(32.2Hz) is similar to that observed in compound 1D(31.88Hz). There is no evidence to suggest a hydride type structure. Further work is necessary to determine the nature of this complex.

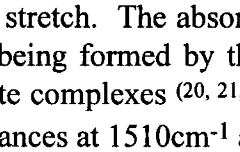
Clearly there is not enough evidence to categorically say what is happening in this reaction. The change in bridge length promotes different reactivity but, without further experimentation, its nature is unclear.

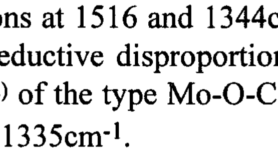
9.4 Use Of 2,2'-Bipyridine(Bipy) Ligand.

The spectroscopic data for this reaction is recorded in section 6.4.8. When 2,2'-bipyridine was used as a ligand in the oxidative coupling reaction, there is no evidence for the formation of the metallacycle (1H), i.e. oxidative coupling of propene/CO_2 has not occurred. The IR spectrum of the solid isolated from the autoclave contains aborbances assigned to the complex $[(Bipy)Ni(CO)_2]$, [v(CO), $1973cm^{-1}$, $1880cm^{-1}$ previously reported (24)].

Strong absorbences in the infra red of the solid at $1516cm^{-1}$ and $1344cm^{-1}$ are indicative of carboxylate and/or carbonates, as shown below for carboxylic acid salts.







The frequencies of vibration are lower than that of the corresponding acids because of the reduction in bond order. The absorbance at $1516cm^{-1}$ is assigned though the frequency is low to the asymmetric stretch and the weaker absorbance at $1344cm^{-1}$ is assigned as being the symmetric stretch. The absorptions at 1516 and $1344cm^{-1}$ may also be ascribed to a carbonate being formed by the reductive disproportionation of CO_2. The molybdenum carbonate complexes (20, 21, Ch.2) of the type $Mo\text{-}O\text{-}C\text{-}(O)_2$ are reported to have broad IR absorbances at $1510cm^{-1}$ and $1335cm^{-1}$.

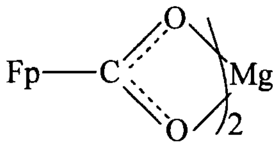
Two other small bands at $1799cm^{-1}$ and $2043cm^{-1}$ remain unassigned. They are possibly metal carbonyl vibrations in metal cluster complexes, i.e. containing more than one nickel atom (24). The remaining absorbances are associated with 2,2'-bypyridine. Mass spectroscopy shows the presence of species corresponding to $[(Bipy)Ni]^+$, $[(Bipy)_2Ni]^+$and $[(BIPY)_3Ni]^+$, the first species being the most intense ion in the spectrum. It is concluded that Bipy coordinates to the nickel as observed in the synthesis of 1H, but the chemistry mediated at the [(Bipy)Ni] centre is more complex than oxidative coupling of propene & CO_2 to yield compound 1H. Analysis of the reaction mixture solution shows predominantly cyclooctadiene; there is no evidence for isomerization of the cyclooctadiene seen previously in systems where oxidative coupling has occurred.

9.5 Use Of N,N' Tetramethylethylenediamine (TMEDA) Ligand

The spectroscopic data for this reaction is recorded in section 6.4.9. When TMEDA was used as a ligand in the oxidative coupling reaction, there is questionable evidence of successful coupling. There is a small absorbance band in the IR spectrum at $1652cm^{-1}$ and another at $1635cm^{-1}$ which are in the correct region of the spectrum for the expected product of oxidative coupling and formation of

$[(TMEDA)\overline{NiCH_2CHCH_3COO}]$ and/or $[(TMEDA)\overline{NiCH(CH_3)CH_2COO}]$. The band at $1652cm^{-1}$ is also present in the IR spectrum of 1,5 cyclooctadiene and may be due to either free cyclooctadiene or cyclooctadiene complexed to the nickel. The major absorbances are associated with a carboxylate/carbonate structure discussed in section 4.40 in the context of Bipy. Broad absorbance bands are observed at $1521cm^{-1}$ and $1380cm^{-1}$ which are not present in the IR spectrum of compound 1H.

The IR spectrum of the CO_2 complex shown below (20 Ch.2)



$Fp = (\eta\text{-}C_5H_5)Fe(CO)_2$

discussed earlier(chapter 2) contains a broad absorbance at $1560cm^{-1}$ and another at $1435cm^{-1}$ assigned as the asymmetric and symmetric stretches of the carboxylate group.

The molybdenum carbonate complexes previously mentioned have IR bands at $1510cm^{-1}$ and $1335cm^{-1}$ and are assigned as being due to unidentate carbonate complexes, e.g. $[L_2NiOCO_2]$. As with the reactions using BIPY, it is most likely these absorbances are from ligand nickel carbonates. However the broadness of the absorbance bands means bridging carbonate structures cannot be ruled out.

Two very weak absorbance bands at $2043cm^{-1}$ and $1998cm^{-1}$ are assigned to the $[(TMEDA)Ni(CO)_2]$ compound expected in the reductive disproportionation of CO_2. These are consistent with literature values (24).

The mass spectrum indicates that no oxidatively coupled product has been formed. The expected ion M/z 261 detected in the preparation of compound 1J was not evident.

Overall, TMEDA favours the reductive disproportionation. Also analysis of the reaction mixture shows no evidence of isomerization of cyclooctadiene seen previously in systems where oxidative coupling has occurred.

9.6 Use Of Tricyclohexyl Phosphine (PCy_3) Ligand.

The spectroscopic data for this reaction is recorded in section 6.4.10. When PCy_3 was used as a ligand (one molar equivalent), there was no evidence for the oxidative coupling reaction or the tetrameric compound 1A. The IR spectrum of the solid isolated from the reaction contained a number of absorbance bands common to $Ni(COD)_2$ the starting material. Also present are weak bands at $1923cm^{-1}$, $1899cm^{-1}$ and $1882cm^{-1}$ associated with metal carbonyls.

It was thought that PCy_3 may possess the right combination of steric and electronic properties to activate CO_2 in the oxidative coupling reaction and that the intermediate if formed, possess coordinative unsaturation thought necessary for β-hydride migration, the first step in the liberation of methacrylic acid from the metal (reverse of oxidative addition).

Analysis by GC-MS of the autoclave reaction mixture shows the presence of cyclooctadiene isomers seen with other phosphine liganded nickel complexes. In this case, though, the presence of isomerization products is not accompanied by oxidative coupling. The products of reaction were $[(PCy_3)Ni(COD)]$, $[(PCy_3)_2Ni(COD)]$, and $[(PCy_3)Ni(CO)_n]$, where $n = 1, 2, 3$, none of which are unexpected. No evidence was found in the IR spectrum for nickel carbonate formation.

For a wider discussion of the results of this section see chapter ten.

TABLE 9.1
ANALYSIS OF PROTON NMR DATA FOR THE SOLID ISOLATED FROM THE REACTION
$Ni(COD)_2$ + DCPE + PROPYLENE + CO_2

δ	**Multiplicity**	**Coupling Constant**	**Assignment**	**Data for Model Compound IC/IF**
0.57	dddd	J 9.28Hz, 9.28Hz, 4.8Hz, 4.8Hz	H_A/H_B M_{ISO}	0.57(dddd, 1H $^2J_{H-H}$ 9.28Hz $^2J_{H-P\ TRANS}$ 9.28Hz $^2J_{H-P\ CIS}$ 4.88Hz $^3J_{H-H}$ 4.88Hz)
1.036	t	7.1Hz	CH_3 C_{ISO}	1.036(t, 3H, $^3J_{H-H}$ 7.1Hz)
1.19	d	6.83Hz	CH_3 M_{ISO}	1.18(d, 3H $^3J_{H-H}$ 6.83Hz)
1.2-2.2	br		ligand CH_2	1.2-2.2(br)
2.39	br		H_C M_{ISO}	2.39(br, 1H)
2.80	dd	16.6Hz, 5.37Hz	H_C C_{ISO}	2.80(dd, 1H, $^2J_{H-H}$ 16.6Hz, $^3J_{H-H}$ 5.41Hz)

C_{ISO} = crotonic isomer = $[(DCPE)NiCH(CH_3)CH_2COO]$
M_{ISO} = methacrylic isomer = $[(DCPE)NiCH_2CH(CH_3)COO]$

TABLE 9.2
ANALYSIS OF CARBON NMR DATA FOR THE SOLID ISOLATED FROM REACTION OF $Ni(COD)_2$ + DCPE + PROPENE + CO_2

δ	Multiplicity	Coupling Constant	Assignment	Data for Model Compound 1C/1F
15.43	s		CH_3 C_{ISO}(a)	15.5(s)
17.63	dd	21.5Hz, 9.2Hz	C_A M_{ISO}(b)	17.65(dd, J 22.25Hz, 9.95Hz)
23.08	dd	61.3Hz, 24.5Hz	DCPE bridge CH_2 M_{ISO}(b)	23.11(dd, J 64.4Hz, 26.1Hz)
24.8	dd	23.0Hz, 23.0Hz	DCPE bridge CH_2 M_{ISO}(b)	24.83(dd, J 24.6Hz, 23.0Hz)
26.5-30.5	br		Cyclohexyl CH_2	26.5-30.28(br)
33.74	d	13.8Hz	Cyclohexyl CH M_{ISO}(b)	33.75(d, J 13.8Hz)
33.88	d	15.4Hz	Cyclohexyl CH M_{ISO}(b)	33.90(d, J 15.3Hz)
35.43	d	16.9Hz	Cyclohexyl CH M_{ISO}(b)	35.44(d, J 16.8Hz)
35.69	d	16.9Hz	Cyclohexyl CH M_{ISO}(b)	35.69(d, J 18.4Hz)
42.28	s		C_B M_{ISO}(b)	42.28(s)
46.77	s		C_B C_{ISO}(a)	46.5(s)
191.03	d	13.8Hz	C=O	192.0(s), M_{ISO}(b) C_{ISO}(a) not observed

a)C_{ISO} = crotonic isomer = [(DCPE)NiCH(CH_3)CH_2COO]

b)M_{ISO} = methacrylic isomer = [(DCPE)NiCH_2CH(CH_3)COO]

TABLE 9.3
DATA RELATING TO THE COUPLING OF PROPENE / CO_2 TO GIVE 3- & 4-METHYL SUBSTITUTED OXANICKELACYCLOPENTANONES

Tecmhique	Solid Fraction	M iso	C iso
P^{31} NMR δ (ppm)	80.5, 68.5, 62.8, 61.2, 60.4	68.84, 60.66	63.09(d, J 4.88Hz) 61.49(d, J 4.88Hz)
FAB^{+VE} ion (m/z)	646(94), 567(60), 566(40), 565(100), 480(42).	646(100), 567(40), 566(30), 565(60), 480(20).	567(85), 566(55), 565(100), 480(55).
I.R.(cm^{-1}) ν_{max}C=O	1623(vs)	1631(vs)	1623(vs)

C_{ISO} = crotonic isomer = [(DCPE)NiCH(CH_3)CH_2COO]
M_{ISO} = methacrylic isomer = [(DCPE)NiCH_2CH(CH_3)COO]

TABLE 9.4
HYDROLYSIS OF REACTION PRODUCTS Ni(COD)$_2$ + PROPYLENE + CARBON DIOXIDE

Ligand	**Condition**	**Yield**	**n:ISO**	**Minor Prods** $^{(a)}$	**Components of** $^{(c)}$ **Reaction Solution**
DCPE	std$^{(b)}$	62%	1 : 2	Butenoic Crotonic	COD isomers$^{(d)}$
DCPE	60°C, 2hrs	43.4%	1:1.45	Crotonic	COD isomers$^{(d)}$
DCPE	Acetonitrile solvent	30.7%	45:55	Butenoic Crotonic Methacrylic	COD isomers$^{(d)}$
DCPY	std$^{(b)}$	80%	23:77	Crotonic Butenoic	COD isomers$^{(d)}$
DMPE	std$^{(b)}$	20.9%			
PCy$_3$$^{(e,h)}$	std$^{(b)}$	Nil	n/a		COD isomers$^{(d)}$
PCy$_3$$^{(e,i)}$	std$^{(b)}$	Nil	n/a		No COD isomers$^{(f)}$
TMEDA$^{(e)}$	std$^{(b)}$	Nil	n/a		No COD isomers$^{(f)}$
BIPY$^{(e)}$	std$^{(b)}$	Nil			No COD isomers$^{(f)}$

a) < 5% Total products. b)std = as per section 4.11 experimental. c) Reaction solution examined by GC-MS d) COD = Cyclooctadiene. e) Hydrolysis not performed. Coupling determined by I.R. and mass spectroscopy comparison of isolated solids to model compounds. f) Only 1,5 Cyclooctadiene present. g) Solid isolated very air sensitive. h) 1 equivalent PCy$_3$. i) 2 equivalent PCy$_3$.

TABLE 9.6

ANALYSIS OF PROTON NMR DATA FROM SOLID FRACTION ISOLATED FROM REACTION

$Ni(COD)_2$ + DCPy + PROPYLENE + CO_2

δ(a)	Multiplicity	Coupling Constant	Assignment	Data in Model Compound IG(b)
0.50	br		H_A/H_B M_{ISO}	0.57(br, 1H)
0.85	br		H_A/H_B M_{ISO}	0.79(br, 1H,
1.10	br		CH_3 M_{ISO}	1.27(br, 3H)
1.2-2.2	br		ligand CH_2	1.3-2.2(br)
2.30	br		H_C M_{ISO}	2.54(br, 1H)
7.1-8.9	m		Pyridyl H	7.1-9.1

(a)

(a) spectra in $CDCl_3$
(b) only M_{ISO} synthesised, data in CD_2Cl_2

TABLE 9.8

EVIDENCE FOR COUPLING OF PROPYLENE / CO_2 TO GIVE 4 METHYL SUBSTITUTED OXA NICKELA CYCLOPENTANONES FROM THE REACTION

$Ni(COD)_2$ + DCPy + PROPYLENE + CO_2

Tecnhique	Solid Fraction	M iso (IG)	C iso
P^{31} NMR	38.28, 34.22(a)	37.31(b)	Compound not synthesised
FAB^{+VE} ion (m/z)	450(42), 448(100), 361(94), 197(27).	450(32), 448(87), 361(51), 197(100)	.
I.R.(cm^{-1}) ν_{max}C=O	1629(vs)	1629(vs)	

(a) data in CD_2Cl_2
(b) data in toluene

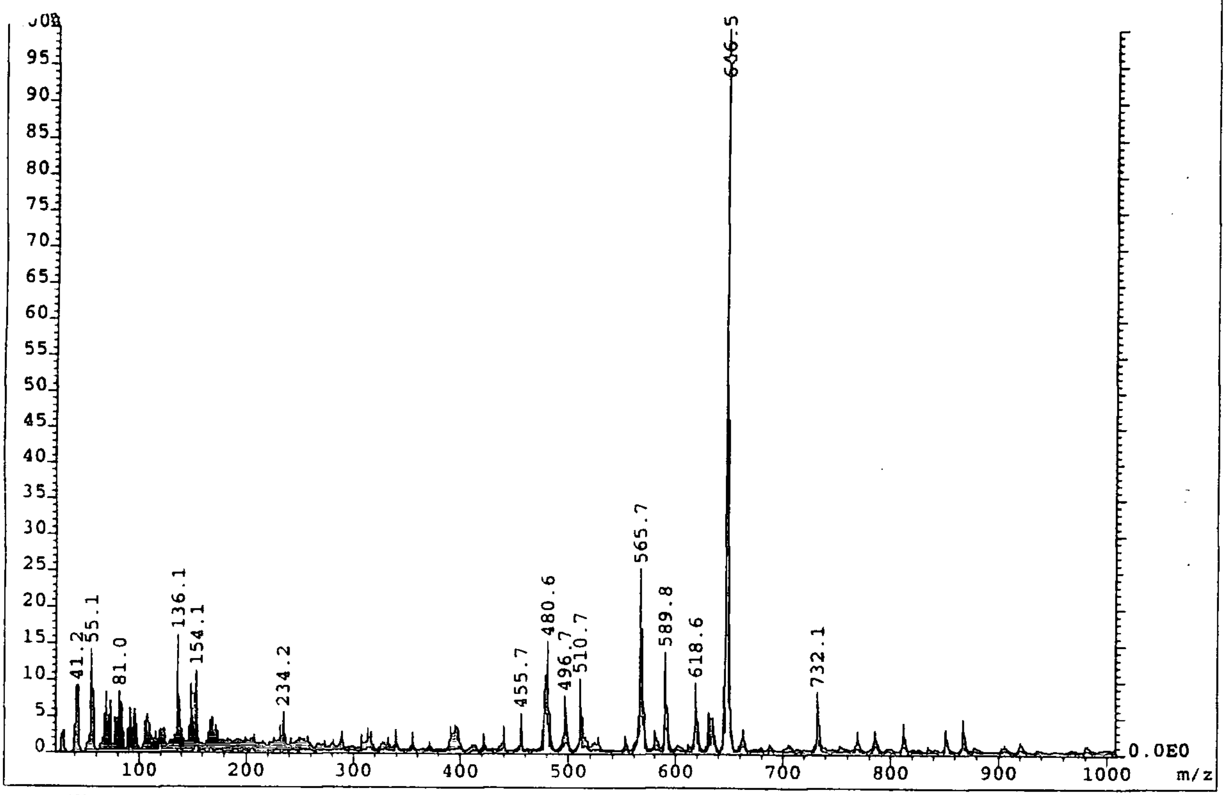
TABLE 9.7
ANALYSIS OF CARBON NMR DATA FROM SOLID FRACTION ISOLATED FROM REACTION OF Ni(COD)$_2$ + DCPy + PROPYLENE + CO$_2$

δ (b)	Multiplicity	Coupling Constant	Assignment	Data in Model Compound (a)
13.56	br		C_A M_{ISO}	12.26(s)
13.76	br		DCPy bridge	12.94(br)
21.58	s		CH_3	21.67(s)
32.5	d	27.7Hz	Cyclohexyl CH	31.77(d, J 27.6Hz)
33.03	d	27.6Hz	Cyclohexyl CH	32.17(d, J 27.6Hz)
35.54	br		DCPy bridge	34.81(s)
43.13	s		C_B	Not Observed

(a) = Spectra taken in DMSO.

(b) = Spectra in $CDCl_3$

FAB(positive ion) Mass Spectrum of the Solid Isolated from Oxidative Coupling at DCPE Liganded Nickel(0), Performed in Acetonitrile



Infra Red Spectrum of the Solid Isolated from Oxidative Coupling at DCPE Liganded Nickel(0), Performed in Acetonitrile

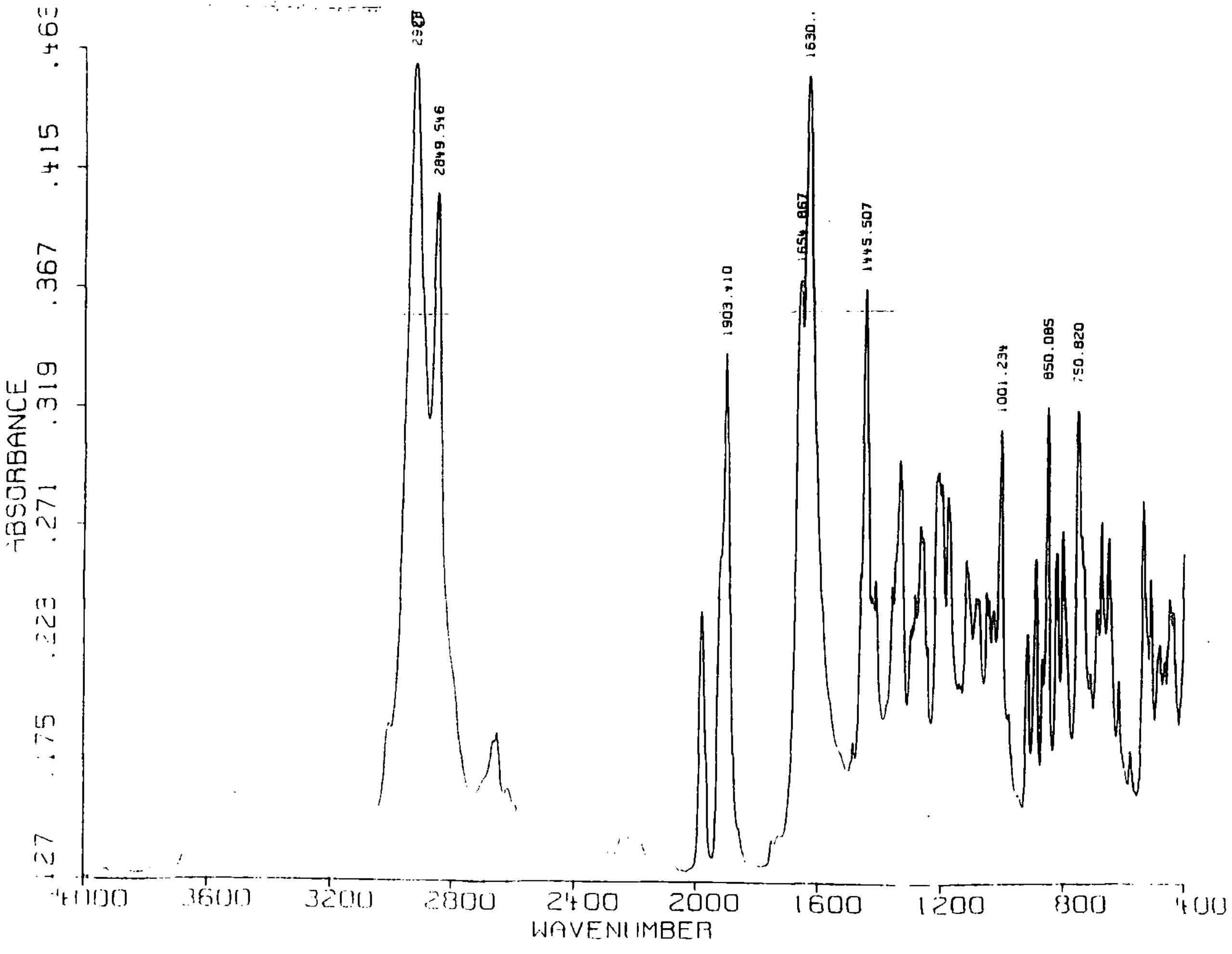


Diagram 9.1

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CHAPTER TEN

CONCLUSIONS

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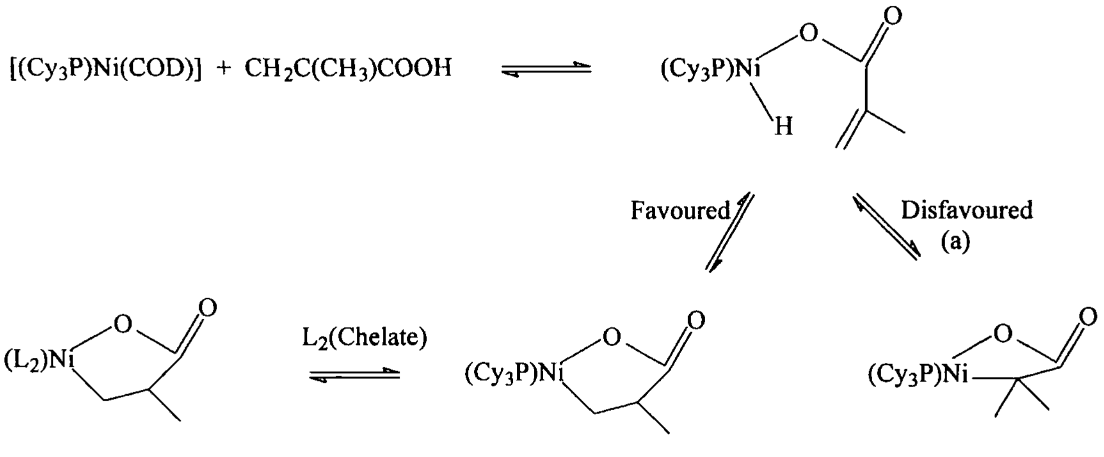
CONCLUSIONS

The important result of this work is the demonstration that the complexes of the type

$[\overline{L_2NiCH_2CH(CH_3)COO}]$ (I) and $[\overline{L_2NiCH(CH_3)CH_2COO}]$, (II) can be synthesised from methacrylic acid (I) and crotonic acid (II) respectively via an extension of the chemistry developed by Yamammoto et al and reviewed in chapter four(1). The same complexes can also be synthesised from propene and carbon dioxide via an oxidative coupling reaction at phosphine liganded nickel(0).

10.1 Oxidative addition of methacrylic/crotonic acid to nickel complexes and the formation of $[(PCy_3)Ni\{CH_2CH(CH_3)COO\}_4]$.

The synthesis of the intermediates (type I and II) from the corresponding carboxylic acid is a two step process. The oxidative addition of methacrylic/crotonic acids to nickel(0) only occurs in the presence of one molar equivalence of tricyclohexylphosphine, a highly electron donating sterically demanding phosphine. Reaction in the presence of greater than one molar equivalence is reported to lead to the formation of π-type complexes(2). Presumably an intermediate of the type $[Cy_3PNi(COD)]$ forms on addition of the phosphine to $Ni(COD)_2$, and this intermediate can oxidatively add the acid. Oxidative additions can proceed by a great variety of mechanisms, but because the electron count increases by two units, a vacant 2-electron site is usually required on the metal. This can mean starting with a 16-electron complex (as above) or generating a 2-electron site from an 18-electron complex by loss of a ligand. The hydrogen of the nickel hydride intermediate (resulting from oxidative addition of methacrylic/crotonic acid, shown below) then presumably adds to the β-carbon of the acid moiety to form the thermodynamically favoured metallacycle. Migration of the hydride ligand to the α-carbon, route(a), would result in a four membered metallacycle structure which would appear on balance to be unfavourable. Stability tends to decrease for metal alkyls in the order $1^0 > 2^0 > 3^0$.



In the absence of any excess ligand it has been shown that the 16-electron tricyclohexylphosphine-nickel metallacycle combines with three other similar molecules to form a tetrameric complex. It is proposed that for the present system the vacant coordination site present on each nickel in $[(Cy_3P)Ni\overline{\{CH_2CH(CH_3)COO\}}]$ is filled by interaction with a carbonyl oxygen of a neighbouring complex molecule in an analogous way to that found for the cyclic amide complex $[(PEt_3)Ni\overline{\{CH_2CH(CH_3)CONH\}}_4]$ (reviewed in chapter 4), the low frequency shift ($\Delta = 62cm^{-1}$) of the carbonyl in the infra red supports this conclusion. The $\nu(CO)$ shift to lower frequencies is a result of a change in electron density in the carbonyl bond resulting from interaction of an oxygen lone pair with the nickel. The donation satisfies the electronic requirements of the nickel and results in a reduction in the bond order of the carbonyl bond observed as a shift in $\nu(C{=}O)$ to lower wave numbers from that observed for

$[L_2Ni\overline{\{CH_2CH(CH_3)COO\}}]$ and/or $[L_2Ni\overline{\{CH(CH_3)CH_2COO\}}]$, eg.

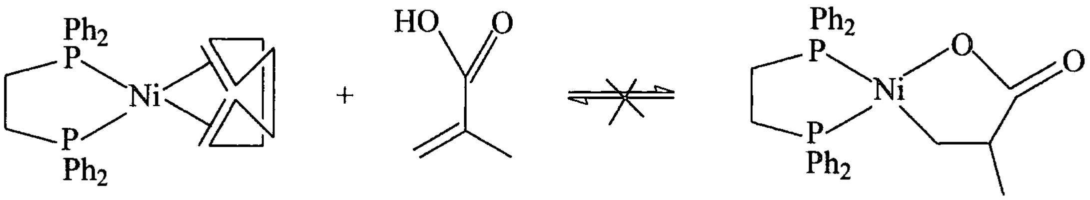
$[(PCy_3)Ni\overline{\{CH_2CH(CH_3)COO\}}_4]$, $\nu(C{=}O) = 1569cm^{-1}$ versus ,

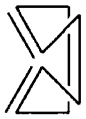
$[(DCPE)Ni\overline{\{CH_2CH(CH_3)COO\}}]$, $\nu(C{=}O)$ $1631cm^{-1}$.

Oxidative addition of methacrylic/crotonic acid to $Ni(COD)_2$ in the presence of DPPE (bidentate phosphine) is reported to result in no synthesis of $[(DPPE)Ni\overline{\{CH_2CH(CH_3)COO\}}]$ and/or $[(DPPE)Ni\overline{\{CH(CH_3)CH_2COO\}}]$(1,2,3). There are two possible reasons for this.

i) The DPPE ligand does not provide the necessary electronic environment at nickel. A highly electron donating phosphine is required for metallacycle formation(2).

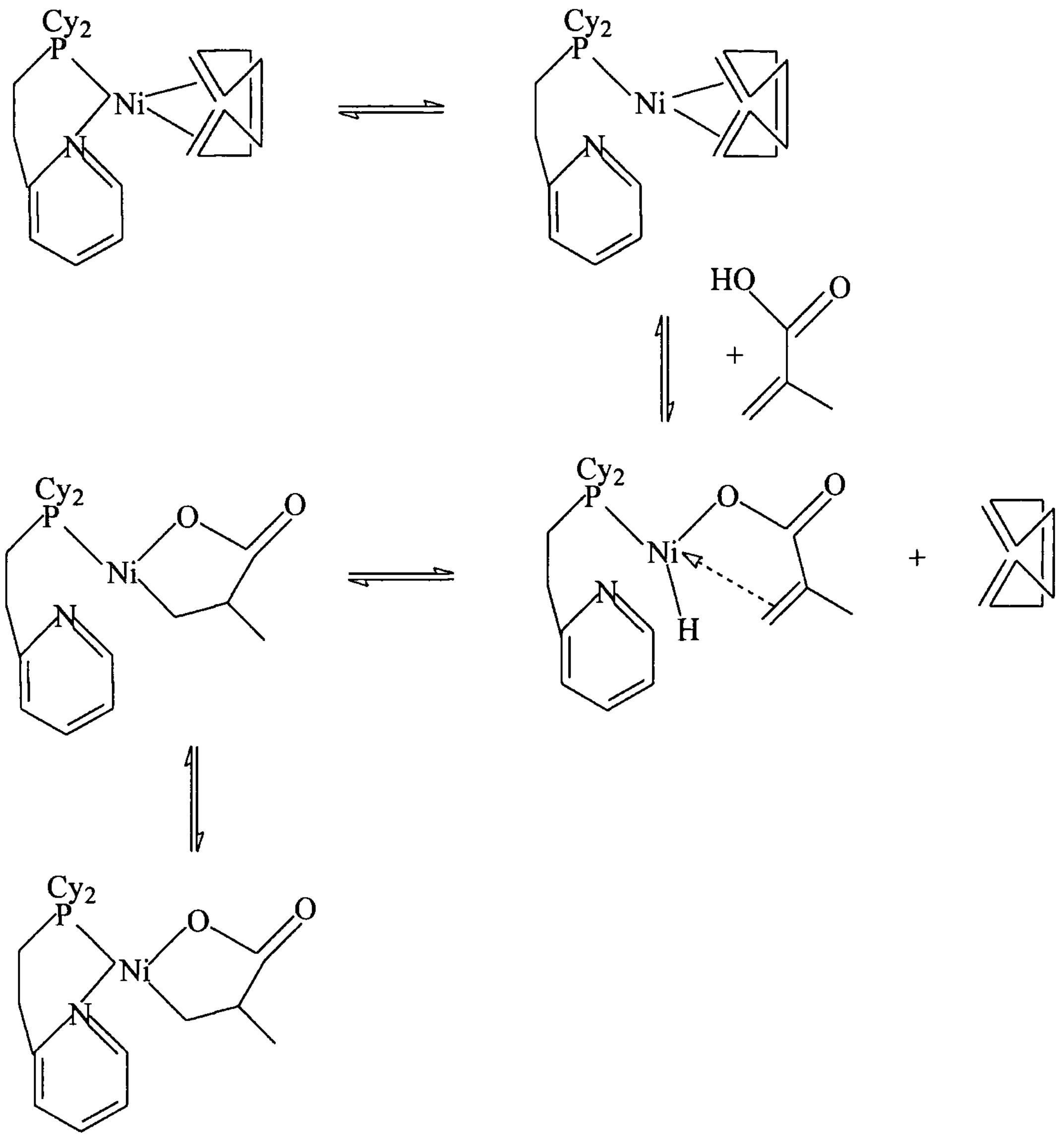
ii) The intermediate generated by the addition of one molar equivalent of DPPE to $Ni(COD)_2$ is an 18-electron complex $[(DPPE)Ni(COD)]$ which may be unable to generate the vacant 2-electron site required for the oxidative addition of methacrylic/crotonic acid. The process is illustrated in the diagram below.




= 1,5 cyclooctadiene

Cyclohexylphosphines have been used extensively in this study, particularily DCPE and DCPy. The oxidative addition of methacrylic/crotonic acid to [(DCPE)Ni(COD)] has not been attempted in this study nor has it been reported as being possible by other workers, it is assumed that the above reaction would not occur because of the unfavourability of the complex [(DCPE)Ni(COD)] to generate vacant coordination sites. Hoberg et al though report the oxidative addition of methacrylic acid to $Ni(COD)_2$ in the presence of DCPy ligand in high yield(4), by mixing $Ni(COD)_2$, DCPy and methacrylic acid at -40°C followed by warming to 20°C. The ligand (DCPy) is thought to be able to form chelate rings on coordination with transition metals in which the pyridine nitrogen is able to detach and generate a vacant coordination site. It is proposed that it is this feature of this ligand which enables oxidative addition of methacrylic acid and the subsequent formation of metallacyclic complexes

$[(DCPy)Ni\{\overline{CH_2CH(CH_3)COO}\}]$ as shown below.



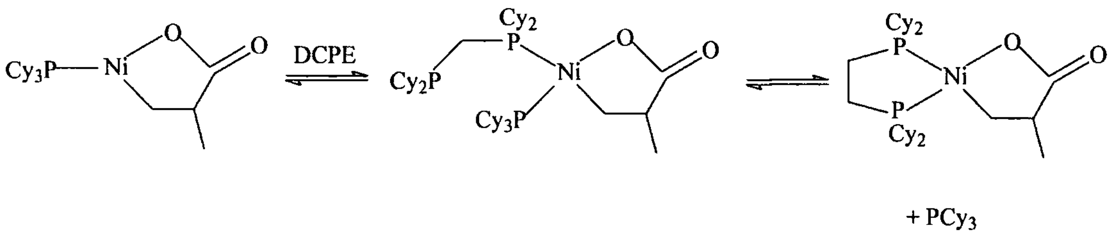
The tetrameric complex $[(PCy_3)Ni\{\overline{CH_2CH(CH_3)COO}\}_4]$, compound 1A, formed in high yield, is very air sensitive and must be stored in an inert atmosphere at all times. It is slightly soluble in tetrahydrofuran, toluene and hexane and recrystalisation from hot hexane was achieved. The crystals grown from hot hexane were small, long thin needles, yellow in colour which turned green on exposure to air. Complete removal of the solvent from the crystals resulted in formation of a powdered material indicating that the solvent is somehow involved in supporting the crystal lattice. Attempts to analyse the crystal structure by X-ray methods proved unsucessful, what appeared to be crystals were mounted in oil on a diffractometer but the analysis showed there was insufficent order in the material to resolve a structure.

10.2 Ligand displacement reactions.

The second reaction to form complexes of the type $[L_2Ni\overline{CH_2CH(CH_3)COO}]$ (I) and

$[L_2\overline{NiCH(CH_3)CH_2COO}]$ (II) is a ligand displacement reaction. The following compounds have been synthesised. Type (I) $[L_2\overline{NiCH_2CH(CH_3)COO}]$ where L_2 = DPPE(1B), DCPE(1C), DCPP(1D), DCPy(1G), Bipy(1H), Phen(1J), TMEDA(1I).

Type (II) $[L_2\overline{NiCH(CH_3)CH_2COO}]$ where L_2 = DPPE(1E), DCPE(1F). The yield and analytical purity of the compound (1B-1J) isolated is related to the ligand used. Two factors are thought to be important in this reaction, i) coordinating ability of the ligand to $[(PCy_3)Ni\{\overline{CH_2CH(CH_3)COO}\}_4]$ or $[(PCy_3)\overline{NiCH_2CH(CH_3)COO}]_n$ where n= 1, 2, 3, and ii) the relative thermodynamics of the ring closure reaction to give the chelate complex as shown below for DCPE.



Using the amines 2,2'-bipyridine, 1,10-phenanthroline and N,N,N',N'tetramethylethylenediamine analytically pure compounds could not be isolated from the ligand displacement reaction. The coordinating ability of Bipy and PEt_3 are reported to be similar toward complexes of the type $L_2Ni(Me)_{2(5)}$. The equilibrium for the following reaction lies somewhere in the middle, approximate equal quantites of the two complexes being in equilibrium.

$$(PEt_3)_2NiMe_2 + Bipy \rightleftharpoons BipyNiMe_2 + 2PEt_3$$

When the diphosphines 1,2-bis(diphenylphosphino)ethane (DPPE) and 1,3-bis(diphenylphosphino)propane (DPPP) are used in place of bipyridine the equilibrium is reported to be over to the right hand side of the equation. The differences observed in this work are most likely related to the thermodynamic favourability of the ring system, the chelate effect.

Because of the presence of a vacant coordination site or one that can be easily formed from the tetramer in solution, the initial coordination is thought to be favourable for both amine and phosphine chelates. The second step though, ring closure and dissociation of PCy_3 is thermodynamically less favourable for the amine complexes even considering the chelate effect.

Using the phosphine 1,3-bis(dicyclohexylphosphino)propane (DCPP) a lower yield is found in the ligand displacement reaction than that obtained using 1,2-bis(dicyclohexylphosphino)ethane (DCPE) and 1,2-bis(diphenylphosphino)ethane (DPPE). This result is thought to arise because of the thermodynamic favourability of the formation of five membered chelate rings versus six membered chelate rings(chapter 7).

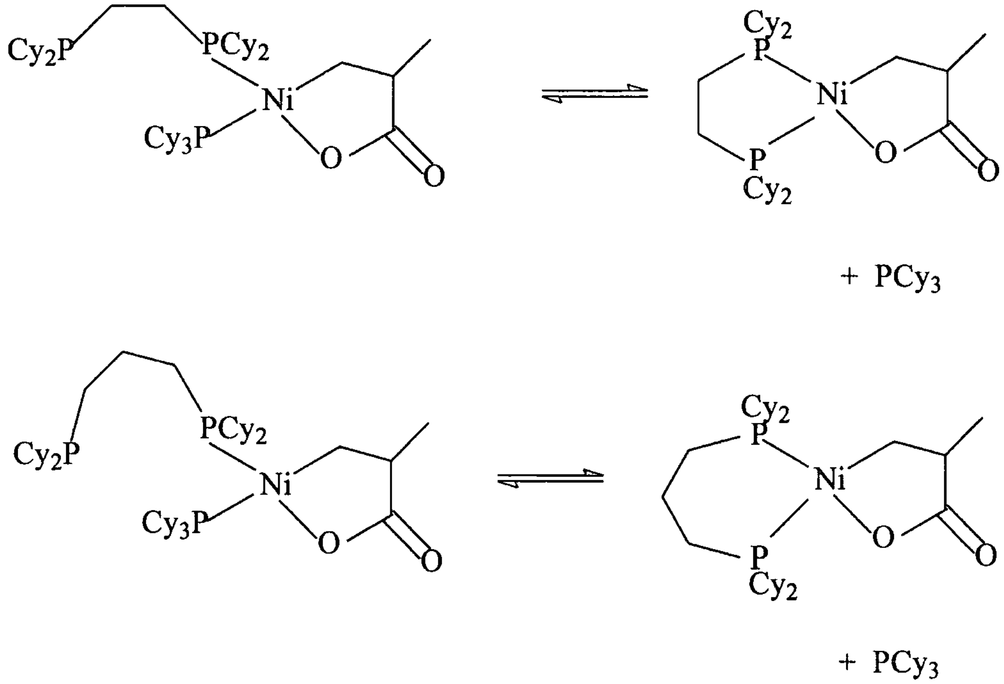
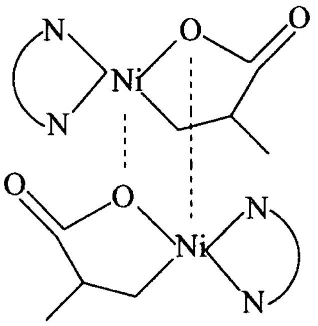


Fig 7.2

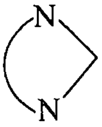
Formation of a five membered chelate ring is energetically more favoured over the formation of the six membered ring ie. $\Delta H_1 > \Delta H_2$.

The complexes of the type $[L_2Ni\{\overline{CH_2CH(CH_3)COO}\}]$ and

$[L_2Ni\{\overline{CH(CH_3)CH_2COO}\}]$ where L_2= DPPE, DCPE, DCPP and DCPy were all yellow in colour and soluble in dichloromethane, chloroform and tetrahydrofuran. The yellow colour is common for square planar phosphine complexes of nickel(II). The complexes isolated where L_2= Bipy or phenanthroline are deep purple in colour. This is suggestive of octahedral geometry around nickel. The complex $[Ni(pyridine)_4(Cl)_2]$ has trans octahedral geometry and is blue in colour, whilst $[Ni(pyridine)_2(Cl)_2]$ resulting from heating $[Ni(pyridine)_4(Cl)_2]$ to 170°C with the evolution of pyridine is yellow/green(6). The complex $[Ni(pyridine)_2(Cl)_2]$ is reported as containing six-coordinate nickel. The TMEDA complex isolated in this study is a yellow green colour and may therefore have square planar or octahedral geometry. In the bipyridine and phenanthroline complexes it is possible the purple colour is arising from an impurity but this is thought unlikely. Complexes involving THF coordinating at trans positions of six coordinate octahedral complexes may be possible to account for the colour, as may stacking as illustrated in the diagram below where planar(bipyridine, phenanthroline) or slim ligands are used.



Stacking



Planar chelate

The complexes have all been characterised by ^1H, ^{13}C and ^{31}P NMR and by IR and FAB positive ion mass spectroscopy. Several points are worthy of note.

i) The frequency at which the α-CH_2 protons of the metallacycle ring resonate in the 4-methyl substituted cyclopentanones $[L_2\overline{Ni\{CH_2CH(CH_3)COO\}}]$ where L_2= diphosphine is relatively insensitive to the substituents on the phosphine. Changing the ligand from DPPE in the complex $[(DPPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ to the more basic, highly electron donating DCPE in the complex $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ has a ~0.04ppm effect on the chemical shift of one of the α-CH_2 protons and ~0.01ppm effect on the other(see Table 7.12). This suggests the magnetic environment of the α-CH_2 protons must be very similar in both complexes.

ii) Also apparent from inspection of the proton nmr data is the greater sensitivity of the β-hydrogen (H_C) frequency to ligand changes. The chemical shift changes from 2.34pppm in $[(DPPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ to 2.54ppm in $[(DCPy)\overline{Ni\{CH_2CH(CH_3)COO\}}]$. A shift of 0.2ppm is quite significant.

iii) Also noticeable in the DCPy complex is the change in the resonance positions of the α-CH_2 protons, one of which is unaffected by the ligand change and one of which is some 0.25ppm shifted to higher frequency. These changes reflect conformational changes in the metallacyclic ring.

iv) In the carbon nmr of the 4-methyl substituted cyclopentanones complexes it is apparent that only the α-carbon frequency is sensitive to ligand changes. It ranges from 22.66ppm in $[(DPPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ to 12.12ppm in $[(DCPy)\overline{Ni\{CH_2CH(CH_3)COO\}}]$, the frequency of resonance falling midway between these values for the amine complexes and the DCPE complex(see Table 7.14). All of the other carbon atoms of the metallacyclic ring are relatively insensitive to the ligand changes in this study. Also the β-carbon (C-H) couplings measured in the DPPE and DCPE complexes and used as a measure of the interaction, if any, of the β-hydrogen with the metal centre, are similar and consistent with there being no interaction. This is consistent with the theory that the metallacycle structure is rigid and orbital overlap between the β-hydrogen and d-orbitals of the metal can not occur. The planar transition state discussed in chapter 2 which is necessary for β-hydrogen elimination can not occur.

v) The ^{1}H nmr data for the 3-methyl substituted complexes is limited to two complexes $[(DPPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$ and $[(DCPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$. It has not proved possible to assign all of the metallacycle protons in $[(DCPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$ but two features which have been assigned are the methyl group protons and one of the β-carbon protons $H_{B/C}$ both of these are significantly shifted from their positions in the complex $[(DPPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$, (see Table 7.7) indicating that the magnitude of the ligand effect is greater in the 3-methyl substituted complex than in the 4-methyl substituted complex. The methyl group protons and the β-carbon proton in the 4-methyl substituted complexes have been shown to be insensitive to the ligand change DPPE to DCPE. The greater sensitivity of the methyl group protons may be a result of the methyl group interacting with the bulky cyclohexyl ligand groups to a greater extent in the 3-methyl substituted cyclopentanones, where the methyl group might be anticipated to be in closer proximity to the cyclohexyl groups. The carbon NMR data shows a similar ligand sensitivity effect in the 3-methyl substituted complexes ie. both the α-carbon and the 3-methyl substituent carbon nmr signals are significantly shifted in changing ligand from $[(DPPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$ to $[(DCPE)\overline{Ni\{CH(CH_3)CH_2COO\}}]$.

vi) Phosphorus NMR of both isomers is sensitive to the changes in substituent at phosphorus. This is perhaps not surprising given the large differences in both electronic and steric properties of the phosphorus substituents in changing from DPPE to DCPE ligands. The phosphorus NMR signal is also sensitive to chelate ring size(see Table 7.10), this effect has been reported by other workers(7).

The phosphorus nmr signals in all the complexes have been sharp, indicating that the phosphine is tightly bound to the nickel on the nmr time scale. This suggests that under the conditions at which the spectra were recorded phosphine flipping off the metal to form vacant sites is not occuring. Exchanging phosphine donors is characterised in the phosphorus nmr by broad signals. Clearly phosphorus nmr does not tell us anything about the ability of the pyridine ring in DCPy to create coordinative unsaturation or whether these processes occur at different temperatures, pressures or reactant stoichiometry.

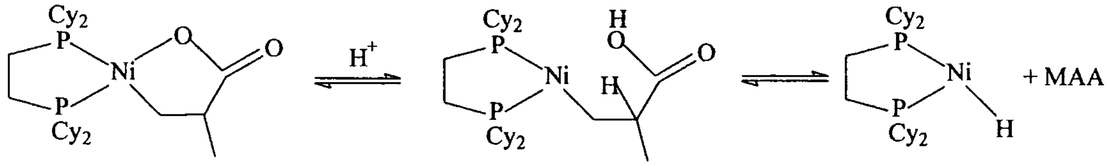
vii) Mass spectroscopic analysis (FAB positive ion) has proved to be a useful technique for the study of these compounds, and coupled with MS-MS, structural information has been revealed. Perhaps the most interesting feature of the mass spectroscopy in general is the tendancy of the chelate phosphine complexes of both isomers to form $[M-H]^+$ ions. It has been shown by MS-MS studies that the process leading to this ion is $[(M+H)-H_2]^+$ or "in beam reduction". The generation of $[M-H]^+$ ions does not occur with the mixed chelate DCPy or with the amine derivatives. Whilst no MS-MS experiments were performed on the amine derivatives the ion corresponding to the complex $[(DCPy)\overline{Ni\{CH_2CH(CH_3)COO\}}]$, m/z 448, was studied. As mentioned, one interesting difference was the absence of $[M-H]^+$ ions. The other interesting difference between it and the corresponding $[M+H]^+$ ion generated from $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ was the absence of fragmentation to yield an ion corresponding to $[M-CO_2]^+$, ie. 44amu loss, the main loss being an 86amu loss corresponding to loss of methacrylic acid. This clearly shows differences in the behaviour of the $[(DCPy)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ complex and related complexes which it is not possible at present to rationalise. The differences in fragmentation, the success of the oxidative coupling reaction achieved using this ligand and its potential to flip off the metal and create vacant coordination sites clearly make this ligand and other mixed heteroatom ligands worthy of further study.

Mass spectroscopic analysis of the prepared complexes proved useful for assessing purity. The common impurites PCy_3 and its oxide, arising from ligand displacement reactions of the starting complex, along with other phosphines/oxides were all amenable to study by this technique. PCy_3 and its oxide were identified as the major impurities in reactions where analytically pure compounds were not isolated. Using mass spectroscopy in conjunction with IR. and phosphorus nmr, it was possible to deduce whether the phosphine was present as bound phosphine or not. Bound phosphine impurities believed to be present in the preparation of the amine derivatives were difficult to remove completely by washing from the sample.

10.3 Decomposition reactions of 1-oxa-2-{1,2-bis(dicyclohexylphosphino) ethyl}nickela-4-methylcyclopentan-5-one. COMPOUND 1C.

A number of complexes have been synthesised which have proven amenable to characterisation by a range of techniques. Data has been presented and discussed in chapters six and seven of this thesis. The complex $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ has been used for further reaction studies, chosen because it has been shown that it can be synthesised from methacrylic acid as well as from propene/carbon dioxide mixtures. Ways were sought to destabilise the metallacycle to liberate methacrylic acid. The addition of maleic anhydride was not sucessful, as it was successful for the related Bipy coordinated nickel(II) complex $[(Bipy)\overline{Ni\{CH_2CH_2CH_2COO\}}]$ (reviewed in chapter 4). One possible explanation for this is the unfavourability of geometry changes in square planer nickel(II) phosphine complexes required for the addition of maleic anhydride. It may be that the mechanism of reaction involves coordination of maleic anhydride involving transient five and six coordinate nickel(II) complexes. Bipy complexes of octahedral 6-coordinate geometry are known as are examples of octahedral complexes of the formulation NiL_2X_2, where L= nitrogen ligands. If the mechanism does involve coordination of maleic anhydride first, either one molecule or two, as seems likely then this may not be possible for a square planar complex having bulky phosphine ligands. The reaction involving the Bipy complex on the otherhand can be easily envisaged as going via a 6-coordinate octahedral intermediate.

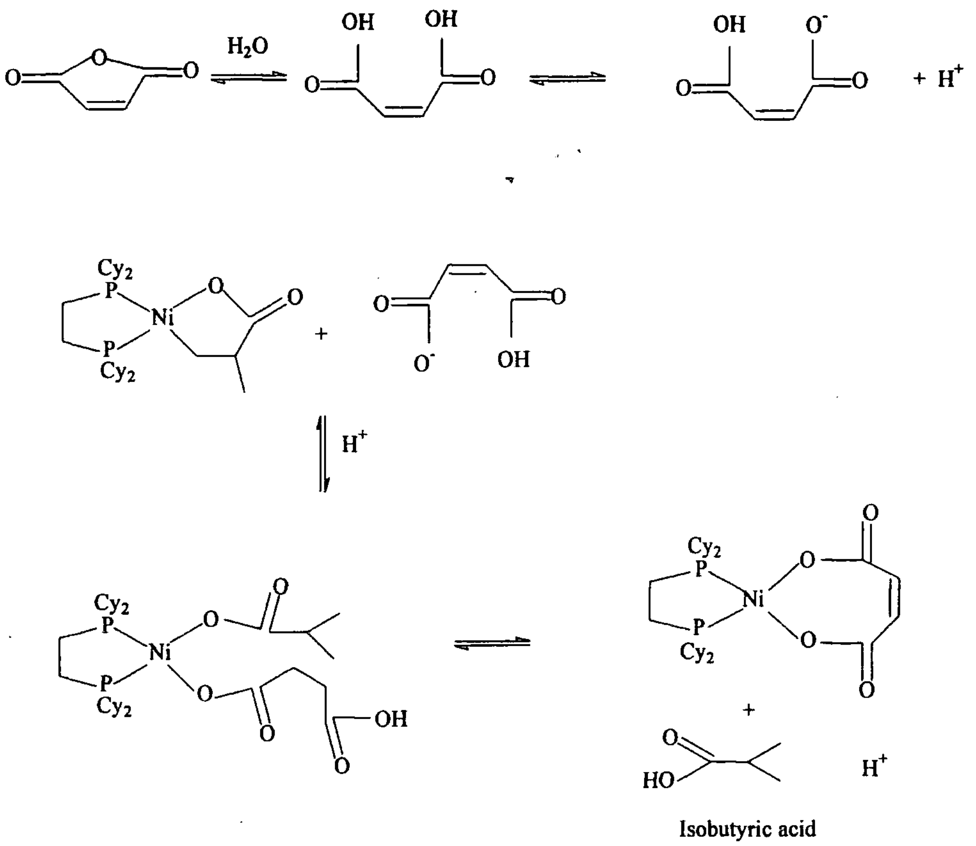
To fit with the above hypothesis there needs to be an alternate mechanism for the formation of methacrylic acid found in this study to that suggested to be operating in the reaction of maleic anhydride with $[(Bipy)\overline{Ni\{CH_2CH_2CH_2COO\}}]$. The production of methacrylic acid found in the reaction of maleic anhydride with $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ (6.3.1) can be rationalised by invoking the presence of small amounts of acid which can protonate the metallacycle $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ at the oxygen producing a nickel alkyl complex as shown below. Rotation of the alkyl group, to facilitate β-hydrogen elimination, results in loss of methacrylic acid as shown below. The acid is thought to arise from from the enolate form of maleic anhydride formed in the presence of small amounts of water present in the maleic anhydride as used.



Free rotation about the nickel-carbon bond in the above intermediate should allow the necessary orbital overlap for β-elimination to proceed, the constraints of the metallacyclic ring no longer being present.

The two other major products of this reaction are iso-butanoic acid and acrylic acid, their formation can also be understood by proposing the following schemes

i) The enolate anion of maleic anhydride and H^+ is postulated as being formed in the presence of water. Protonation of the α-carbon of $[(DCPE)\overline{Ni\{CH_2CH(CH_3)COO\}}]$ followed by attack of carboxylate anion producing a thermodynamically favourable nickel oxygen bond in place of a nickel carbon bond followed by ring closure to yield the observed solid product and iso-butanoic acid as shown.



ii) Oxidative addition of maleic anhydride to Ni(0) generated in situ followed by decarbonylation to give the metallacycle $[(DCPE)\overline{Ni\{CH_2CHCOO\}}]$, which can liberate acrylic acid via acid hydrolysis. There is some precedent in the literature for this (6). The complex Ni(Bipy)(cod) reacts with glutaric anhydride to give $[\overline{(Bipy)Ni\{CHCH_2CH_2COO\}}]$ + CO. There is also literature precedent for reaction of nickel(0) with other anhydrides via oxidative addition and ring contraction isomerisation induced by ligand exchange(3).

$[(Bipy)NiCH_2CH_2CH_2COO]$ + DPPE ———> $[(DPPE)NiCH(CH_3)CH_2COO]$

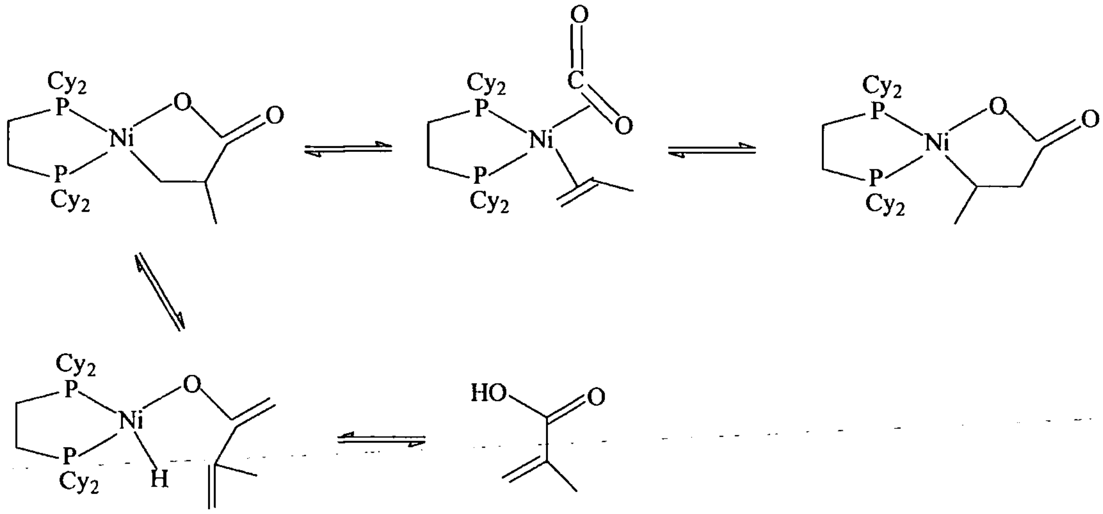
The conclusion to come out of this section of the study is that the original idea of using high pressure of propylene to effect liberation of methacrylic acid from the metallacycle

$[\overline{(DCPE)Ni\{CH_2CH(CH_3)COO\}}]$ does not work probably for the same reason that maleic anhydride does not work, octahedral geometry is not favoured for these complexes involving bulky phosphines.

Attempts have also been made to thermally liberate methacrylic acid from the complex

$[(DCPE)Ni\{\overline{CH_2CH(CH_3)COO}\}]$. Under a nitrogen atnosphere heating the complex to 110°C resulted in the detection of a nickel hydride, presumably the result of β-hydride migration to the nickel. Two other sources are possible but less likely i) α-hydride migration ii) ortho-metallation or insertion into the C-H bond of the ligand. The second of these two proceses is known to occur readily using triphenylphosphine type ligands but is less well documented for alkyl-phosphines. This reaction warrants further study. The solid (A, section 6.3.2) analysed showed minor absorbances which could be assigned to free carboxylic acid groups. This conclusion was not supported by proton nmr. The reason for the apparent discrepancy may be that in the drying of the solid under vacuum the carboxylic acids were removed apart from traces detectable by IR.

Heating the metallacycle $[(DCPE)Ni\{\overline{CH_2CH(CH_3)COO}\}]$ under an atmosphere of 1:1 propene: carbon dioxide (total pressure 8 Bar) did not result in the detection of any hydride species. The metallacycle was recovered intact in virtually 100% yield. Also no isomerisation occurred to give the 3-methyl substituted complex. The equilibria at the metal centre shown below are relevant here



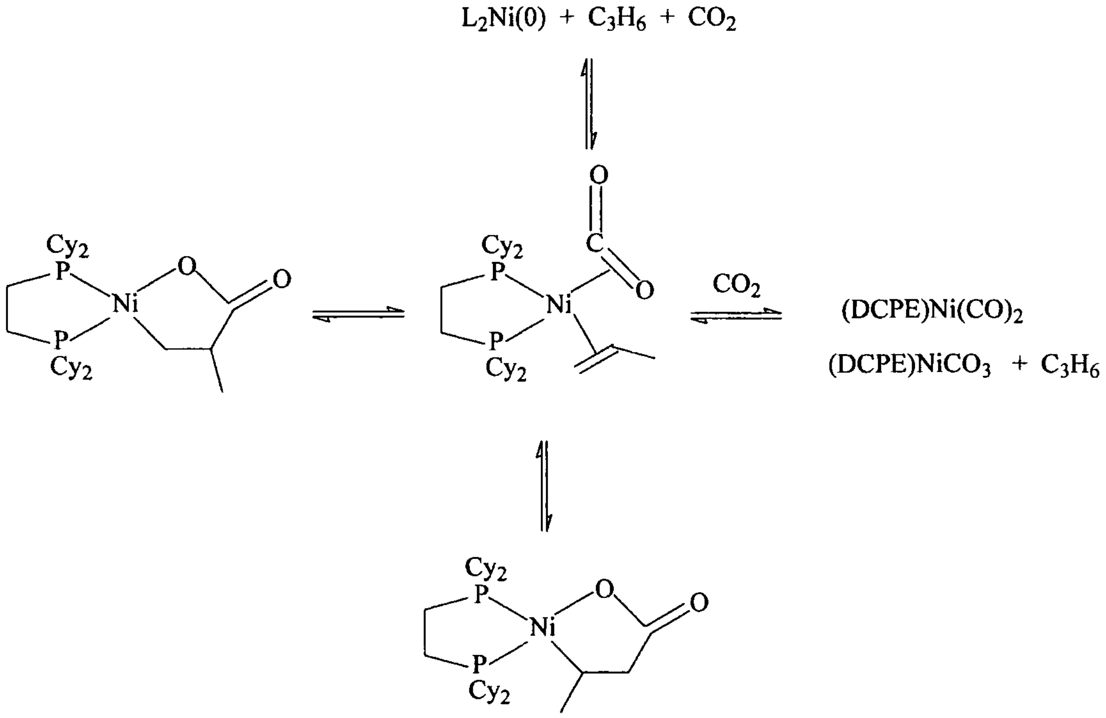
The absence of the 3-methyl isomer in the reaction product is perhaps not surprising, the equilibrium being forced over to the left hand side (metallacycle formation) in the presence of propene and carbon dioxide under pressure. The explanation for the absence of nickel hydride in this system is uncertain, as it was detected in the related experiment where $[(DCPE)Ni\{\overline{CH_2CH(CH_3)COO}\}]$ was heated under a nitrogen atmosphere(1Bar). It may be that the propene or carbon dioxide at pressure is occupying any vacant coordination sites generated at elevated temperature by the breakdown of the phosphine-nickel chelate ring and so preventing β-hydride migration. In Hobergs work on catalysis involving phenyl isocyanates and alkenes (reviewed chapter 4) a series of requirements for catalysis have been deduced, these requirements are, i) monodentate phosphine, ii) nickel:ligand ratio not exceeding 1:2, iiii) The isocyanate is always added using a metering pump (starve fed) to prevent reductive disproportionation type reactions. These conditions demonstrate that vacant coordination sites are required for catalysis, most likely for β-hydride migration to occur, and that increased levels of the isocyanate reduce catalytic yields, probably by competing irreversibly for these sites. The implications in this case are similar. i) The bidentate phosphine DCPE does not readily detach from the metal to generate vacant coordination sites, and when it does, β-hydride migration is indicated, but only in the absence of excess competing ligand which blocks the sites. These kinds of thermal decomposition studies are needed for other metallacycles of the type

$[L_2Ni\{\overline{CH_2CH(CH_3)COO}\}]$, most importantly where L_2=(DCPy).

10.4 Alkene carbon dioxide coupling reactions

The final section of this work involved the oxidative coupling of propene and carbon dioxide at liganded nickel(0). Sucessful coupling in high yield was obtained using the ligands DCPE and DCPy only. A small degree of coupling was indicated using DCPP but this was only a minor component of the nickel containing species isolated at the end of the reaction. The amine ligands tried all appeared to form carboxylates and/or carbonates as indicated by the IR spectra of the solids isolated. This may again be a function of these complexes to attain octahedral geometry if they do not already posses it. Equally it may be that these reductive disproportionation reactions involving carbon dioxide are the favoured reactions of square planar complexes of these ligands. The use of monodentate tricyclohexylphosphine in the coupling reaction did not result in any oxidative coupling or nickel carbonates.

Using DCPE and DCPy ligands the reactions proceeded smoothly in high yield (see Table 10.4). The ratio of n-butanoic:iso-butanoic resulting from acid hydrolysis of the intermediate metallacycles demonstrates the selectivity to coupling at the central carbon of propene, though significant amounts of the isomer resulting from coupling at the terminal carbon are present. The effect of heating the reaction solution to 60^{0}C has been to change the n:iso ratio in an unfavourable way, increasing the proportion of n-butanoic acid. This change in n:iso ratio must be a result of temperature influencing the equilibria shown below, the assumption being that if the reaction had not been heated to 60^{0}C for 2 hours the n:iso ratio would be unchanged from the standard reaction using DCPE. Other workers have reported a favourable change in n:iso ratio on heating.

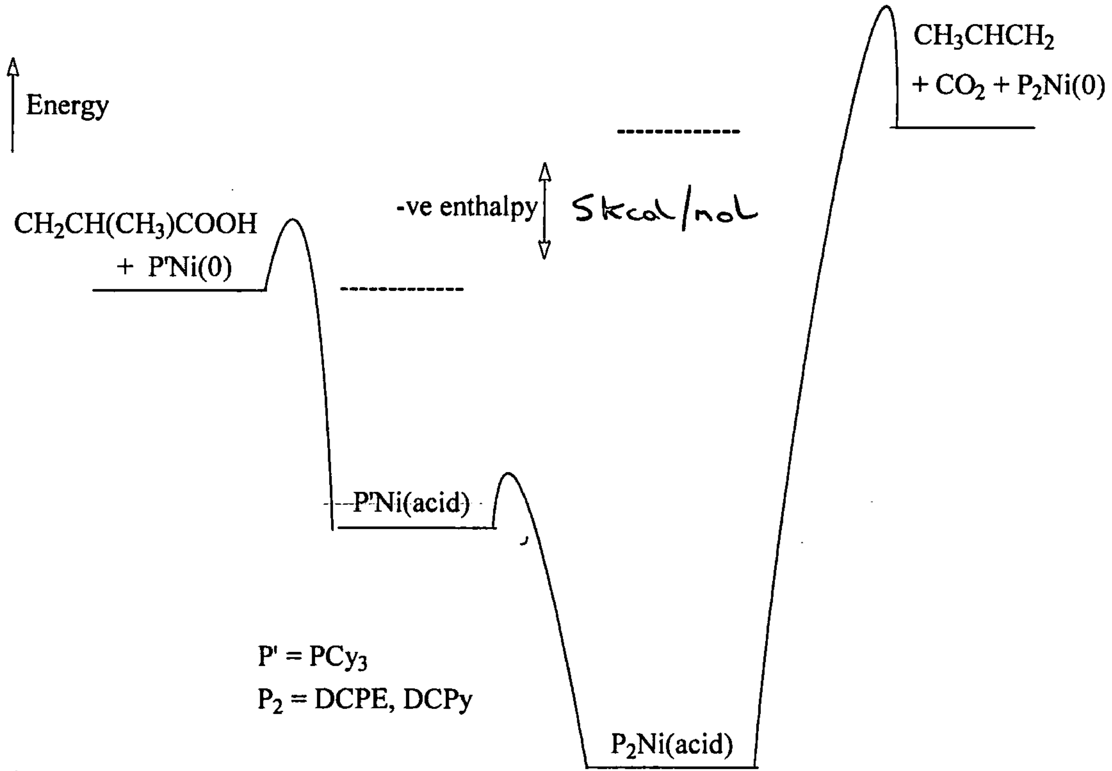


The efffect of undertaking the coupling reaction in acetonitrile solvent also reduces the n:iso ratio. Interestingly the nickel appears to be involved in two reactions i) oxidative coupling to generate metallacyclic complexes, which yield n and iso butanoic acid after acid hydrolysis and ii) reductive disproportionation of carbon dioxide to give metal carbonyls. This is the only circumstance in this study where this is apparent. The other observation peculiar to this system is the presence of small amounts of methacrylic acid after acid hydrolysis. This is interesting because it suggests that acetonitrile may be able to influence β-hydride migration. Only methacrylic acid is detected and not crotonic or linear butenoic indicating the effect is on the methacrylic isomer(4-methyl substituted cyclopentanone). The acetonitrile is known to have coordinating ability and is acting as a reversibly coordinating ligand influencing the equilibria by competing for vacant coordination sites. Clearly in this case the presence of acetonitrile is having a negative effect on yield.

The highest yields of carboxylic acids and n:iso ratios favouring iso-butanoic acid formation were obtained using the P-N ligand DCPy. No evidence for catalysis was found with this ligand and also no evidence for methacrylic acid after acid hydrolysis. This suggests two possibilites. i) DCPy is not able to generate a vacant coordination site thought necessary for β-hydride migration. ii) DCPy is able to generate a vacant coordination site but β-hydride migration is not favoured. Other workers have reported the use of beryllium chloride (discussed in chapter nine) to produce unsaturated acids after acid hydrolysis and it is suggested that this may interact with the pyridine nitrogen or the carboxylate moiety of the metallacycle to assist formation of vacant coordination sites.

The results of this study coupled with information in the literature on similar systems indicates that chelate ligands, capable of generating vacant coordination sites, are a most likely component of a catalyst to generate methacrylic acid from propene and carbon dioxide. This is indicated by, i) high yields of $(DCPy)Ni\{\overline{CH_2CH(CH_3)COO}\}]$ in the ligand displacement reaction,. ii) the report by Hoberg et al that the oxidative addition of methacrylic acid to [(DCPy)Ni(COD)] occurs in high yield, iii) high yields of $[(DCPy)Ni\{\overline{CH_2CH(CH_3)COO}\}]$ have been demonstrated in this study to form from propene and carbon dioxide. Nickel(0) complexes are shown to oxidatively add methacrylic acid and oxidatively couple propene and carbon dioxide.

From the results of this study the following reaction profile is proposed as a model for rationalising the chemistry.



The model takes account of the following, i) The reaction of carbon dioxide and propene proceeds at -50^{0}C, ii) the reaction P'Ni(0) + methacrylic/crotonic acid proceeds at -10^{0}C, as does the ligand displacement P'Ni(acid) + P_2 to give $P_2Ni(acid)$ iii) the overall thermodynamics and kinetics are favourable, ΔH -ve.

This model is consistent with the experimental results. It places the intermediate metallacycles synthesised by both routes in an energy well. It also clearly demonstrates that the complex to which methacrylic acid is oxidatively added and the complex to which oxidative coupling takes place are different. This reinforces the suggestions made earlier about the need for in situ coordinative unsaturation.

Tricyclohexylphosphine in the presence of $Ni(COD)_2$ has the required properties for the oxidative addition but cannot oxidatively couple propene and CO_2, instead the predominant reaction products are isomers of cyclooctadiene. Successful oxidative coupling occurs at [DCPENi(COD)] but not at [$Cy_3PNi(COD)$]. This may be because one tricyclohexylphosphine ligand attached to nickel is unable to provide a sufficently electron rich centre for CO_2 coupling to occur, . The vacant site is necessary for the oxidative addition of methacrylic/crotonic acid and by the theory of microreversibility, a vacant site is also necessary for β-hydride migration and reductive elimination of methacrylic acid.

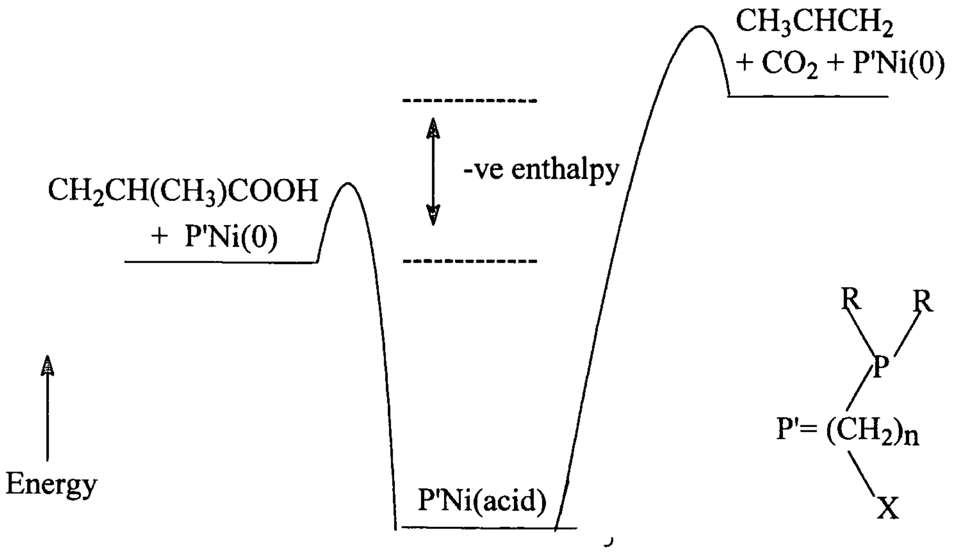
A balance is required between the need for strongly electron rich ligands to activate the nickel towards CO_2 coupling reactions, achieved using, for example, two phosphorus centres each attached to two strongly electron donating groups, but not by one Cy_3P ligand, and the need for a degree of coordinative unsaturation. A monodentate appears not to have sufficent donor strength on its own account to couple propene and CO_2, and an alternative approach of using an unsymmetrical bidentate monophosphine having an electron rich phosphorus atom as well as a weaker donor atom capable of detachment from the metal to give a vacant coordination site, needs to be tested. Such ligands worthy of study are shown below.

$R_2P(CH_2)_n—N<$ $R_2P(CH_2)_n—O/$ $R_2P(CH_2)_n—AsR_2$

$R_2P(CH_2)_n—P(CF_3)_2$ $R_2P(CH_2)_n—CN$ $R_2P(CH_2)_n—$furyl

R= Cyclohexyl, t-butyl (n = 1, 2, 3)

The potential catalytic system could be modelled as shown below.



Possible ways of linking the catalysis cycle involve lowering the energy barrier between the metallacyclic intermediate and the products, P'Ni(0) + methacrylic acid. The methods used to destabilise the metallacycle $[(\mathrm{DCPE})\overline{\mathrm{Ni}\{\mathrm{CH_2CH(CH_3)COO}\}}]$ in this study namely thermal and the use of π acids would be valid and should be tried in any future work.

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