Studies of transition metal phosphine complexes relevant to catalysis

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Studies of Transition Metal Phosphine Complexes Relevant to Catalysis.

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Department of Chemistry
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This thesis is dedicated to my family and friends, who have helped me get this far; and a curse on those who have hindered me.

And the days are not full enough,
And the nights are not full enough,
And life goes by like a field mouse,
Not shaking the grass.

Ezra Pound

Acknowledgements

I would like to thank Dr. Mel Kilner for his help, encouragement and ideas throughout the project. I am also grateful to my co-workers (past and present, in no particular order): Nicky Moore, Pete Ellis, Dave Bryant, Dr. Simon Crabtree and Emma Rivers for preventing me from teetering over into insanity. Thanks are also due to the rest of the inorganic chemists at Durham, especially Pat, Mark, Andy J., Andy K., Lynn, Tom, Sarah and Richard. My sympathy goes out to those who were not in our section who sat with us during the coffee breaks where we discussed halibuts and cheese. I also want to thank Simon and Rob who were not in my section but found out the joy of photography at annual dinners.

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Finally, I would like to say thank you to my family for their support over the last twenty eight years.

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

Abstract

Two areas related to catalysis have been explored.

Methoxycarbonyl compounds of the type [Pd(X)(CO_2Me)(L_2)] **(1)** and [Pd(X)(CO_2Me)$(L)_2$] **(2)** were used as models in the work related to hydroesterification using methyl formate instead of CO and MeOH. The behaviour of the complexes **(1)** and **(2)** in solution was examined, as was their behaviour in the presence of alkenes and nucleophiles. Many of these derivatives were too unstable to isolate, forming the corresponding dichloride complexes [Pd$(X)_2$(L_2)] **(3)** and [Pd$(X)_2$$(L)_2$] **(4)**. Several crystal structures of such complexes were obtained. The cationic complex [Pd(CO_2Me)(MeCN)$(PPh_3)_2$](BF_4) **(5)** was synthesised from **(2)** by removal of the chloride ligand with silver tetrafluoroborate. This is the first isolated cationic methoxycarbonyl complex of palladium. A crystal structure of **(5)** was obtained. Some of the factors which affected the stability of methoxycarbonyl complexes were examined. Some of these systems were used as precursors for catalytic studies of hydroesterification.

The second part of the work involved the chemistry of an unusual phosphine ligand and some of its analogues. The bidentate ligand dppn **(6)** has been reacted with some first row transition metal halides to give novel complexes such as [$NiCl_2$(dppn)] **(7)** and [$CoCl_2$(dppno)] **(8)**. The ligand **(6)** also reacted with [Pd$(MeCN)_4$]$(BF_4)_2$ **(9)** to give [Pd$(MeCN)_2$(dppn)]$(BF_4)_2$ **(10)**. Upon addition of dppe to **(10)**, the acetonitrile and dppn ligands were entirely replaced by dppe to give the complex [Pd$(dppe)_2$]$(BF_4)_2$ **(11)**. When dppe was added to the nickel complex **(7)**, the dppe displaced the chelating dppn ligand to give [$NiCl_2$(dppe)] **(12)** and free dppn. The cyclohexyl analogue of dppn, called dcpn **(13)** was synthesised. The complexes [$PdCl_2$(dcpn)] **(14)** and [Pd$(MeCN)_2$(dcpn)]$(BF_4)_2$ were made using the ligand **(13)**. The phosphine oxides of **(6)** and **(13)** were made by exposure to air in solution. These compounds are called dpno **(15)** and dcno **(16)** respectively. Preliminary catalytic work using the ligand **(6)** was carried out.

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List of Abbreviations

Ar	aromatic group
bipy	bipyridine
calc	calculated
cat	catalyst
dba	dibenzylideneacetone
dcpe	1, 2-bis(dicyclohexylphosphino)ethane
dcpn	1, 8-bis(dicyclohexylphosphino)naphthalene
dcno	1, 8-bis(dicyclohexyl-oxo-phosphino)naphthalene
DMF	dimethylformamide
dmso	dimethyl sulphoxide
dppe	1, 2- bis(diphenylphosphino)ethane
dppm	1, 1-bis(diphenylphosphino)methane
dppn	1, 8-bis(diphenylphosphino)naphthalene
dpno	1, 8-bis(diphenyl-oxo-phosphino)naphthalene
dppno	{1-(oxo-diphenylphosphino), 8-(diphenylphosphino) (naphthalene)}
dppp	1, 3-bis(diphenylphosphino)propane
dtbpp	1, 3-bis(ditertiarybutylphosphino)propane
HOTf	Trifluoroacetic acid (CF_3CO_2H)
L	generic 2 electron ligand
mes	mesitylene group
PR_3	generic monophosphine
pnp	2, 6 bis(diphenylphosphinomethyl)pyridine
thf	tetrahydrofuran
Triphos	($Ph_2\mathbf{P}CH_2CH_2\mathbf{P}(Ph)CH_2CH_2\mathbf{P}Ph_2$)
triphos	generic tridentate phosphine ligand
CHN	Carbon, hydrogen and nitrogen elemental analysis
GC	Gas Chromatography

IR	-	Infrared Spectroscopy
MO	-	molecular orbital
MS	-	Mass Spectroscopy
NMR	-	Nuclear Magnetic Resonance
psi	-	pounds per square inch
ppm	-	parts per million
rt	-	room temperature

Chapter 1

Literature Review

Action without study is fatal.
Study without action is futile.

Mary Beard (1876 - 1958)

1.1 Hydroesterification of olefins using carbon monoxide and methanol

For some time, there has been a good deal of interest[1] in hydroesterification: the catalytic production of methyl propanoate from ethylene, CO and methanol (see Figure 1.1). One of the reasons that this process is of interest is that methylmethacrylate can be obtained from the product.[2] One currently favoured catalyst precursor for hydroesterification is [$PdCl_2(PPh_3)_2$]; this is a metal complex that is relatively easy to prepare (or can be bought) and, as it is air stable, relatively simple to use. It has been found for this catalyst that addition of some HCl accelerates the reaction.[3]

$$\boxed{\mathrm{HOMe} + \mathrm{CO} \xrightarrow[\text{Catalyst (e.g. } \mathrm{PdCl_2(PPh_3)_2}\text{)}]{=} \mathrm{CH_3CH_2CO_2Me}}$$

Figure 1.1

For alkenes longer than ethene, both linear and branched esters are formed (see Figure 1.2). There are a number of factors that govern the normal (linear)/ iso (branched) ratio. Use of a bidentate phosphine will give more of the linear ester than using PPh_3, for example.[4]

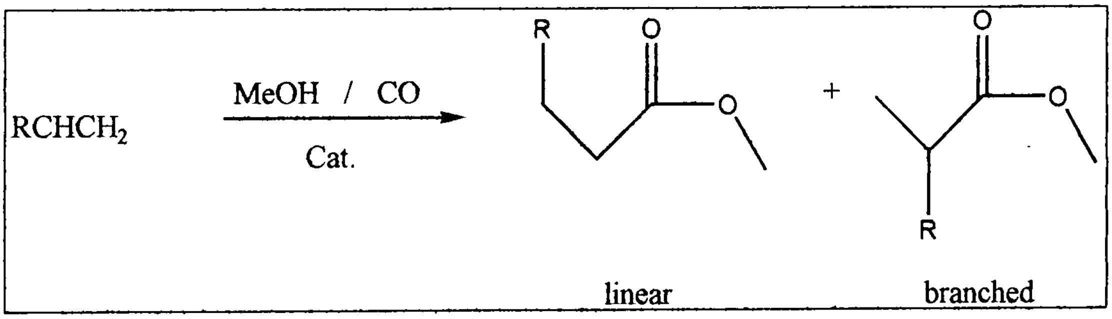


Figure 1.2

Using $SnCl_2$ or $GeCl_2$ as a co-catalyst also favours the formation of linear over branched esters.[5] There are also some systems which, utilising chiral phosphines, can perform asymmetric carbonylation.[6] The optical yields for these systems have tended to be rather poor. Recently, however, there have been a few publications[7] where both stereoselectivity and yield have been reasonable or good.

1.2 Use of methyl formate in hydroesterification and other catalytic processes.

In the light of the above, why should we use methyl formate (HCO_2Me) when the CO/ MeOH route has been found to work? The main reason for this is that carbon monoxide is a hazardous gas, and so any process that can eliminate or reduce the need for its use would be advantageous.

There has been a considerable amount of attention to the methyl formate based hydroesterification process. The two metal systems that seem to catalyse the formation of ester from alkyl formate and olefin most effectively are Ru and Pd. These systems are now compared.

1.2.1 Ruthenium catalysed hydroesterification using alkyl formate.

The first example of formation of methyl propanoate from methyl formate was published by Isnard and co-workers in 1983.[9] This system, based on the ruthenium complex $RuCl_2L_3$, was believed to proceed by initial decarbonylation of the methyl formate to CO and MeOH. Their discovery stemmed from their own work in the synthesis of diethyl ketone from ethene and CO, where alcohols were used as a hydrogen source. In the absence of CO, it was found that MeOH acted not only as a source of hydrogen, but also as a source of carbon, giving rise to the formation of methyl propanoate in the presence of ethene. This was already known. [10] It was noted, however, that considerable amounts of methyl formate were always found in the reaction mixture. This discovery prompted the investigation of the interaction between methyl formate, ethene and the catalytic precursor $RuCl_3$. The formation of methyl propanoate, by decomposition of the methyl formate, could not be extended to higher olefins or other alkyl formates.

In 1990, however, Nahmed and Jenner found a system that could catalyse reactions involving higher olefins. [11] These workers used dodecacarbonyltriruthenium with alkyl phosphines to give a system that did not require any additional CO pressure. Their choice of catalyst was based on work showing the system to be a highly efficient decarbonylation catalyst for alkyl formates. [12] This would suggest that the hydroesterification depended on the *in situ* decarbonylation of alkyl formate. Similar results were obtained by Kondo and co-workers. [13]

Other work by Legrand and co-workers [14] was based on a $RuCl_3$ complex with an amine and an amine salt as co-catalysts. This system was reported as having a considerably better turnover frequency than previous systems, and needed no additional carbon monoxide. One interesting aspect about this system was that the authors claimed that the formation of methyl propanoate was not based on decarbonylation of the formate, but rather on the oxidative addition of the HCO_2Me

to the metal followed by association and insertion of the olefin (see Figure 1.3). The basis for this argument was a deuterium labelling study using d^4 methanol, where no deuterium was found in the product ester. This process was patented.[15]

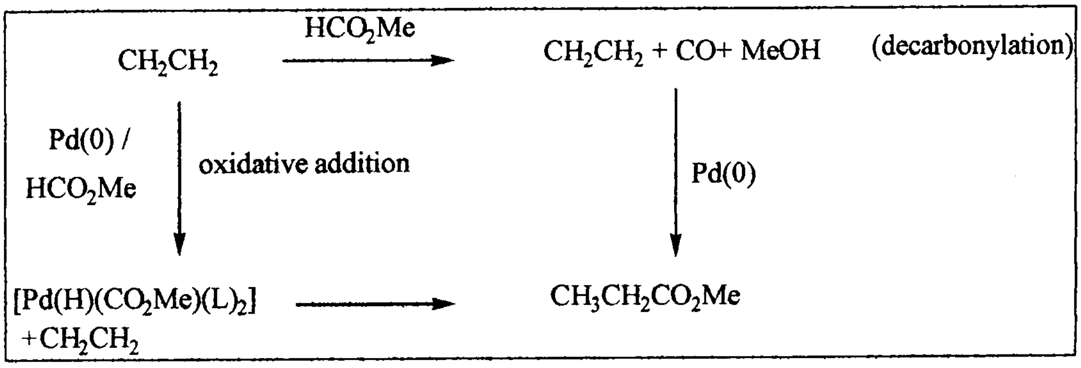


Figure 1.3

Lugan and co-workers[16] claimed an even more efficient system obtained by concentrating on the promoting effects of chloride ions on a ruthenium complex. The key to this improvement seemed to be the choice of solvent. It was found that dimethylformamide produced a remarkable improvement in activity, giving selectivity and conversion close to 100%.

1.2.2 Palladium catalysed hydroesterification using alkyl formate

Palladium based systems did not appear until somewhat later. In 1987 Mlekuz and co-workers[17] published a paper in which the hydroesterification of various alkenes was carried out using conditions closely related to the Wacker process.[18] The system seemed applicable to a wide variety of alkyl formates, including methyl formate, and a variety of olefins. No mention, however, was made of ethene as the substrate. The best results were obtained for a 18/5/1 mixture of olefin/$CuCl_2$/$PdCl_2$. Just as for the Wacker process, oxygen was required to re-oxidise the CuCl to $CuCl_2$.

In 1989, Keim and Becker published some work on esterification involving methyl formate and alkenes. [19] The paper contained work on both a palladium and a ruthenium system. The ruthenium system was reported as being more efficient then that of Isnard. [9] The palladium system reportedly esterified butadiene effectively to the methyl ester of pentenoic acid.

In the same year, Lin and Alper [20] developed a more general palladium based system. This work investigated the effect of the oxidation state of the catalytic precursor complex on the nature of the product. It was found that using Pd(0) phosphine or dibenzylideneacetone (dba) complexes would give more of the linear ester, while using a Pd(II) phosphine dichloride complex would produce more branched product. No indication was given as to whether or not the system had been tested on ethene and methyl formate. Further investigations were made by Lin and co-workers [21] when the effect of adding hydrogen to the Lin and Alper palladium based system was studied. The reason put forward for the improvement was that the addition of H_2 provided more hydridic palladium species for olefin insertion to occur. The modified system (like the original one) was thought to proceed without decomposition of the alkoxycarbonyl intermediate. The processes both used CO pressure, but no methanol. It was found that the addition of hydrogen improved the process, increasing the yield by up to 46% in some cases. One of the puzzles with both of these systems was the need for additional CO pressure when there seemed to be no need to add CO for the reaction to work. It was proposed that the CO helped stabilise the palladium intermediates, and indeed, upon addition of CO, the precipitation of palladium metal was inhibited. Once again, however, there seemed to be no use of methyl formate with ethene.

A more recent paper [29] on a similar system, however, found that the methyl formate was not the source of the CO although the MeOH from the decarbonylation of the formate was involved. More recently, Grevin and Kalck [22] developed a palladium based system that claimed to use methyl formate and ethene to give a high yielding methyl propanoate system. The turnover, however, was only moderately good. The result was significant in that no carbon monoxide was needed. The reaction was carried out in MeOH to give best yields and so, since CO was found at the end of the reaction, it is probable that the methyl formate decarbonylates (thus giving high yields in the presence of methanol). The use of methyl formate was, however, found to be more effective than simply using MeOH and CO.

In 1996, a paper by Pennequin and co-workers[23] outlined an oxidative carbonylation of alkenes using a mixed system of palladium and copper (presumably by a Wacker type process, recalling Alper's earlier work[20]). The workers found that the best conversion was obtained with some initial CO pressure and after that with lithium methoxide in solution, to cause partial decarbonylation of the methyl formate (by setting up an equilibrium such as shown in Figure 1.4 below) so that the palladium species did not decompose.

$$\boxed{HCO_2Me \xrightleftharpoons[OMe^-]{} CO \quad + \quad MeOH}$$

Figure 1.4

1.2.3 Other reactions involving methyl formate

In a recent review[24] Jenner outlined the various types of reaction that methyl formate is known to undergo. In the same review, Jenner discussed the synthesis of methyl formate from methanol and CO.[25] In the presence of a suitable system, methyl formate can also be converted to acetaldehyde, or to ethyl formate.[26] In one case, where a rhodium species was used in neat methyl formate, conversion to acetic acid was almost quantitative.[27] Comparable results were achieved with certain palladium and cobalt catalysts. The mechanism for acetic acid formation is not clear, but it is thought that the actions of a hard and soft Lewis acid on the formate may be beneficial.[28] One of the other areas discussed in Jenner's review was the decarbonylation of methyl formate, catalysed by a wide variety of systems based on rhodium, iridium, osmium, copper, and ruthenium. It is the ruthenium and osmium catalysts that seem to be most effective, however.

The formate can also be used in the conversion of alkyl and aryl halides to acids[29] or esters.[30] This reaction is catalysed by palladium or ruthenium complexes. The latter paper, dealing with conversion to esters, by Carpentier and co-workers also examines the activation of the methyl formate towards decarbonylation. This work implies that the CO needed for the reaction does not actually come from the methyl formate, but has to be pumped in at pressure. The methyl formate is thought to be important as a source of MeOH for the reaction. Carrying out the reaction in methanol, however, is less efficient than using methyl formate as the solvent.

Another important reaction in which methyl formate can be used as a substrate is hydroformylation. This reaction can lead to either hydroformylation or hydrogenation in the presence of water as the solvent.[31] Alkenes of longer chain length tended towards hydrogenation, whereas, shorter or cyclic alkenes were hydroformylated. It was observed that internal alkenes isomerised to terminal alkenes prior to hydroformylation.

In summary, methyl formate is a versatile substrate for several reactions, and can be regarded as equivalent to MeOH and CO. The reactions discussed are summarised in Figure 1.5.

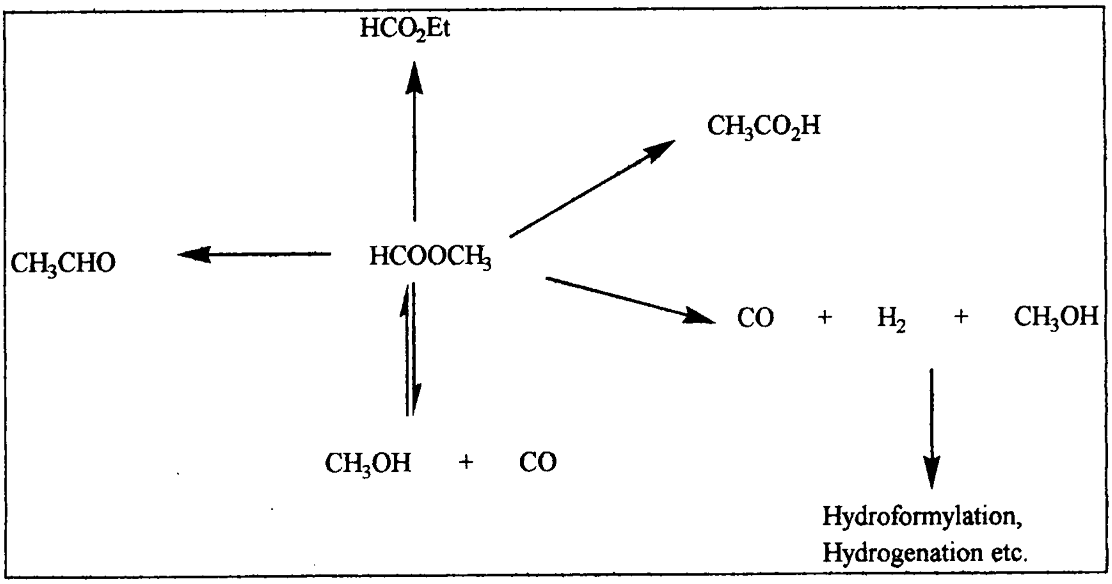


Figure 1.5

1.3 Methoxycarbonyl complexes and their role in catalysis.

From the above discussion, there seems to be no clear pattern to predict how the formate reacts once it is activated in a given system, although the decarbonylation route does seem to predominate. It was felt that, because of the proposed oxidative addition of HCO_2Me to Pd(0) (see Figure 1.3), an attempt to understand the role of methoxycarbonyl (CO_2Me) complexes should be made. These complexes are relevant not only to this reaction but to other carbonylations.[32]

1.3.1 Palladium and platinum alkoxycarbonyls.

In 1968 Fitton and co-workers[33] synthesised the ethoxycarbonyl complex $[Pd(Cl)(CO_2Et)(PPh_3)_2]$. This was achieved by the oxidative addition of ethylchloroformate to tetrakis(triphenylphosphine)palladium(0). No experimental details were published with it. Meanwhile, Clark and co-workers[34] had synthesised platinum alkoxycarbonyl derivatives of the form $[PtX(CO_2R)(PPh_3)_2]$, by addition of neat methanol or ethanol to cationic carbonyl species $[PtX(CO)(PPh_3)_2]^+$. The alkoxycarbonyls formed in this reaction were found to react with water to give the platinum halohydride complex. Later, in 1971, Beck and Werner[35] published a paper that showed synthesis of platinum alkoxycarbonyls from isocyanate complexes (see Figure 1.6).

$$\boxed{[Pt(NCO)_2(PPh_3)_2] + 2\ ROH + CO \xrightarrow[CH_2Cl_2]{} [Pt(NCO)(CO_2R)(PPh_3)_2] + H_2NCO_2R}$$

Figure 1.6

In 1972 a short paper by Otsuka and co-workers[36] described the synthesis of nickel and palladium halo-formates by oxidative addition of the alkylchloroformates to the zero valent metal. This was followed the next year by a full paper.[37]

In the same year, Hidai and co-workers [38] also made $[Pd(Cl)(CO_2Me)(PPh_3)_2]$, but this time it was synthesised using a CO/MeOH/tertiary amine system on the palladium dichloride phosphine complex. Use of a tertiary amine seems to be important, as using primary or secondary amines gave carbonyl complexes instead.

In 1974, Vitagliano [39] published some work showing the synthesis of platinum alkoxycarbonyl diene complexes. The synthesis was based, once again, on nucleophilic attack by MeO^- on coordinated CO. Another paper, [40] in the same year, examined the nature of the methoxycarbonyl moiety. The study was prompted by an unusual feature of a bis(alkoxycarbonyl)platinum complex. The feature, which puzzled the authors, was a *trans* configuration for the alkoxycarbonyl ligands. In platinum complexes, such an arrangement for two Pt-C bonds is unusual. The authors play down the possibility of steric interactions from the triphenylphosphine ligands, and instead claim that the alkoxycarbonyl ligand acts as a relatively hard ligand. To explain this they cite Pearson's rationalisation of the instability caused in a system by two soft *trans* ligands on a soft metal. [41]

Little other work that was concerned with palladium methoxycarbonyls appears until 1978 when Rivetti and Romano [42] synthesised the dimethoxycarbonyl $[Pd(CO_2Me)_2(PPh_3)_2]$, and the acetate complex $[Pd(OAc)(CO_2Me)(PPh_3)_2]$. The study was concerned with the behaviour of palladium(II) phosphine systems in alcohols when exposed to CO. The authors found that when the reaction was carried out at elevated temperature and pressure, there was formation of dimethyl oxalate (MeOC(O)C(O)OMe). The acetate complex was synthesised by the addition of silver acetate to the complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$. The bis-methoxycarbonyl was synthesised as shown in Figure 1.7.

$$[Pd(Cl)(CO_2Me)(PPh_3)_2] \quad + \quad NaOCH_3 \quad \xrightarrow{CO} \quad [Pd(CO_2Me)_2(PPh_3)_2]$$

Figure 1.7

There has been some more attention paid to palladium methoxycarbonyl systems in recent years.[43] In 1988, for example, Yamamoto *et al.*[44] made a palladium alkoxycarbonyl complex from CO insertion into a metal alkoxide. The alkoxides of palladium are normally very unstable; however the use of fluorinated alkoxides produced a stable OR group.[44]

The study of methoxycarbonyls has not been limited to palladium and platinum, however. A brief discussion of the chemistry of other transition metal methoxycarbonyl complexes follows.

1.3.2 Alkoxycarbonyls of transition metals other than palladium and platinum.

Most of the middle to late transition metals have at least some examples of alkoxycarbonyl complexes.

There are published examples of alkoxycarbonyl complexes of all of the group nine metals. Cobalt systems were synthesised by Bao and co-workers[47] from $[CpCo(dppe)CO]^{2+}$ and nucleophilic alkoxide. Keim and co-workers[48] synthesised methoxycarbonyl derivatives of rhodium and iridium. These reactions are interesting because they show direct oxidative addition of methyl formate to a metal centre (see Figure 1.8).

$$\boxed{(PMe_3)_3RhCl \xrightarrow[HCO_2Me]{} Rh(PMe_3)_3(Cl)(H)(CO_2Me)}$$

Figure 1.8

The above example (Figure 1.8), and a similar reaction observed with iridium, clearly demonstrates the oxidative addition potential of methyl formate. Another iridium methoxycarbonyl complex $[IrCl(CO_2Me)(dppe)_2][BF_4]$ was made by Lilga and Ibres [49] by nucleophilic attack on co-ordinated carbon monoxide.

Methoxycarbonyl complexes of nickel have also been made (in the same paper as the synthesis of the palladium chloro-methoxycarbonyl species). [31] The Ni complexes were reportedly thermally unstable and very air sensitive. This behaviour contrasts with the air stable palladium complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$. Nickel ethoxycarbonyl complexes have been reported by Bianchini and co-workers. [50] These compounds were synthesised by the oxidative addition of ethylcyanoformate to Ni(0).

A rare example of a group eleven alkoxycarbonyl complex was produced by Komiya *et al.*[51] when they synthesised a gold(III) complex containing an alkoxycarbonyl ligand, [*cis*-$AuMe_2(CO_2R)(PPh_3)$].

With the advent of numerous crystal structures of platinum, palladium and other transition metal complexes containing methoxycarbonyl ligands, the existence of these ligands has been well established. Part of the purpose of this study is to try to clarify their reactivity and their role within the hydroesterification reaction, particularly with reference to the methyl formate route, and to observe their reactivity.

1.3.3 Role of methoxycarbonyl ligands in other reactions.

The methoxycarbonyl ligand has been observed in many reactions, either as a side product or as an intermediate. [52] The reaction of greatest interest to this work is that of hydroesterification of alkenes. This has already been covered in section 1.2. Therefore, in this section we will (briefly) discuss the occurrence and role of methoxycarbonyl complexes in some related systems.

In the synthesis of dimethyl oxalate, the intermediate is believed to be a bis methoxycarbonyl species such as that shown in Figure 1.9.[53]

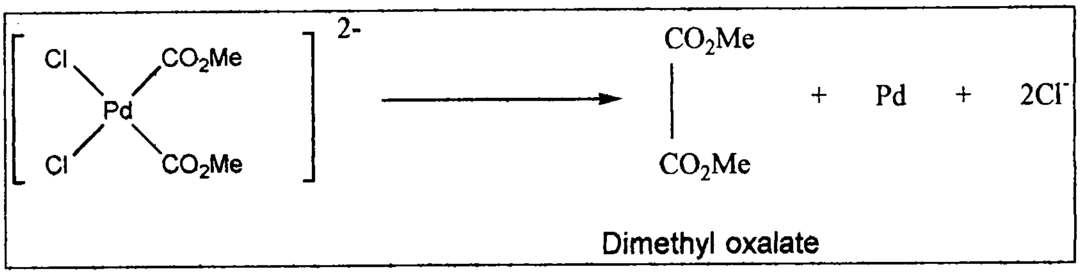


Figure 1.9

For catalysis to occur in this type of system the palladium must be re-oxidised by a reagent such as $CuCl_2$. This is reminiscent of the Wacker process and the technique of adding a re-oxidant has been applied in similar situations.[54]

One of the major fields of study that involves palladium methoxycarbonyl intermediates is the currently fashionable area of polyketone catalysis.[55] Initiation in the polyketone process (see section 1.4.2.4) can occur though the insertion of ethene into the Pd-CO_2Me bond of palladium methoxycarbonyl complexes.

1.4 Palladium phosphine chemistry

Palladium metal is found in Group 10 of the periodic table and in the middle period of the transition elements (hence it is a 4d metal). It was discovered in 1803 by W.H. Wollaston in South Africa. It is a rare metal, and is normally found with platinum and usually occurs as the metal but can also occur with sulphur, antimony and mercury. The three main sources of the metal are South Africa, Canada and Russia. Principal uses of the metal are reliant on its corrosion resistant nature, making it useful in dental alloys, jewellery and electrical contacts. It is also one of the chemist's favourite catalytic metals. It has six naturally occurring isotopes: ^{102}Pd (1%); ^{104}Pd(11%); ^{105}Pd(22.2%); ^{106}Pd(27.3%); ^{108}Pd(26.7%) and ^{110}Pd(11.8%).[56] The only isotope that has a nuclear magnetic moment is ^{105}Pd. The spin of I = 5/2 means that it is quadropolar, and probably because of this, coupling to palladium has not been observed in NMR studies.

There are very many palladium phosphine complexes. Complexes of the type $Pd(PR_3)_n$ where n is 3 or 4 tend to be air sensitive yellow solids. These compounds can be readily made by the reduction of $PdCl_2$ (by, say, hydrazine) in the presence of the phosphine ligand. [57] Having a zero oxidation state, they readily undergo oxidative addition reactions (e.g. see Figure 1.10). The structure of some of these palladium(0) compounds (especially for those compounds with bulky ligands such as PPh_3) is not entirely clear, one reason for this being an equilibrium in solution (Figure 1.11).

$$\begin{array}{ccc} [Pd(PPh_3)_4] & \xrightarrow[RX]{\hspace{3em}} & [Pd(X)(R)(PPh_3)_2] \\ \\ Pd(0) & & Pd(II) \end{array}$$

Figure 1.10

The other common oxidation state for palladium is Pd(II), shown in Figure 1.10 to result from oxidative addition to Pd(0) complexes. The +2 state (d^8) is the most common for palladium, and since it is d^8, is invariably square planar, or nearly so (the energy level diagram based on the Crystal Field model is shown in Figure 1.12).

$$Pd(PPh_3)_4 \rightleftharpoons Pd(PPh_3)_3 + PPh_3$$

Figure 1.11

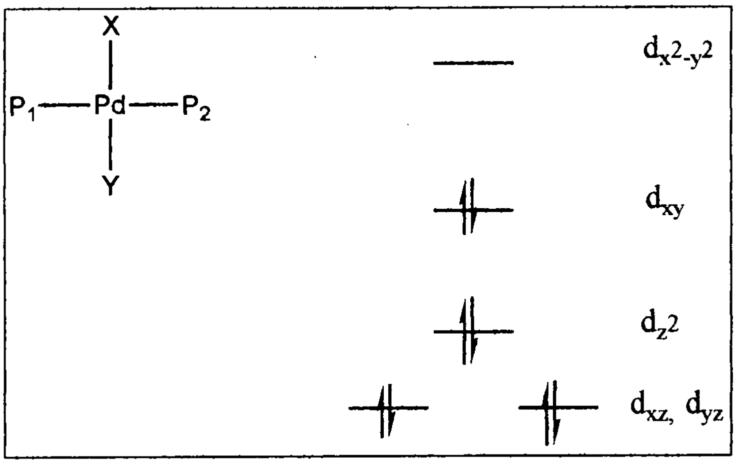


Figure 1.12

1.4.1 Bonding in Palladium Phosphine Complexes.

The generally accepted picture of metal-phosphine bonding is shown in Figure 1.13. The lone pair on phosphorus forms a sigma (σ) bond with the metal while a d_π orbital on the metal back donates synergically into the σ^* orbital from the P-C bond.

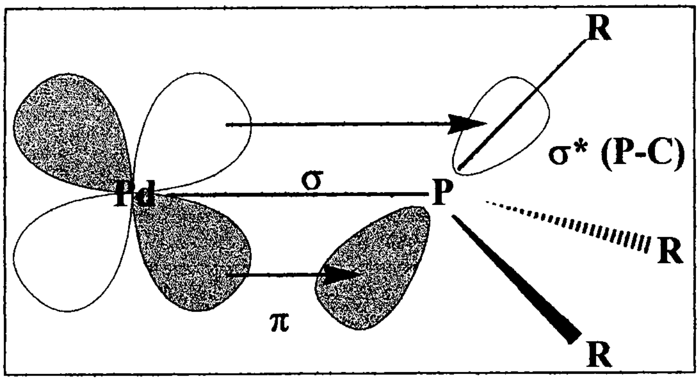


Figure 1.13

One consequence of this bonding model is that the length of the P-C bond increases with greater back donation from the metal.[58] The degree of back donation which occurs depends not only on the π-basicity, and oxidation state, of the metal, but also on the substituents (R) on the phosphorus. The extent of back donation to the phosphine PR_3 decreases in the order $PF_3 >> P(OR)_3 > P(Ar)_3 > P(alkyl)_3$.[59] As the R group becomes more electronegative, the energy of the P-R bond becomes lower (i.e. more stable), leading to a lowering in $\sigma^*_{(P\text{-}C)}$ energy.[59] This means that the orbital overlap for something such as PF_3 is very great. In fact the back donation for PF_3 is very close to that observed for CO.[59]

1.4.2 ^{31}P NMR in analysis of palladium species.

The ^{31}P nucleus has a nuclear spin $I = 1/2$ and is practically 100% abundant. The ^{31}P sensitivity is quite high, but is lower than the sensitivity of the ^{1}H nucleus. This means that longer acquisition times are usually required for ^{31}P NMR than for proton NMR. The chemical shift of the free phosphine can be estimated from the groups present on the phosphorus. These so-called group contributions can be surprisingly accurate for the estimation of chemical shift. One fairly early study by Grim and co-workers[60] showed a good comparison between the calculated and the observed shift for a variety of phosphine ligands.

^{31}P {^{1}H} NMR is an extremely useful tool in the probing of phosphine ligands in palladium and other metal complexes. The chemical shift and coupling constants of species under study can give useful structural information. One particularly useful rationale is the coordination chemical shift. Upon coordination to a metal, a phosphine ligand's ^{31}P NMR signal generally moves to a higher chemical shift. The degree to which this occurs seems to be predictable. There appears to be a linear relationship between the coordination chemical shift (see below) and the chemical shift of the free phosphine for a given metal system.[61]

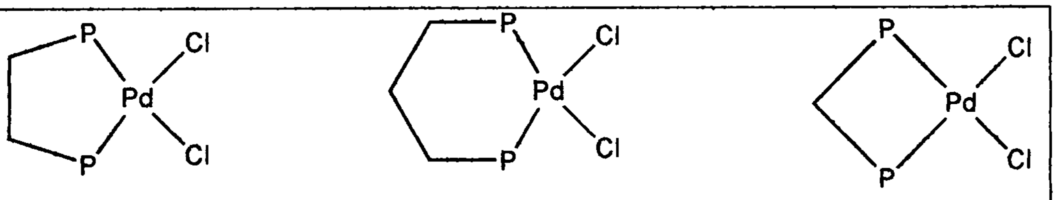
The size and direction of the shift is modified when chelating phosphines are used as there is a 'chelate effect' that is practically diagnostic of chelation. Consider the following example. Free dppe gives a signal at approximately -13 ppm in the ^{31}P{^{1}H} NMR spectrum. When it coordinates to $PdCl_2$ the observed chemical shift in the spectrum is at 65 ppm. This difference is known as the *coordination chemical shift* and is given the symbol Δ. In the case of the dppe complex $\Delta = 65 - (-13) = 78$ ppm. It is interesting to compare this with the coordination chemical shift for PPh_3 ($\delta = -6$ ppm) in $[PdCl_2(PPh_3)_2]$ ($\delta = 23.5$ ppm). In the latter case $\Delta = (23.5 - (-6)) = 29.5$ ppm.

The effect of the chelate ring is quantified by a factor called the *ring contribution* to the chemical shift given the symbol Δ_R. The ring contribution can be estimated by considering the closest analogue of the chelating phosphine complex as two non-chelating ligands. An example taken from Garrou's review[63] (Table 1.1) shows this.

Table 1.1 Comparison of chelating and non-chelating phosphine chemical shifts

	δ_P	$\delta_{P\text{ free ligand}}$	Δ
$[PtCl_2(dppe)]$	54.5 ppm.	-13.3 ppm.	67.7 ppm.
$[PtCl_2(MePh_2P)_2]$	6.4 ppm.	-28.0 ppm.	34.4.ppm.

Evaluating the difference between the entries in the last column gives the ring contribution, i.e. $\Delta_R = 67.7 - 34.4 = 33.3$ ppm. For chelating phosphine complexes with ring sizes other than five (see Figure 1.14) the magnitude and sign of the coordination effect can be different. Dppm complexes, for instance, (with a ring size of four) tend to have a negative coordination chemical shift as well as being of a greater magnitude than the dppe analogues. The ring contribution is very useful if we are trying to determine whether or not chelation has occurred, especially with dppm which has a high tendency to bridge metals.



2 carbon backbone, ring size = 5

3 carbon backbone, ring size =6

1 carbon backbone, ring size = 4

Figure 4.14

In summary, the reasons for this additional shift are not altogether understood, but can be quantified. It was originally thought that the steric strain in the bound ligands would explain the phenomenon. This seems unlikely from a comparative study of the shift for five membered rings (as for $PtCl_2$(dppe) above) with four and six membered rings.[62] It is, however, clearly a useful tool if we are unsure as to whether or not a ligand has formed a chelate complex. Garrou's review, from which much of the above information has been gleaned, deals with the causes and consequences of the chelation on phosphorus NMR spectra.[63]

1.4.3 Reactions of Palladium Phosphines.

Palladium phosphine chemistry is almost entirely that of four coordinate square planar Pd(II) or of Pd(0), which can be planar $[Pd(L_3)]$, linear $[Pd(P^tBu_3)_2]$ or possibly tetrahedral $[Pd(PPh_3)_4]$. The structure of the tetrakis complex is hard to ascertain as there is an equilibrium in solution, as was shown in Figure 1.11. The $14e^-$ $[PdL_2]$ complexes are thought to show a reasonable stability because of the large steric contribution of the sorts of groups that form these complexes, for example $P(^tBu)_3$.

1.4.3.1 Oxidative Addition/ Reductive Elimination

As mentioned above, one of the most common reactions in palladium phosphine chemistry is oxidative addition. Oxidative addition to Pd(0) gives Pd(II) complexes. The reverse reaction (reductive elimination) is also fairly facile. This aspect of palladium chemistry is absolutely critical to its behaviour as a catalyst; reductive elimination is the last step in many postulated catalytic cycles. Oxidative addition, however, has been better documented.[64] There are several possible mechanisms for oxidative addition. Non-polar molecules, such as hydrogen, are thought to undergo three-centre-addition with the metal. For alkyl halides S_N2 mechanisms are thought to predominate (see Figure 1.15). For 18 electron palladium(0) species, loss of a ligand is observed before oxidative addition takes place (as illustrated in Figure 1.15).[65]

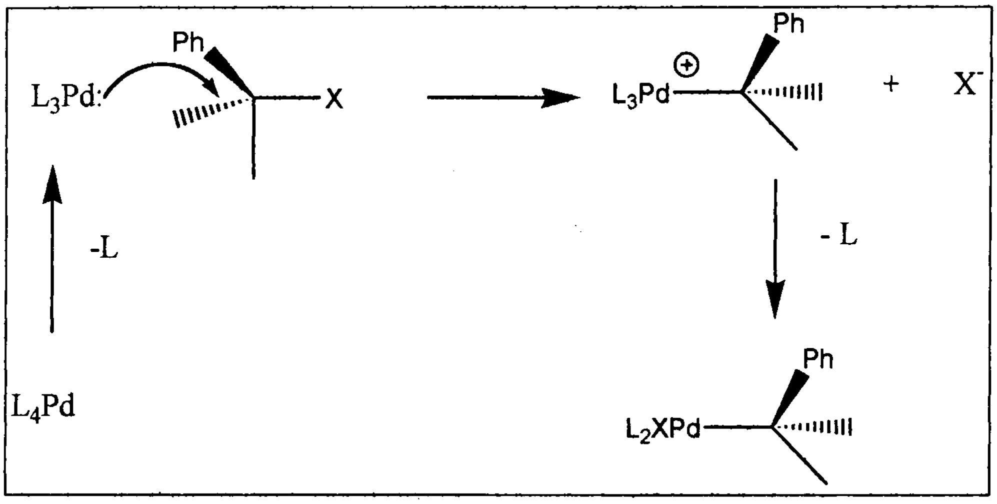


Figure 1.15

As illustrated above, palladium can readily undergo oxidative addition with alkyl (or acyl) halides. When this happens, a species of the type $[Pd(X)(R)(PR_3)_2]$ is formed. This is often a crucial step in catalytic reactions, such as in the hydrocyanation reaction where an olefin is converted to an organic cyanide *via* $[Pd(H)(CN)L_2]$, for example. If the HCN is added directly to the palladium (0) complex without an alkene present, then a double oxidative addition leads to an unstable Pd(IV) intermediate, to give $Pd(CN)_2L_2$ and H_2.[66]

The oxidative addition process of palladium is also the first catalytic step in the Heck reaction.[67] This reaction has proved popular with synthetic organic chemists since it is a very useful method for creating carbon-carbon bonds (for example see Figure 1.16).

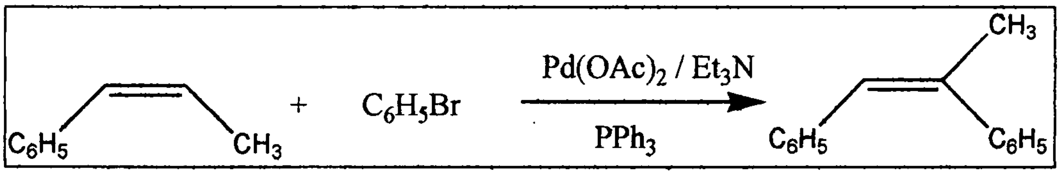


Figure 1.16

Reductive elimination is the reverse process, and is frequently the terminating step in a catalytic reaction. In the Heck process for example, Pd(0) is re-generated by reductive elimination of HBr from [Pd(H)(Br)L_2] to give PdL_3 in the presence of L.

1.4.3.2 Alkene and CO Insertion

The insertion of olefins into palladium hydride bonds is an important postulated step in catalysis. In the esterification reaction, it is a crucial step for ester formation[68] (see Figure 1.17). There has been some debate[60,69] as to whether the olefin inserts into the Pd-H or into the Pd-C bond of a methoxycarbonyl complex. The currently favoured thinking is that it inserts into the Pd-H bond. The insertion into Pd-C bonds, though, is certainly possible for olefins as shown by the Heck reaction.

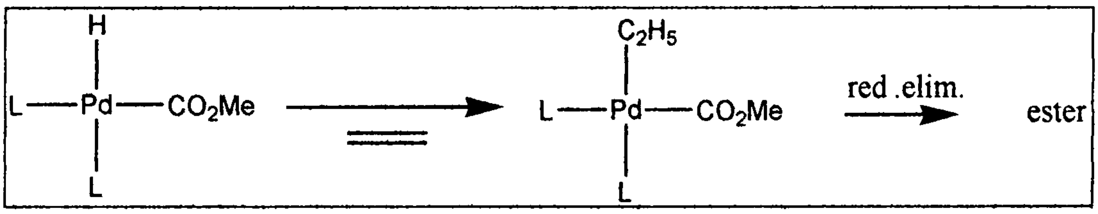


Figure 1.17

One of the other most common types of insertion, of course, is that of CO (see Figure 1.18). In polyketone synthesis, this is a very important step.

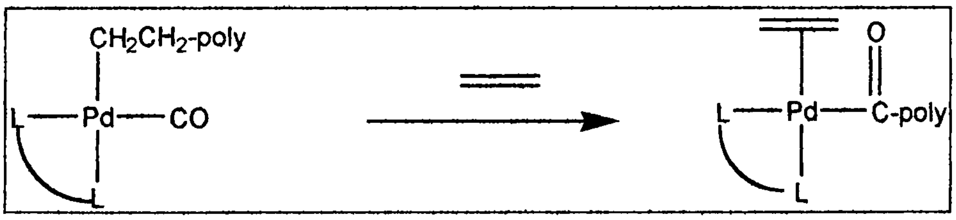


Figure 1.18

The polyketone reaction is particularly interesting[70] in that the insertions of CO and of C_2H_4 are perfectly alternating. CO inserts into Pd-CH_2CH_2-polymer, and CH_2CH_2 inserts into Pd-C(O)-polymer. Double insertion of CO is disfavoured, as is the double insertion of ethene.[71] This means that there are very few instances where the chain of the polymer will have units such as $C(O)\text{-}C(O)\text{-}CH_2CH_2\text{-}C(O)$ or $CH_2CH_2\text{-}CH_2CH_2\text{-}C(O)$.

1.4.3.3 Olefin oxidation and other catalytic processes

Several references have been made in the above text to catalytic reactions (e.g. Heck, polyketone synthesis) and the steps that constitute these processes. In this section we take a closer look at some of these reactions.

Palladium(II) systems (e.g. $PdCl_2$) form π- complexes with olefins. Upon coordination, the olefin is more prone to nucleophilic attack. The attack of a nucleophile followed by the formation of a Pd-C σ bond is called *palladation*. When the nucleophile is water, the reaction constitutes part of the Wacker process. After nucleophilic attack, one of two things generally happens; either the palladium eliminates to give Pd(H)(Cl) and the organic moiety; or else there is substitution of the palladium by another nucleophile (see Figure 1.19). The nucleophile can come from a variety of reagents, e.g. H_2O, RO^- and NR_3.
When propene is used, propanaldehyde is not formed, but acetone is. Indeed, terminal olefins generally are oxidised to the methyl ketone. [72]

The importance of the Wacker process is somewhat on the wane now, as the process found its main use in the generation of acetaldehyde for oxidation to acetic acid. Acetic acid production is now mostly carried out using the Monsanto process, a system based on rhodium.

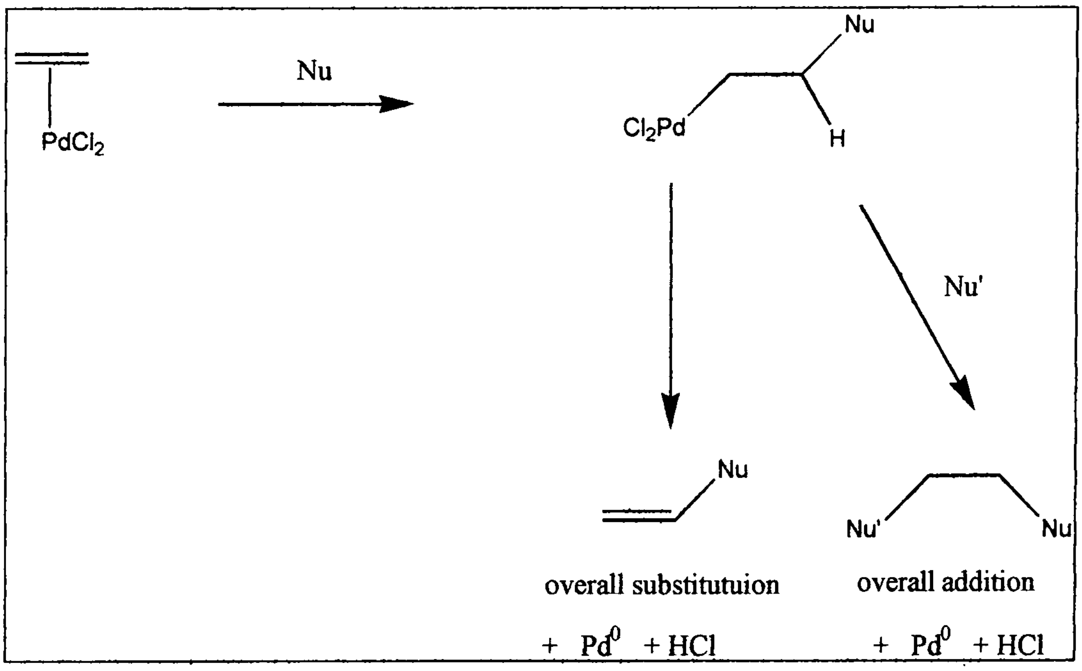


Figure 1.19

Originally, the Wacker process was simply the conversion of ethene into acetaldehyde. A summary of what occurs in the reaction is shown below. There has been much discussion about the intimate mechanism of the Wacker process. [73]

$$CH_2{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2\,HCl$$

$$Pd + 2\,CuCl_2 \longrightarrow PdCl_2 + 2\,CuCl$$

$$2\,CuCl + 2\,HCl + 1/2\,O_2 \longrightarrow 2\,CuCl_2 + H_2O$$

$$CH_2{=}CH_2 + 1/2\,O_2 \longrightarrow CH_3CHO$$

Palladation reactions are not limited to water based systems, however. Using amines, for example, it is possible to get amino palladation (see Figure 1.20) to get tertiary amines. [74]

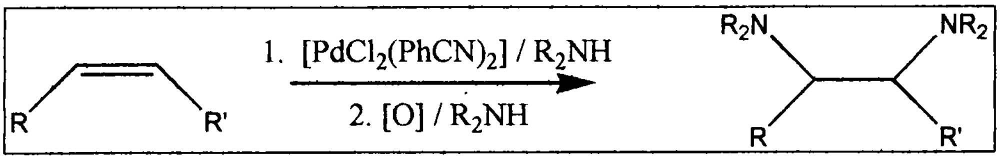


Figure 1.20

Esterification of olefins also comes into this category (i.e. olefin oxidation), but has been dealt with previously. Another carbonylation reaction that is relevant is bis-alkoxycarbonylation[75] such as is shown in Figure 1.21. This is a useful route to succinate derivatives.

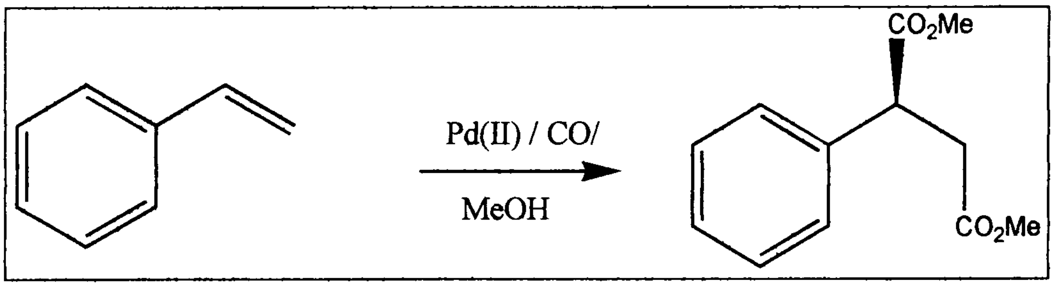


Figure 1.21

Heck reactions[67] are now widely used in organic synthesis. The Heck process is mainly used for functionalisation of olefins by means of an alkyl halide and a Pd(II) salt. The Pd(II) is reduced *in situ* to Pd(0).[76] There is then oxidative addition of an alkyl halide to the Pd(0) centre. The alkyl halide must be free of available β hydrogens or the only products observed are olefins as β elimination products. The triethylamine has two functions. Apart from the reduction mentioned above, it also 'mops up' the HX which is generated in the last step. The catalytic cycle[77] for the Heck reaction is shown in Figure 1.22. Because the last step is a *syn* elimination, the reaction goes with a high degree of stereochemical control. The reaction works most effectively with alkyl bromides and iodides. Chlorides do not seem to react very efficiently.

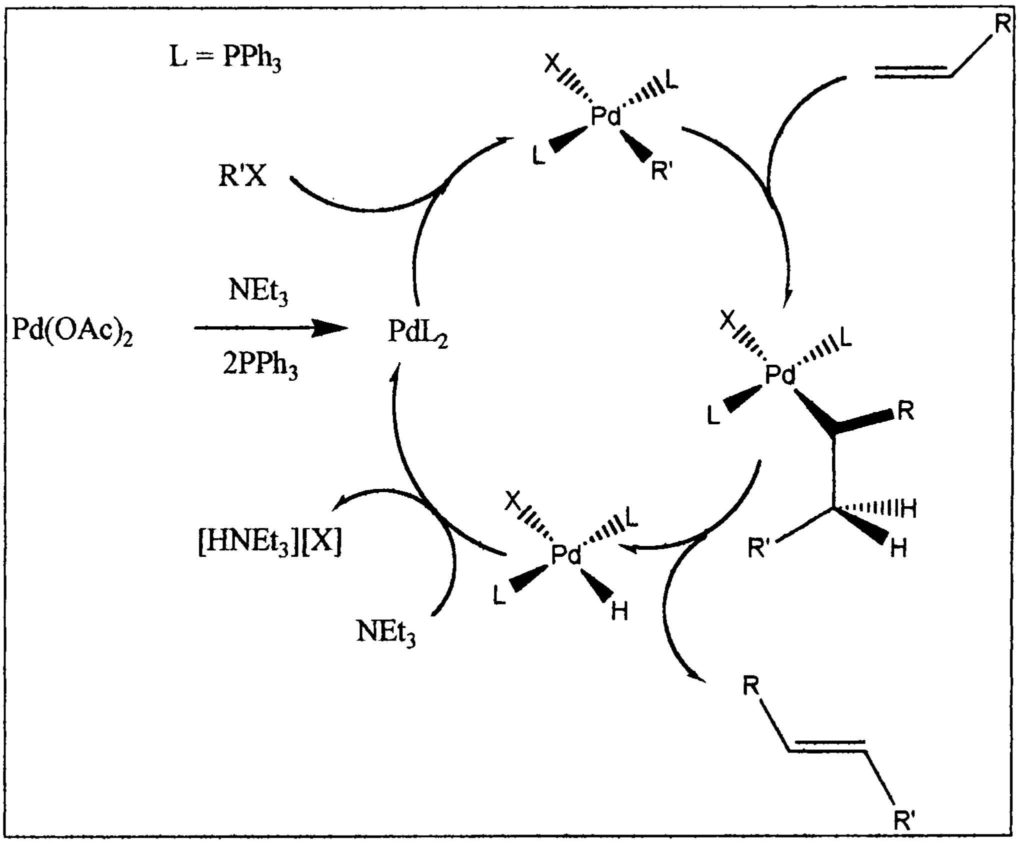


Figure 1.22

An increasingly wide application of palladium catalysis in organic synthesis is that of cyclisation. Much of this work has been carried out and reviewed by Trost and co-workers.[78] An example of this reaction is shown in Figure 1.23.

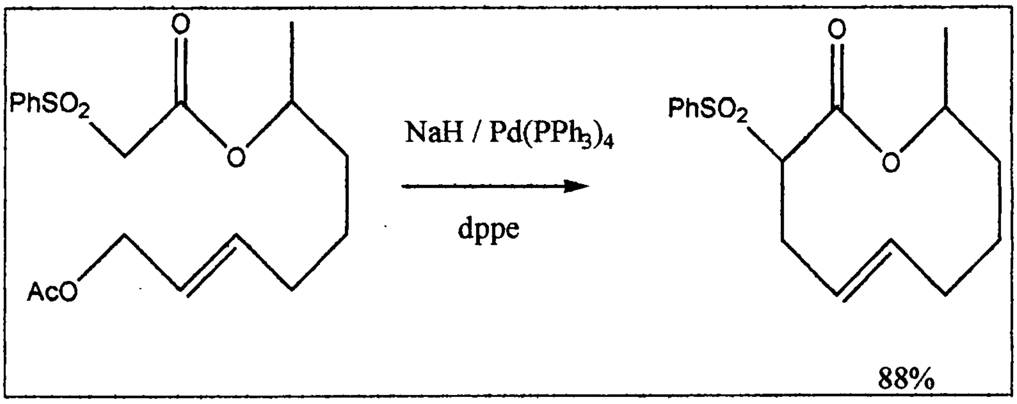


Figure 1.23

1.4.3.4 Polyketone synthesis and related reactions.

The last of the reactions that will be discussed here is that of polyketone synthesis. Polyketone is the alternating copolymer of ethene and CO. It is an attractive material because it has useful properties and the starting materials are readily available. The usefulness of the product comes from the potential that the functionalised backbone offers. The carbonyl functionality means that the polymer may be photo-degradeable, [79] making it more environmentally friendly. In addition, the carbonyl group has the potential to be functionalised (e.g. by reduction to polyalcohol),[80] and the reaction has now been modified to other alkenes (e.g. norbornene) with a measure of success. [81]

The basic reaction has been known for several years [82] but often the product yields were too low for industrial polyketone production. The turning point came in 1991 when Drent and co-workers published a paper [55] that gave the ethene/CO polyketone in high yield with almost perfect selectivity and at a good rate. There has been much investigation into the reaction mechanism and indeed, some of the work in this thesis is concerned with this reaction. A subsequent review [83] on the so-called Drent process has been published recently. The catalytic precursor is derived from palladium acetate with a chelating bidentate phosphine with a three carbon backbone. The suggested catalytic species is cationic, and this is a common feature in much, if not all, of the polyketone work published. As mentioned above, there has been much study of the mechanism of copolymerisation. In particular, the reasons that cause such good alternation to occur has been under scrutiny. Brookhart [84] and Sen [85] determined that the fundamental reason was a balance of thermodynamic and kinetic factors. The double insertion of CO is unfavourable both kinetically and thermodynamically, whereas the insertion of ethene into a Pd-CO bond is favoured. By a similar argument, it was discovered that the double insertion of ethene was kinetically unfavourable. Other work, carried out by Vrieze and co-workers [86] helped to verify that the mechanism proposed by Drent was probably correct, by producing stepwise insertion reactions.

A palladium methoxycarbonyl species is thought to be involved in the initiation step of the polymerisation, especially at higher temperatures.[83] It was an esterification system that Drent was working on when the discovery of the polyketone catalyst was made. For this reason, the polyketone reaction is of particular interest to this work.

There are many examples of palladium catalysis. The above examples are representative of the utility and flexibility of the metal in homogeneous catalysis.

1.4.3.5 Co-ordinating modes of Phosphines.

Monodentate phosphines co-ordinate simply to the metal except when, on occasion, cyclometallation is observed. This phenomenon can also occur with bidentate ligands.[87] Bidentate ligands can bind in several manners.

In the case of ligands such as ($Ph_2P(CH_2)_nPPh_2$), with short backbones such as dppe (with n=2) the mode of attachment tends to be *cis*-chelating (Figure 1.24a) rather than bridging. The first member of the series, dppm (with n=1), however, is the exception to this rule. Dppm will behave readily as a bridging ligand between two metals (see Figure 1.24b).[88] Bidentate phosphines of longer backbone length (usually with n > 6) can sometimes chelate to a metal centre in a *trans* configuration (see Figure 1.25).[89]

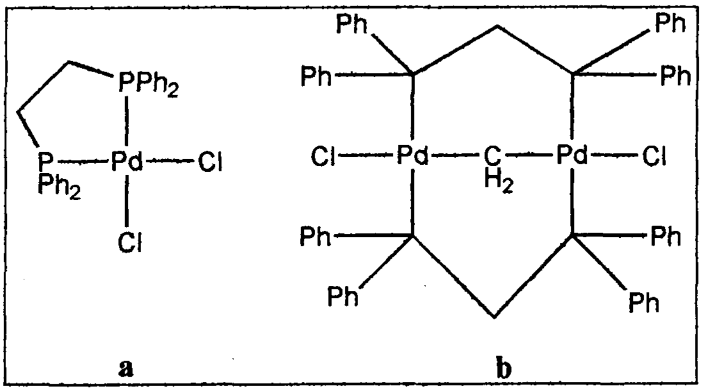


Figure 1.24

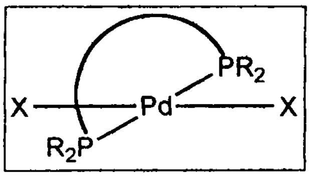


Figure 1.25

1.4.4 Synthesis of Palladium Phosphine Complexes.

The monodentate phosphine dichloride complexes can be made by the addition of the phosphine to $PdCl_2$ or to the pre-prepared benzonitrile complex $[PdCl_2(PhCN)_2]$. In each case, the resulting product is a complex of the form $[PdCl_2(PR_3)_2]$. There are many examples of this type of reaction. [90] The same results can be achieved from the $[MCl_4]^{2-}$ salt with the addition of phosphine to give the $[M(PR_3)_2Cl_2]$ and two moles of chloride salt.

Palladium complexes bridged by metal halides can also be prepared. $PdCl_2$ is boiled in ethanol or chloroform with the tetrachloropalladate salt. [91] This produces the species $[Pd(Cl)_2(PR_3)]_2$, which takes on the form shown in Figure 1.26.

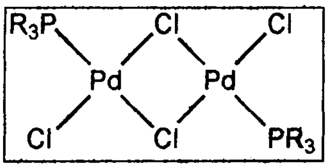


Figure 1.26

Synthesis of the bidentate phosphine dichloride complexes can be achieved in the manner described above, simply by the addition of the diphosphine to the metal chloride or to the benzonitrile complex $[PdCl_2(PhCN)_2]$. It can also be made from monodentate phosphine complexes, where the incoming diphosphine displaces two outgoing monodentate ligands.

As mentioned before, the synthesis of Pd(0) species can be readily achieved by reduction of $PdCl_2$ in the presence of the desired phosphine.

Another route to palladium phosphine complexes is to add phosphines to the dimeric Pd(0) complex $[Pd_2(dba)_3.CHCl_3]$. The added phosphines displace the dba ligands to give Pd(0) phosphine complexes. This dba complex is a convenient starting material for several reactions, and is also catalytically active for certain reactions.[92] We return to this in Chapter 2.

Cationic palladium species such as $[Pd(R)(Solv.)(L)_2]^+$ can be prepared from the palladium halide complex and a silver (or thallium) salt of a non-coordinating anion. One common method uses $AgBF_4$ in a coordinating solvent such as acetone, acetonitrile or methanol. These cationic species are more prone to nucleophilic attack due to the presence of the charge on the metal species. The charged species can also undergo more rapid carbonyl insertion reactions than the corresponding neutral complex.[93] In the light of this improved behaviour, it is not surprising that they have been studied and used as catalysts for several systems.[94]

Some syntheses of simple palladium complexes may be found in Hartley's book.[95]

1.5 Organometallic Chemistry of Palladium.

1.5.1 σ - Bonded Organometallic Complexes of Palladium

Although $Ni(CO)_4$ is known, no monoleptic equivalents exist for palladium or platinum. Even the nickel complex readily decomposes to give CO. The reason for this may be the reduced ability of later transition metals to act as π bases to the CO anti-bonding orbitals, due to the lower energy of the d orbitals towards the end of the transition series.[96] In addition, the promotion energy (i.e. the energy needed to excite a species by promotion of an electron) of nickel(0) is smaller than that of platinum(0) or palladium(0). The value for Ni(0) is approximately 1.7eV compared to about 4eV for Pd and 3eV for platinum. This is thought to imply a greater ability of nickel to promote electrons to the CO anti-bonding orbital.[97] Despite the lack of monoleptic palladium carbonyls, there are some known zero valent palladium carbonyl phosphines; for instance, $[Pd(PPh_3)_3CO]$.[98]

Alkyl complexes of palladium can be prepared from Grignards, organolithium and organomercury agents. An example is shown in Figure 1.27.

$$[PdCl_2(PR_3)_2] + 2(BrMgMe) \xrightarrow[\text{Ether}]{} [Pd(Me)_2(PR_3)_2] + 2\,MgBrCl$$

Grignard Reaction

Figure 1.27

Alternatively, oxidative addition to the Pd(0) species as outlined in section 1.4.2.2 is an effective method for the production of palladium acyl, methoxycarbonyl and alkyl complexes with groups which cannot β-hydrogen eliminate.

Complexes of the form $[Pd(R)_2L_2]$ can undergo reductive elimination leading to decomposition of the complex to give Pd(0) and R-R. It is partly this ability which makes Pd such an attractive metal for catalysis.

1.5.2 π - Bonded Organometallic Complexes of Palladium.

The first palladium olefin complexes were prepared in 1938.[99] These complexes were unstable and decomposed rapidly. The longest lived of these were $[PdCl_2(olefin)]$ complexes with olefin = cyclohexene and styrene. These could be stored in a desiccator at room temperature, and only decomposed slowly. Olefin complexes of Pd(0) species have been studied more recently. Such complexes have been prepared from $[Pd(PPh_3)_4]$ by the addition of an olefin in THF or benzene.[100]

Acetylene complexes of palladium have also been prepared, again by the substitution of PR_3 by the unsaturated species. This is particularly effective when the acetylene is substituted with electron withdrawing groups like CO_2Me or CF_3.[101]

1.5.2.1 Bonding in olefin π- complexes.

The bonding in metal olefin complexes shows some similarity to that exhibited by metal carbonyl bonding. There is a donation of electron density from the π bond of the olefin and a synergic back donation by the metal into the π^* anti-bonding orbital, following the Dewar-Chatt-Duncanson model (see Figure 1.28).[102]

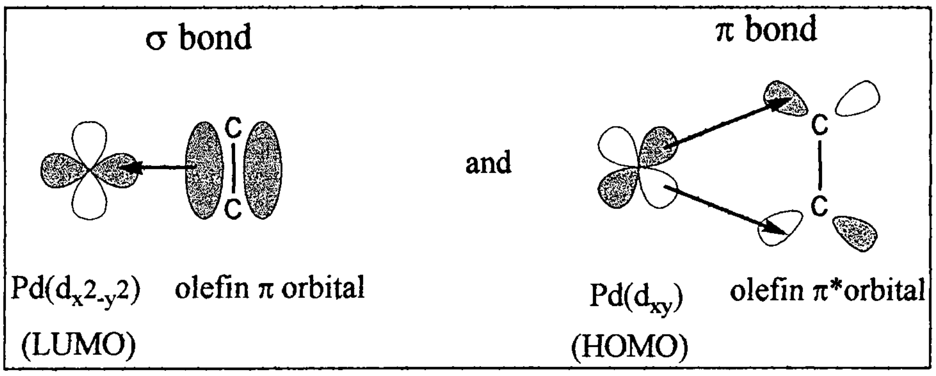


Figure 1.28

1.5.2.2 Reactions of olefin complexes.[103]

There are several reaction types that the olefin complexes can undergo. The olefin is a ligand with a high *trans* effect and thus the ligand *trans* to the olefin is often labilised and thus undergoes more facile substitution. Alternatively, the olefin can be replaced by another ligand, such as a tertiary phosphine, ammonia or even another olefin or acetylene. The exchange of unsaturated ligands is driven by the relative volatility of the unsaturated species.

Complexes of coordinated olefins can undergo nucleophilic attack, at either the metal centre or at the olefin. When attack at the olefin occurs, it is normally on the side of the olefin opposite to the metal (so called *exo* attack). Examples of this type of reaction have been discussed in section 1.4.2.4.

1.5.3 Palladium allyl complexes

Allyl complexes of palladium are quite an important class of intermediates in organic reactions.[104]

π-allyls can be made readily by the addition of allylic halides to Pd(0). These allylic palladium complexes can then be further reacted to give an organic moiety, *e.g.* see Figure 1.29 below.

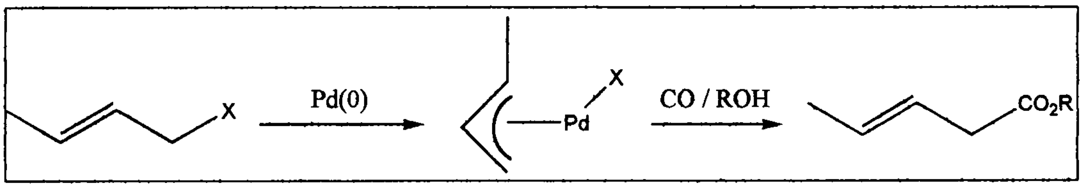


Figure 1.29

Allyls can be made in several ways,[105] one of the other better known being the addition of 1,3 dienes to Pd(II) as in Figure 1.30.

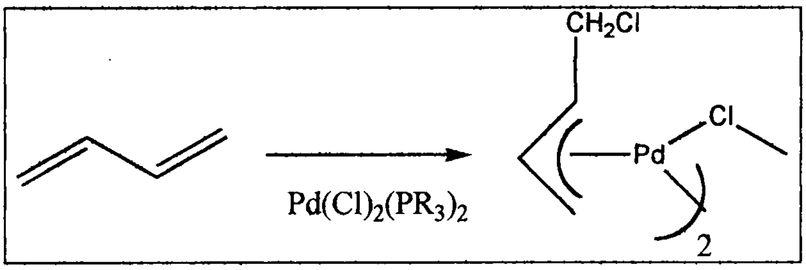


Figure 1.30

In summary, palladium chemistry is a vast and burgeoning field. It would be impracticable to attempt a more in-depth coverage than has been carried out here. There are several excellent references[3,53,56,59,77,87,90] from which much of the above material has been gleaned and these should be consulted for a more in-depth review of the subjects.

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Chapter 2

Synthesis of Starting Materials

Thinking is easy, acting is difficult, and to put one's thoughts into action is the most difficult thing in the world.

Goethe (1749 - 1832)

2.1 Introduction and aims

In this chapter, the attempted and successful synthetic approaches to the preparation of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (**1**) are described. It was already known that the oxidative addition of methylchloroformate ($ClCO_2Me$) to $[Pd(PPh_3)_4]$ (**2**) gave the chloromethoxycarbonyl adduct (see Figure 2.1).[1]

$$\boxed{[Pd(PPh_3)_4]\ (\mathbf{2}) \xrightarrow[ClCO_2Me]{} [Pd(Cl)(CO_2Me)(PPh_3)_2]\ (\mathbf{1})}$$

Figure 2.1

Although the reaction was documented, few experimental details were published with it. This route was initially unsatisfactory for two main reasons; the original reaction was carried out in benzene, which is a toxic solvent, and the starting complex $[Pd(PPh_3)_4]$ is air and light sensitive. We wanted to make the process safer to use and to have it produce high yields of the target complex (**1**).

In addition, it was found that there was a dearth of oxidative addition reactions of methylchloroformate to Pd(0) in the literature. Some examples, which occur in literature and are discussed later in this chapter, have been outlined in Chapter 1.

Most examples of methoxycarbonyl species recorded were synthesised using nucleophilic attack of MeOH on an intermediate metal carbonyl complex in the presence of base (see Figure 2.2).[2]

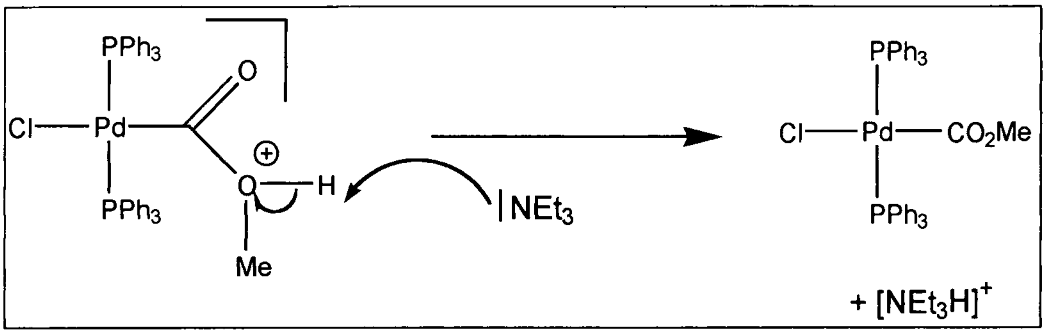


Figure 2.2

The main aim of the work in this chapter was to create a simple, reliable route to the $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ compound so that we could explore the reactivity of this species, as well as study any catalytic properties that it may have.

2.2 Experimental Section

Unless otherwise stated, all experimental work was carried out in a dry, inert atmosphere (N_2) using standard glove box, vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen. $Pd_2(dba)_3{\cdot}CHCl_3$ was kindly donated by ICI, as were some of the more unusual phosphines (dtbpp, dcpe); these were used as supplied without further purification. Other chemicals were synthesised as described or bought from one of Aldrich, Acros or Lancaster. Further details can be found in Appendix 5 - Experimental Parameters.

Experiment 2.2.1

Reaction of $[Pd_2(dba)_3{\cdot}CHCl_3]$ with PPh_3 and $ClCO_2Me$

$[Pd_2(dba)_3.CHCl_3]$ (0.18g, 0.18 mmol) and PPh_3 (0.26 g, 0.99 mmol) were placed in a clean, dry, nitrogen filled, 2-necked, round bottomed flask and then dissolved in dry, degassed and distilled toluene (50 ml). The resulting orange / brown solution was stirred overnight at room temperature. At this point, methylchloroformate (0.039g, 20 µl, 0.40 mmol) was added *via* a syringe to the [Pd(dba)(PPh$_3$)$_2$] formed *in situ*. After 1 hour of stirring, the solution had developed a yellow / gold colouration. The solvent was removed under reduced pressure before drying the residue *in vacuo*. The yellow residue was washed with ether (2 x 10ml) and hexane (2 x 10ml). Analysis showed that the solid was [PdCl$_2$(PPh$_3$)$_2$] (yield 0.07g, 28%). Found C, 61.31; H, 4.39%. $C_{36}H_{30}Cl_2P_2Pd$ requires C, 61.60; H, 4.31%. $^{31}P\{^1H\}$NMR (toluene) $\delta = 23.5$ (s) ppm. ^1H NMR (CDCl$_3$) $\delta =$ 7.3 - 7.7 (**30H**, m, Ph). IR (nujol /KBr) $\nu_{P\text{-}C} = 1465$ cm^{-1}; $\nu_{Pd\text{-}Cl} =$ 338 cm^{-1}.

Experiment 2.2.2

Reaction of [Pd$_2$(dba)$_3$·CHCl$_3$] with dppe and ClCO$_2$Me

[Pd$_2$(dba)$_3$.CHCl$_3$] (0.10g, 0.11 mmol) and dppe (0.08g, 0.20 mmol) were placed in a 2-necked round bottomed flask which had been pre-flushed with nitrogen. The starting materials were then dissolved in dry, degassed toluene (50 ml). The solution was stirred for two hours, until an orange colouration appeared, before one equivalent of methyl chloroformate (ClCO$_2$Me, 0.02g, 21 µl, 0.23 mmol) was added slowly to the solution *via* a syringe. The solution turned yellow and was stirred briefly before solvent was removed under reduced pressure. The resulting off-white solid was washed with ether (2 x 10 ml) and hexane (2 x 10 ml) before drying *in vacuo*. The resulting white solid was analysed as [PdCl$_2$(dppe)]. Found C, 54.10; H, 4.05%. $C_{26}H_{24}Cl_2P_2Pd$ requires C, 54.24; H, 4.20%. $^{31}P\{^1H\}$ NMR (CDCl$_3$) $\delta = 59.0$ ppm. ^1H NMR (CDCl$_3$) δ= 7.2-7.7 (**20H**, m, Ph), $\delta = 2.1$ (**4H**, m, PCH_2CH_2P). IR $\nu_{P\text{-}C} = 1456$ cm^{-1}; $\nu_{Pd\text{-}Cl} = 325$ cm^{-1}.

Recrystallisation from $CDCl_3$ produced a crystal suitable for X-ray analysis. This crystal was analysed by Dr. A.S. Batsanov as $[Pd(Cl)_2(dppe)\cdot(CDCl_3)_3]$ (**3**). Selected bond lengths and angles follow in Tables 2.1 and 2.2 respectively. Supplementary data can be found in Appendix 1. The crystal structure is shown in Figure 2.3

Table 2.1 Selected Bond Lengths for $[PdCl_2(dppe)\cdot(CDCl_3)_3]$ (3)

Bond	Length/Å (error)	Bond	Length/Å (error)
Pd(A)-P(2A)	2.238(3)	Pd(A)-P(1A)	2.256(3)
Pd(A)-Cl(2A)	2.360(3)	Pd(A)-Cl(1A)	2.365(3)
P(1A)-C(11A)	1.807(11)	P(1A)-C(21A)	1.813(10)
P(1A)-C(1A)	1.835(10)	P(2A)-C(31A)	1.794(11)
P(2A)-C(41A)	1.814(9)	P(2A)-C(2A)	1.818(10)
C(1A)-C(2A)	1.522(13)	C(11A)-C(16A)	1.397(14)
C(11A)-C(12A)	1.41(2)	C(12A)-C(13A)	1.38(2)
C(13A)-C(14A)	1.41(2)	C(14A)-C(15A)	1.37(2)
C(15A)-C(16A)	1.397(14)	C(21A)-C(22A)	1.389(14)
C(21A)-C(26A)	1.409(14)	C(22A)-C(23A)	1.40(2)
C(23A)-C(24A)	1.37(2)	C(24A)-C(25A)	1.41(2)
C(25A)-C(26A)	1.39(2)	C(31A)-C(32A)	1.41(2)
C(31A)-C(36A)	1.41(2)	C(32A)-C(33A)	1.39(2)
C(33A)-C(34A)	1.37(2)	C(34A)-C(35A)	1.37(2)
C(35A)-C(36A)	1.38(2)	C(41A)-C(42A)	1.38(2)
C(41A)-C(46A)	1.39(2)	C(42A)-C(43A)	1.39(2)
C(43A)-C(44A)	1.37(2)	C(44A)-C(45A)	1.38(2)
C(45A)-C(46A)	1.38(2)		

Table 2.2 Selected Bond Angles for [PdCl$_2$(dppe)·(CDCl$_3$)$_3$] (3)

Atoms	Angle/°	Atoms	Angle/°
P(2A)-Pd-P(1A)	85.60(10)	P(2A)-Pd-Cl(2A)	176.3(1)
P(1A)-Pd-Cl(2A)	99.99(10)	P(2A)-Pd-Cl(1A)	89.7(1)
P(1A)-Pd-Cl(1A)	175.20(11)	Cl(2A)-Pd-Cl(1A)	91.8(1)
C(11A)-P(1A)-C(21A)	104.8(5)	C(11A)-P(1A)-C(1A)	106.3(5)
C(21A)-P(1A)-C(1A)	106.8(5)	C(11A)-P(1A)-Pd(A)	121.1(4)
C(21A)-P(1A)- Pd(A)	110.3(3)	C(1A)-P(1A)-Pd(A)	106.7(3)
C(31A)-P(2A)-C(41A)	108.9(5)	C(31A)-P(2A)-C(2A)	105.0(5)
C(41A)-P(2A)-C(2A)	104.4(4)	C(31A)-P(2A)-Pd(A)	113.2(4)
C(41A)-P(2A)-Pd(A)	116.3(4)	C(2A)-P(2A)-Pd(A)	108.1(4)
C(2A)-C(1A)-P(1A)	107.0(7)	C(1A)-C(2A)-P(2A)	108.0(6)
C(16A)-C(11A)-C(12A)	119.6(10)	C(16A)-C(11A)-P(1A)	120.8(8)
C(12A)-C(11A)-P(1A)	119.4(8)	C(13A)-C(12A)-C(11A)	119.3(11)
C(12A)-C(13A)-C(14A)	120.6(12)	C(15A)-C(14A)-C(13A)	120.1(10)
C(14A)-C(15A)-C(16A)	119.9(11)	C(11A)-C(16A)-C(15A)	120.4(11)
C(22A)-C(21A)-C(26A)	119.6(10)	C(22A)-C(21A)-P(1A)	121.2(8)
C(26A)-C(21A)-P(1A)	119.2(8)	C(21A)-C(22A)-C(23A)	119.2(11)

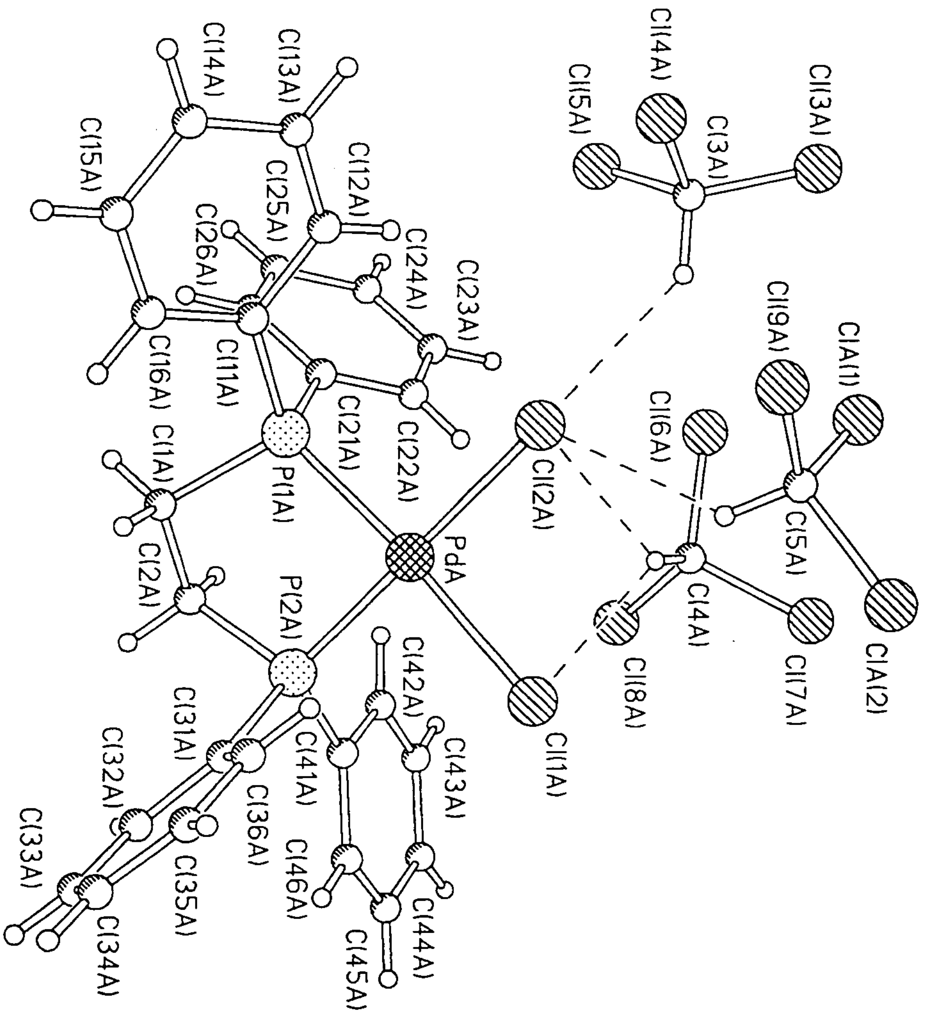
C(24A)-C(23A)-C(22A)	121.5(11)	C(23A)-C(24A)-C(25A)	119.6(11)
C(26A)-C(25A)-C(24A)	119.4(10)	C(25)-C(26A)-C(21A)	120.6(10)
C(32A)-C(31A)-C(36A)	116.9(10)	C(32A)-C(31A)-P(2A)	121.6(9)
C(34A)-C(33A)-C(32A)	121.2(12)	C(35A)-C(34A)-C(33A)	119.5(12)
C(34A)-C(35A)-C(36A)	120.6(12)	C(35A)-C(36A)-C(31A)	121.4(11)
C(42A)-C(41A)-C(46A)	118.9(9)	C(42A)-C(41A)-P(2A)	117.9(8)
C(46A)-C(41A)-P(2A)	123.1(8)	C(41A)-C(42A)-C(43A)	121.3(12)
C(44A)-C(43A)-C(42A)	119.3(12)	C(45A)-C(44A)-C(43A)	119.4(11)
C(44A)-C(45A)-C(46A)	122.0(12)	C(45A)-C(46A)-C(41A)	119.0(11)

Experiment 2.2.3

Reaction of [$Pd_2(dba)_3 \cdot CHCl_3$] with dcpe and $ClCO_2Me$.

[$Pd_2(dba)_3.CHCl_3$] (0.15 g, 0.16 mmol) and dcpe (0.14 g, 0.32 mmol) were placed in a clean, dry, nitrogen filled, 2-necked, round bottomed, 100 ml flask before being dissolved in dry, degassed toluene (40 ml). The orange solution was stirred for three hours before one equivalent of methylchloroformate ($ClCO_2Me$, 0.03g, 30 µl, 0.32 mmol) was added slowly (*via* a syringe against a counter flow of N_2). The

Figure 2.3 Crystal structure of [$PdCl_2$(dppe)]·($CDCl_3$)$_3$



orange solution was observed to turn yellow almost immediately, and was stirred for another thirty minutes before a small quantity of precipitate was observed. The solvent was removed under reduced pressure. The remaining white solid was washed with ether (2 x 10 ml) and hexane (2 x 10 ml) before drying *in vacuo* and weighing. The white solid was found to be [PdCl$_2$(dcpe)] (yield 0.05g, 26 %). Found C, 51.71; H, 8.23%. $C_{26}H_{48}Cl_2P_2Pd$ requires C, 52.05; H, 8.06 %. $^{31}P\{^{1}H\}$NMR (dimethylformamide) $\delta = 95.1$ ppm (s). ^{1}H NMR (CDCl$_3$) 1.2 - 2.0 ppm (**48H**, m, Cy & PCH$_2$CH$_2$P). IR $\nu_{P\text{-}C} = 1463$ cm^{-1}; $\nu_{Pd\text{-}Cl} = 330$ cm^{-1}.

Experiment 2.2.4

Reaction of [Pd$_2$(dba)$_3$·CHCl$_3$] with dtbpp and ClCO$_2$Me.

To a clean, dry, 2-necked, round bottomed, 100 ml flask were added [Pd$_2$(dba)$_3$.CHCl$_3$] (0.20 g, 0.21 mmol) and dtbpp (0.20g, 0.44 mmol). To the flask was then added dry, degassed toluene (50 ml) before stirring for three hours at room temperature. To the stirred, orange solution was added methylchloroformate (0.045g, 43 µl, 0.43 mmol) *via* a syringe. The resulting yellow solution was stirred for a further thirty minutes at room temperature before the solvent was removed under reduced pressure. The yellow solid was washed with ether and hexane (2 x 10 ml portions each) before drying *in vacuo*. The solid was found to be [PdCl$_2$(dtbpp)] (yield 0.06g, 28%). Found C, 44.72; H, 8.22%. $C_{19}H_{42}Cl_2P_2Pd$ requires C, 44.76; H, 8.30%. $^{31}P\{^{1}H\}$NMR (CH$_2$Cl$_2$) $\delta = 38.2$ ppm (s) ^{1}H NMR (CDCl$_3$) $\delta = 1.3 - 2.2$ ppm (**42H**, m, ^{t}Bu &(PCH$_2$CH$_2$CH$_2$P)).

Experiment 2.2.5

Synthesis of $[Pd(PPh_3)_4]$ [3]

A mixture of $PdCl_2$ (6.0g, 0.034 mol), triphenylphosphine (32.75g, 0.17 mol) and dimethylsulphoxide (400 ml) was placed in a 1 litre, 2 necked flask equipped with a magnetic stirrer bar. A rubber septum and vacuum / nitrogen system were connected to the outlets. The whole system was placed under nitrogen with provision for release of excess pressure. The yellow mixture was heated in an oil bath, with stirring, until complete dissolution occurred (~140 °C). The bath was then taken away and the solution was stirred rapidly for a further fifteen minutes. Hydrazine monohydrate (6.7 g, 013 mol) was then added slowly over about a minute *via* a syringe. A vigorous reaction, resulting in the release of N_2, ensued. The flask containing the dark solution was immediately cooled in a water bath until crystallisation of the yellow product commenced. At this point, the water bath was removed and the solution was allowed to cool naturally. Upon reaching room temperature, the mixture was filtered under N_2 through a sinter before the canary yellow solid was washed with 2 portions of ethanol (35 ml each) and 2 portions of ether (35 ml each). The product was dried by passing N_2 through the sinter, overnight, before drying *in vacuo* (yield 26.8 g, 86 %). Found C, 74.34; H, 5.10%. $C_{72}H_{60}P_4Pd$ requires C, 74.83; H, 5.23%. ^1H NMR (CD_3CN) δ =7.2 - 7.7 ppm (**60H**, m, Ph). IR $\nu_{P\text{-}C}$ = 1460 cm^{-1}.

Experiment 2.2.6

Synthesis of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (2) [1]

$[Pd(PPh_3)_4]$ (5g, 4.3 mmol) was placed in a 100ml, 2-necked, round bottomed flask before being dissolved in dry, degassed toluene (100ml) with heating to 80°C in an oil bath. Once all the tetrakis(triphenylphosphine)palladium(0) had dissolved, to give a clear solution, methylchloroformate (0.41g, 0.35 ml, 4.3 mmol) was added slowly to the stirring solution at 80 °C. After several minutes a white precipitate had formed and stirring was continued, for a total of five hours, at the same temperature. At the end of this time, the cream coloured, air stable solid formed was separated by filtration using a glass sinter and washed with several aliquots of diethyl ether (3 x 10 ml) before drying *in vacuo* (yield 1.91g, 70%). Found C, 62.67; H, 4.68, Cl, 5.32%. $C_{38}H_{33}ClO_2P_2Pd$ requires C, 62.91; H, 4.58; Cl, 4.89%. $^{31}P\{^1H\}$NMR (dimethylformamide) $\delta = 19.3$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 2.3$ ppm (**3H**, s, OCH_3), 7.2-7.7 ppm (**30H**, m, Ph). IR ν_{CO}(max) = 1671 cm^{-1}, 1654 cm^{-1}.

Experiment 2.2.7

Synthesis of [$PdCl_2$(dcpe)]

[$PdCl_2(PhCN)_2$] (0.1g, 0.26 mmol) was placed in a clean, dry, 2-necked, nitrogen filled flask before the addition of THF (20 ml, dry, degassed) and stirring at room temperature until dissolution was complete. To the stirring solution was added an equivalent of dcpe (0.11g, 0.27mmol). The reaction was stirred for a further hour before a sample was removed for $^{31}P\{^1H\}$ NMR analysis. The signal obtained matched that which was found in Experiment 2.3 for [$PdCl_2$(dcpe)]. $^{31}P\ \{^1H\}$, $\delta =$ 94.7 ppm (s), further confirming the identity of the species.

2.3 Discussion

The choice of [$Pd_2(dba)_3 \cdot CHCl_3$] (**4**) as starting material for the synthesis of the chloroformate adduct (**1**) was made for several reasons. The [$Pd_2(dba)_3 \cdot (CHCl_3)$] species is air stable and easy to handle. This is in contrast with [$Pd(PPh_3)_4$] which is air and light sensitive. $Pd_2(dba)_3$ is a useful catalytic precursor in its own right, and has found several applications. These include the coupling of aryl systems, [4] hydroesterification of alkynes [5] and conversion of alcohols to esters. [6] The isolation of the methylchloroformate adduct (**1**) from the oxidative addition to the dibenzylideneacetone phosphine precursor (**4**), however, was found to be more difficult than first thought. Frequently, the reactions would give a mixture of products, such as the palladium dichloride phosphine complex, free dba and the starting material, which proved very hard to separate. In addition, the dba phosphine complexes were found, as noted by Herrmann and co-workers, [9(b)] to be fluxional, making the *in situ* species difficult and time consuming to identify.

Dibenzylideneacetone complexes of palladium have been known for some years and their chemistry has been studied. [7] [$Pd_2dba_3 \cdot CHCl_3$] is a dimeric palladium species with three bridging dba ligands, as shown in Figure 2.4. Synthesis of the palladium dba complexes may be achieved by adding sodium acetate to a solution of palladium chloride followed by addition of dibenzylideneacetone. The product, [$Pd(dba)_2$], is then recrystallised from chloroform to give the solvated dimer (**4**). [8] [$Pd(dba)_2$] was used as an alternative source of Pd(0) in the reactions 2.2.1 and 2.2.2, the same reactions being observed.

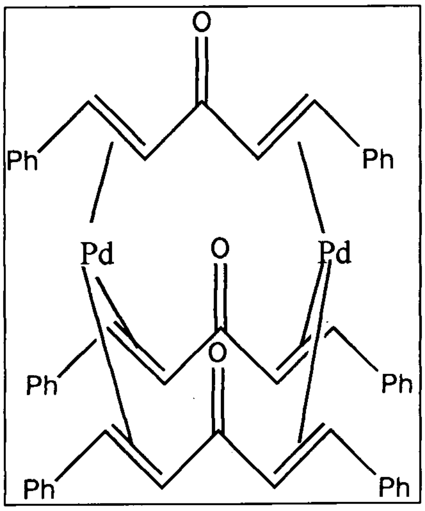


Figure 2.4

One of the project aims was to reduce the need for air sensitive starting materials. The dibenzylideneacetone (dba) complex is a useful starting material since it is a rare example of an air stable Pd(0) complex. Other Pd(0) species (those based on phosphine ligands) tend to decompose in air. Our proposed synthetic route was as outlined in Figure 2.5.

$$[Pd_2(dba)_3] \xrightarrow[4\ PR_3]{} 2\,[Pd(PR_3)_2(dba)] \xrightarrow[2\ ClCO_2Me]{} 2[Pd(Cl)(CO_2Me)(PR_3)_2]$$

Figure 2.5

The first step (i.e. the addition of the phosphine ligands) had already been established by Herrmann and co-workers.[9(b)] A variety of phosphine ligands have been employed to give species of the type $[Pd(PR_3)_2(dba)]$ or [Pd(diphos)(dba)] where diphos is a chelating phosphine.[9] Our intention was to produce a relatively easy route to a wide variety of methylchloroformate adducts.

Work carried out by Jutand and co-workers [10] was concerned with the problem of oxidative addition to *in situ* mixtures of $[Pd(dba)(L)_2]$ complexes. Their conclusions were that it was not possible to get a clean, oxidative addition product in such a situation and that, effectively, the addition of excess phosphine to produce the $[Pd(PR_3)_4]$ species was required. The findings of the present work bear this out. In addition to these problems, identification of the products was made difficult by the large number of stretches in the 1550 cm^{-1} - 1670 cm^{-1} region of the IR spectrum (see Table 2.3).

Table 2.3 Comparison of IR stretches for starting materials and products

IR spectra in nujol / KBr matrix	IR Stretches (in cm^{-1})
dibenzylideneacetone [3]	1657, 1651, 1627, 1591
$[Pd_2(dba)_3\cdot(CHCl_3)]$ [3]	1620, 1615, 1591, 1550
$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ [2]	1672,1654

In each case where the oxidative addition was carried out, the only isolated product was the palladium dichloride adduct of the phosphine being used. The reason for this may lie in the olefinic nature of the dibenzylideneacetone ligand. The insertion into ester metal bonds is known, [11] and it is possible that the palladium methoxycarbonyl species has formed, only to then undergo insertion and then decomposition to the observed palladium metal, as well as the dichloride which was found. There was some tenuous evidence for this in that the IR spectrum showed what may have been an ester stretch at 1744 cm^{-1} in a sample obtained from Experiment 2.2.2.

One of the practical difficulties associated with this oxidative addition route was that the addition of even a slight excess of the methylchloroformate seemed to hasten the formation of the dichloride complex of palladium. The desired product (i.e. $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (**1**)), once isolated, was found to be unstable with respect to the palladium dichloride complex. This phenomenon was always observed if the chloroformate adduct (**1**) was left in solution for more than a few minutes, particularly in the presence of a chloride source. This is also discussed in later chapters.

The crystal structure of $[Pd(Cl)_2(dppe)(CDCl_3)_3]$ (**3**) was obtained from crystals grown in an NMR sample of the products of Experiment 2.2.2. This structure is shown in Figure 2.3. The structure is of interest because it shows an example of deuterium bridging between the chlorine atoms of the palladium complex. There have been two previously published structures of dppe palladium dichloride. The first structure was recrystallised from dichloromethane. [12] The other structure crystallised without any solvent retained in the crystal. [13] Some selected bond lengths and angles are now compared (Table 2.4). Figure 2.6 is a general schematic for all the palladium dichloride dppe complexes shown in Table 2.4.

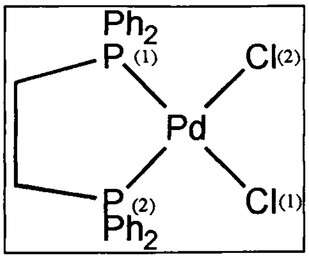


Figure 2.6

Table 2.4 Comparison of crystal data for [$PdCl_2$(dppe)] complexes

	(3)	(4)	(5)
Pd-Cl(1)	2.365(3) Å	2.361(2) Å	2.415(3) Å
Pd-Cl(2)	2.360(3) Å	2.357(2) Å	2.394(3) Å
Pd-P(1)	2.256(3) Å	2.233(2) Å	2.284(3) Å
Pd-P(2)	2.238(3) Å	2.226(2) Å	2.264(3) Å
P(1)-Pd-Cl(1)	175.20(11)	175.14(7) °	172.4(1) °
P(2)-Pd-Cl(1)	89.7(1) °	89.73(7) °	88.5(1) °
P(1)-Pd-Cl(2)	92.99(10) °	90.33(7) °	87.6(1) °
P(2)-Pd-Cl(2)	176.3(1) °	175.48(7) °	175.5(1)°
P(1)-Pd-P(2)	85.60(10) °	85.82(7) °	88.3(1) °
Cl(1)-Pd-Cl(2)	91.8(1) °	94.19(7)°	95.8((1) °

Key to Table 2.4: (3) [$PdCl_2$(dppe)$\cdot$($CDCl_3$)$_3$][14] (4) [$PdCl_2$(dppe)$\cdot$$CH_2Cl_2$][12] (5)[$PdCl_2$(dppe)][13]

As can be seen from Table 2.4, the Cl-Pd-Cl bond angle in the new structure is about three degrees smaller than the other two structures (approximately 92° *vs.* 95°). This is attributed to Cl---D---Cl interaction in the crystal lattice (see Figure 2.3). The data of the new structure bear a stronger resemblance to the Steffen and Palenik structure (**4**) than to the one published by Singh and co-workers (**5**). This is perhaps not very surprising as the former structure (**4**) was found to have crystallised with dichloromethane, whereas Singh's structure (**5**) was solvent free. Comparison with other known Pd-Cl lengths of *cis*-phosphine palladium dichloride complexes shows that the Pd-Cl length of the new structure is fairly typical.[7] The structure (**5**), however, has slightly longer than average Pd-Cl bonds. The NMR and analytical data are summarised in Table 2.5.

Table 2.5 Data for compounds of the type $[PdCl_2(L)_2]$ {or $[PdCl_2(L_2)]$}

Ligand (Compound)	^{31}P (ppm)	^{1}H (ppm)	CHN actual (calc)
PPh_3 (**6**)	δ = 23.5 (s)	δ = 7.3-7.7(m)	C: 61.31(61.36)% H: 4.39(4.27)%
$PPh_2(CH_2)_2PPh_2$ (**7**)	δ = 59.0 (s)	δ = 7.2-7.7(m) δ = 1.9 (s, br)	C: 54.10(54.22)% H: 4.05(4.17)%
$^tBu_2P(CH_2)_3P^tBu_2$ (**8**)	δ = 38.2 (s)	δ = 1.6-1.8(m) δ = 2.3(m)	C: 44.72(44.76)% H: 8.22(8.24)%
$Cy_2P(CH_2)_2PCy_2$ (**9**)	δ = 95.1 (s)	δ = 1.2-2.0(m)	C: 51.71(52.10)% H: 8.23(8.10)%
PCy_3 (**10**)	δ = 48.5 (s)	δ = 1.2-2.0(m)	C: 51.31(52.05)% H: 8.19 (8.06)%

More success with the synthesis of the chloroformate adduct (**1**) was achieved when the oxidative addition literature route was adapted by using toluene instead of benzene. The literature preparation, by oxidative addition of $ClCO_2Me$ to $[Pd(PPh_3)_4]$, went smoothly at 80°C giving (**1**) in a 70 % yield. It was found that small impurities in either the $[Pd(PPh_3)_4]$ or in the methylchloroformate detrimentally affected the yield and purity of the product to a surprisingly large extent. Best results were obtained using freshly distilled $ClCO_2Me$ and newly prepared tetrakis(triphenylphosphine)palladium(0). The data for the palladium chloroformate product have been reported in the literature. [2] The results of the experiment carried out in this work and the literature values are compared in Table 2.6. For convenience, the aromatic protons have been omitted.

Table 2.6 Data for the complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$(1)

Source	^{31}P (ppm)	^{1}H (ppm)	ν_{CO} (cm^{-1})
This work	δ = 19.3(s)	δ = 2.32(s)	1654, 1672
Literature [2]	δ = 1.91(s)	δ = 2.41(s)	1650, 1670

In the paper cited in Table 2.6, the authors suggested there was some evidence for the existence of two separate isomers in the solid state, shown by the two C=O stretches in the IR spectrum. A similar observation was made in the same work for the ethylchloroformate analogue. Other alkyl chloroformates did not exhibit this phenomenon. In solution state, however, there was only one observed carbonyl band in the IR, found at 1657 cm^{-1}. Also, in the ^1H NMR spectrum, only one singlet was observed. The authors believed that two conformers were responsible for the different IR stretches (see Figure 2.7). The authors cite the similar observations made for the alkoxalyl complexes [Pd(COCOOMe)ClL_2] and [Pd(COCOOEt)ClL_2].[15]

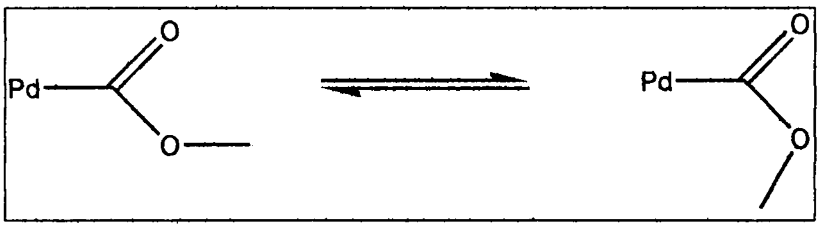


Figure 2.7

2.4 Summary

In summary, the synthetic routes attempted from the dibenzylideneacetone complex (**4**) seem to be impractical, requiring effectively the *in situ* formation of [Pd(PR_3)$_{3 \text{ or } 4}$]. In addition, the [$Pd_2(dba)_3$] route did not produce a smooth conversion to the desired product. It was decided therefore to start from the [$Pd(PPh_3)_4$] complex. The air and light sensitive nature of this species made its synthesis and handling more difficult than for (**4**). Despite these problems, the oxidative addition with methyl chloroformate proceeded quite smoothly. As noted above, it was found that the conditions had to be followed fairly rigorously and the use of pure starting materials was essential to maintain product purity and to produce high yields. This route was used as the standard method for producing the chloroformate adduct throughout this project.

Several palladium dichloride species were produced in the course of the work described here. The dichloride species were generally yellow or white, both of which are common colours for this type of species. Examination of the $^{31}P\{^1H\}$ NMR for the dichlorides showed the following. As expected, the alkyl phosphine complexes had higher chemical shift values than the aryl (compare $[PdCl_2(PPh_3)_2]$ $\delta_p = 23.5$ ppm with $[PdCl_2(PCy_3)_2]$ $\delta_p = 48.5$ ppm). Also demonstrated was the so called 'chelate effect' (discussed in Chapter 1) the result of which is to change the value of the phosphorus NMR chemical shift for chelating ligand complexes. Table 2.5 shows this quite clearly. The tertiary butyl phosphine, with a three carbon backbone (dtbpp), seemed to be an exception, but it has been found that three carbon backbone chelating phosphines do not produce so large a difference in chemical shift as phosphines with 2 carbon backbones.[16] Most of the products were obtained in good analytical purity.

Most of the complexes could be obtained pure by recrystallisation from either toluene or dichloromethane. One exception, the PCy_3 complex (**10**), was not obtained in a pure form due to its much greater solubility in a variety of solvents. The other dichlorides were insoluble in solvents such as ether, which allowed ready separation by either recrystallisation or simply precipitation from solution. The complexes were all stable, even those of the alkyl phosphines, and could be readily handled in air.

Two new species have been reported in this chapter. The crystal structure (**3**) of the dppe dichloride complex is new because of the bridging $CDCl_3$ molecules, making the Cl-Pd-Cl angle some three degrees smaller than for the previously reported structures of this molecule. The other product which is thought to be new is the complex $[PdCl_2(dtbpp)]$. Despite much effort, no mention of the complex could be found in open literature, although some platinum complexes have been reported.[17]

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ is an air stable off-white solid which is insoluble in most common solvents at room temperature. It dissolves better in polar solvents and decomposes in chlorinated solvents to give the complex $[PdCl_2(PPh_3)_2]$ and palladium black. A summary of the reactions carried out in this chapter is given below. Details can be found in the experimental section.

Reaction Summary

$$\begin{tikzcd}
{[Pd_2(dba)_3{\cdot}CHCl_3]} \arrow[r, "2\ PR_3"] \arrow[ddr, "R_2P(CH_2)_nPR_2"'] & {[Pd(dba)(PR_3)_2]} \arrow[r, "ClCO_2Me"] & {[Pd(PR_3)_2Cl_2]} \\
 & & \text{(e.g.[} Pd(PPh_3)_2Cl_2\text{])} \\
 & {[Pd(dba)(R_2P(CH_2)_nPR_2)]} \arrow[r, "ClCO_2Me"] & {[PdCl_2(R_2P(CH_2)_nPR_2)]} \\
 & & \text{(e.g. } [PdCl_2(^tBu)_2P(CH_2)_3P(^tBu)_2)]\text{)}
\end{tikzcd}$$

$$PdCl_2 \xrightarrow{\qquad} [Pd(PPh_3)_4] \xrightarrow{ClCO_2Me} [Pd(Cl)(CO_2Me)(PPh_3)_2] \quad \mathbf{(1)}$$

2.5 References

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Chapter 3

Reactivity of [Pd(Cl)(CO_2Me)(PR_3)$_2$]

The cause is hidden, but the effect is evident.

Ovid (43BC - 18AD)

3.1 Introduction.

In this chapter the reactivity of the complex [Pd(Cl)(CO_2Me)(PPh_3)$_2$] (**1**) is examined.

There were several intended schemes for study. We planned to substitute the phosphine ligands of (**1**) to provide a range of methoxycarbonyl complexes for structural and catalytic studies. We also intended to remove the halide group and modify the coordination site to make for easier access to the metal centre, making the system more reactive and hence more catalytically interesting. Additionally, we wished to examine the general reactivity and stability of all of these species.

One of the aims for the synthetic work was the generation of potential precursors for catalysis. In addition, we wanted to study the behaviour of methoxycarbonyl species under a variety of conditions.

A brief overview of methoxycarbonyl chemistry was presented in Chapter 1.

3.2 Experimental.

Unless otherwise stated, all experimental work was carried out in a dry, inert atmosphere (N_2) using standard glove box, vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen. All chemicals were bought, or for some of the phosphines (e.g. $(^tBu_2)PCH_2CH_2CH_2P(^tBu)_2$ and $Cy_2PCH_2CH_2PCy_2$), kindly donated by ICI, and used without further purification. Experimental parameters can be found in appendix 5.

Experiment 3.2.1

Synthesis of [Pd(Cl)(CO$_2$Me)(dppe)]

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.1g, 0.14 mmol) was placed in a clean, dry, 2-necked, round bottomed flask. The flask was then evacuated and back-filled with nitrogen three times before dry, degassed tetrahydrofuran (THF) (40 ml) was added to the flask *via* a syringe. The stirred suspension was then heated to 50°C, ensuring all the starting material had dissolved. At this point a slight excess (0.07g, 0.18mmol) of 1,2-bis-diphenylphosphinoethane was added. There was rapid formation of a white precipitate. The solution was stirred for a total of one hour before the white solid was separated from the solution by cannula filtration and then washed several times with THF and ether (in 10 ml portions). The white solid was dried *in vacuo* before weighing (yield 0.06g, 72%). Found C, 55.74; H, 4.51 %. $C_{28}H_{27}ClO_2P_2Pd$ requires C, 56.10; H, 4.50 %. $^{31}P\{^1H\}$ NMR (dimethylformamide) $\delta = 33.7$ ppm (d, $J_{pp} = 32.4$ Hz); 48.4 ppm (d, $J_{pp} = 32.4$ Hz). $^{13}C\{^1H\}$NMR (DMF) $\delta = 30.8$ ppm (s, DMF), 36.0 ppm (s, DMF), 129.5 ppm (d, Ph), 132.2 ppm (s, Ph), 133.1 ppm (s, Ph), 134.8 ppm (s, Ph). IR (nujol/KBr): ν_{CO}(max.) = 1653 cm^{-1}; ν_{COC}(max.) = 1044 cm^{-1}.

Electrospray MS(CH_2Cl_2): m/z (+ve ions) 997 (**A**, 10 %), 982 (**B**, 30 %), 938 (**C**, 25 %), 825 (**D**, 100 %) (see Figure 3.1 below). The identity of **A** was supported by the observed isotope pattern, which suggested the presence of both Pd and Cl in the species.

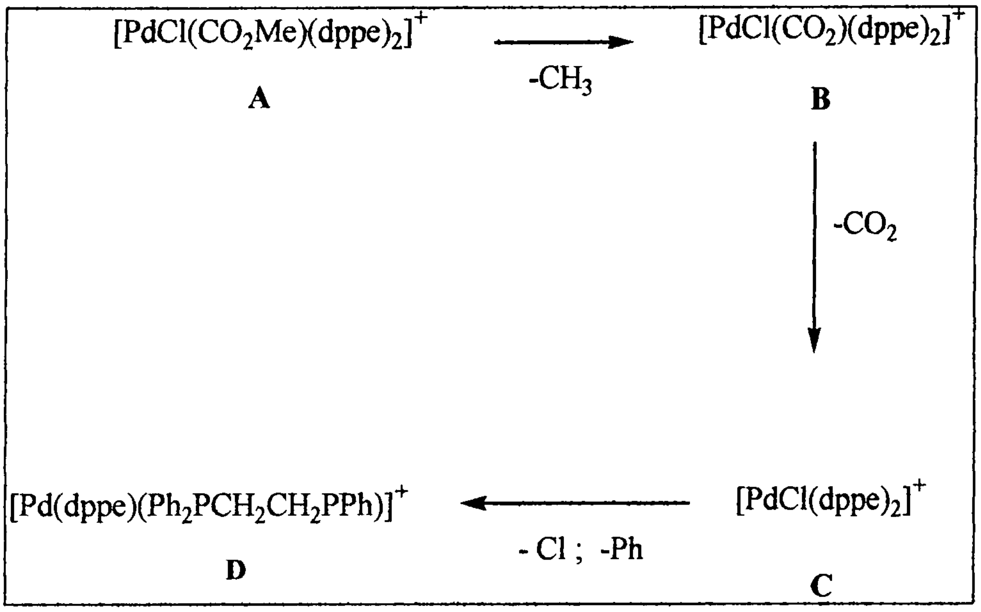


Figure 3.1

Experiment 3.2.2

Synthesis of $[Pd(Cl)(CO_2Me)(dcpe)]$

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.1g, 0.14 mmol) was placed in a clean, dry, 2-necked, round bottomed flask. The flask was then evacuated and back-filled with nitrogen three times before dry, degassed tetrahydrofuran (THF) (40 ml) was added to the flask *via* a syringe. The stirred suspension was then heated to 50°C, ensuring all the starting material had dissolved. At this point a slight excess (0.08g, 0.19 mmol) of bis-1,2-dicyclohexylphosphinoethane (dcpe) in THF (5 ml) was added. The pale solution was stirred for a total of one hour before volume reduction under reduced pressure followed by drying *in vacuo.*

The oily residue was recrystallised from toluene by dropwise addition of hexane and cooling to below 0°C overnight. The white solid formed was separated by filtration and then washed with hexane and ether (in 10 ml portions). The white solid was dried *in vacuo* before weighing (yield 0.053 g, 0.085 mmol, 61%). Found C, 51.58; H, 8.73%. $C_{28}H_{51}ClO_2P_2Pd$ requires C, 52.13; H, 8.59%; $^{31}P\{^1H\}$ NMR (THF) $\delta = 63.5$ ppm (d, $J_{pp} = 20.1$Hz), 73.3 ppm (d, $J_{pp} = 20.1$ Hz). ^1H NMR (CD_3CN) $\delta = 2.4$ ppm (**3H**, s, CO_2CH_3); $\delta =$ 1.2 - 2.0 ppm (**48H**, m, br, Cy, & PCH_2CH_2P). IR (nujol/KBr) ν_{CO} (max) = 1653cm^{-1} ν_{COC}(max) = 1045 cm^{-1}.

Experiment 3.2.3

Synthesis of $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$.

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.20g, 0.28 mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask before wrapping the flask with aluminium foil to exclude light. One equivalent of silver tetrafluoroborate (0.057 g, 0.29mmol) was added. At this point, dry, degassed, distilled acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask to prevent the silver salt reacting with light. After this time, a precipitate (AgCl) had formed in the orange solution. The solution was filtered by transferring the liquid to a filter stick, with a pad of celite, by means of a cannula. The orange solution was reduced in volume producing an off-white precipitate. The solution was reduced further to about 10-15 ml before the entire flask was re-filled with nitrogen and then cooled overnight below 0°C to complete precipitation. The grey/white solid was found to be very air and moisture sensitive. Slow crystallisation of the remaining mother liquor obtained from filtration produced crystals which melted rapidly at room temperature. Crystals obtained were shown by X-ray diffraction to be the cationic complex $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$. Elemental analysis was not possible due to rapid decomposition of the product when removed from solution. $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 24.9$ ppm(s). ^1H NMR (CD_3CN) $\delta =$ 1.97 (s, br, CD_3CN), 2.06 (**3H**, s, br, CD_3CN), 2.38 (**3H**, s, br, OMe), 7.65 (**30H**, s, br, Ph). IR (nujol/KBr) $\nu_{CO}(max) = 1675$ cm^{-1}, $\nu_{BF}(max) = 1050$ cm^{-1}, $\nu_{CN}(max) = 2318$ cm^{-1}.

X-ray analysis was carried out by Dr. C.W. Lehmann. Tables 3.1 and 3.2 below show bond lengths and angles respectively. The numbering refers to the crystal structure shown in Figure 3.2

Table 3.1 Selected Bond lengths for $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$

Bond	Length/Å(error)	Bond	Length/Å(error)
Pd-C(4)	1.984(3)	Pd-N(1)	2.111(2)
Pd-P(1)	2.3418(7)	Pd-P(2)	2.3470(7)
P(1)-C(31)	1.824(3)	P(1)-C(11)	1.824(3)
P(1)-C(21)	1.826(3)	P(2)-C(41)	1.819(3)
P(2)-C(61)	1.819(3)	P(2)-C(51)	1.823(3)
N(8)-C(9)	1.131(4)	C(9)-C(10)	1.448(5)
C(10)-H(10A)	0.98	C(10)-H(10B)	0.98
C(10)-H(10C)	0.98	B-F(1)	1.433(5)
B-F(2)	1.349(5)	B-F(3)	1.356(5)
B-F(4)	1.386(4)	C(2)-C(3)	1.463(4)
C(3)-H(3A)	0.98	C(3)-H(3B)	0.98
C(3)-H(3C)	0.98	C(4)-O(5)	1.212(3)
C(4)-O(6)	1.355(3)	O(6)-C(7)	1.464(3)
C(7)-H(7A)	0.98	C(7)-C(7B)	0.98
C(7)-C(7C)	0.98	C(11)-C(12)	1.394(4)
C(11)-C(16)	1.397(4)	C(12)-C(13)	1.391(4)
C(12)-H(12)	0.95	C(13)-C(14)	1.384(4)
C(13)-H(13)	0.95	C(14)-C(15)	1.384(4)

C(14)-H(14)	0.95	C(15)-C(16)	1.397(4)
C(16)-H(16)	0.95	C(21)-C(22)	1.397(4)
C(21)-C(26)	1.394(4)	C(22)-C(23)	1.388(4)
C(22)-H(22)	0.95	C(23)-C(24)	1.381(4)
C(23)-H(23)	0.95	C(24)-C(25)	1.390(4)
C(24)-H(24)	0.95	C(25)-C(26)	1.394(4)
C(25)-H(25)	0.95	C(26)-H(26)	0.95
C(31)-C(32)	1.387(4)	C(31)-C(36)	1.409(4)
C(32)-C(33)	1.403(4)	C(32)-H(32)	0.95
C(33)-C(34)	1.380(5)	C(33)-H(33)	0.95
C(34)-C(35)	1.372(5)	C(34)-H(34)	0.95
C(35)-C(36)	1.388(4)	C(35)-H(35)	0.95
C(36)-H(36)	0.95	C(41)-C(42)	1.401(4)
C(41)-C(46)	1.403(4)	C(42)-C(43)	1.387(4)
C(42)-H(42)	0.95	C(43)-C(44)	1.390(4)
C(43)-H(43)	0.95	C(44)-C(45)	1.381(4)
C(44)-H(44)	0.95	C(45)-C(46)	1.391(4)
C(45)-H(45)	0.95	C(45)-H(45)	0.95
C(51)-C(52)	1.390(4)	C(51)-C(56)	1.394(3)
C(52)-C(53)	1.395(4)	C(52)-H(52)	0.95
C(53)-C(54)	1.386(4)	C(53)-H(53)	0.95
C(54)-C(55)	1.380(4)	C(54)-H(54)	0.95
C(55)-C(56)	1.388(4)	C(55)-H(55)	0.95
C(56)-H(56)	0.95	C(61)-C(62)	1.390(4)
C(61)-C(66)	1.400(4)	C(62)-C(63)	1.402(4)
C(62)-H(62)	0.95	C(63)-C(64)	1.382(5)
C(63)-H(63)	0.95	C(64)-C(65)	1.382(5)
C(64)-H(64)	0.95	C(65)-C(66)	1.388(4)
C(65)-H(65)	0.95	C(66)-H(66)	0.95

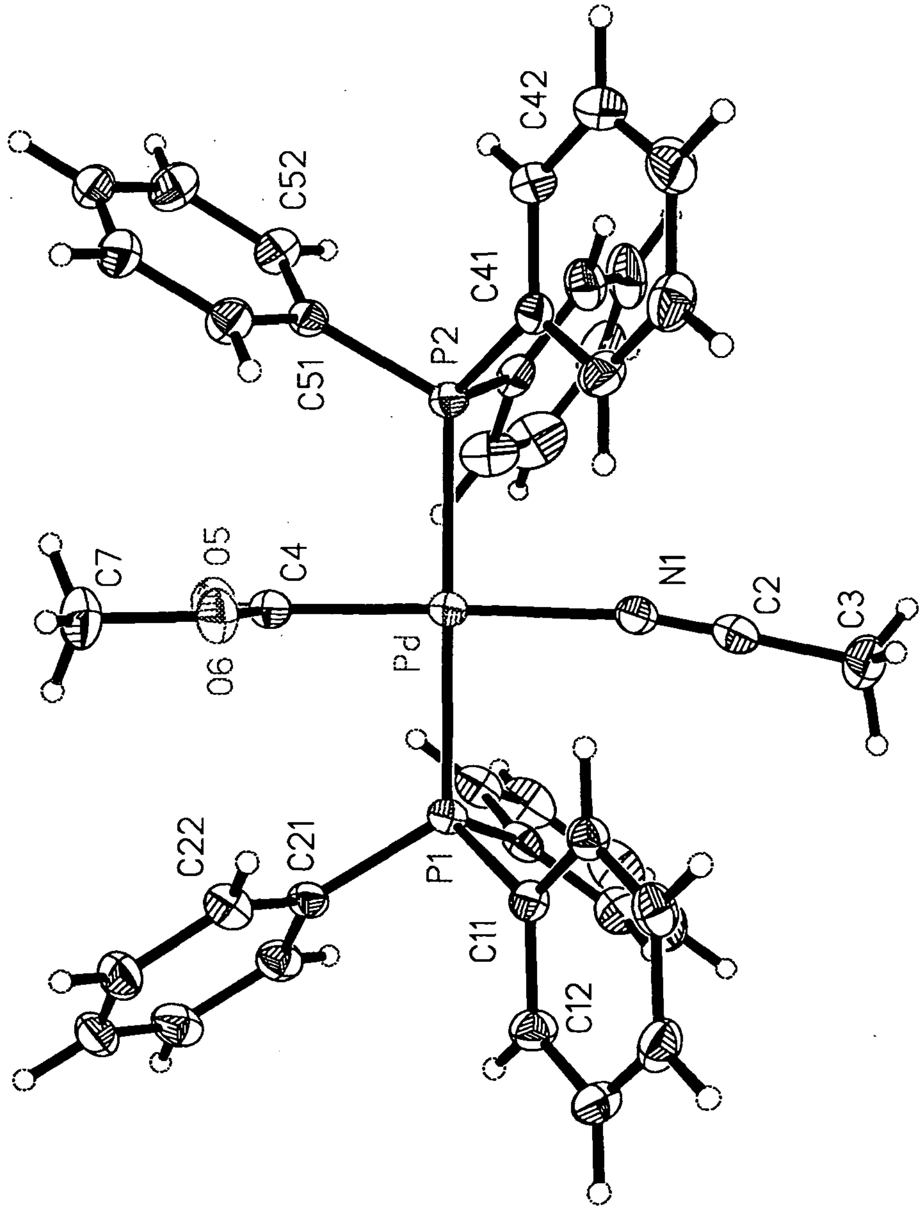
Table 3.2 Selected Bond angles of [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4)

Atoms	Angle/° (error)	Atoms	Angle/° (error)
C(4)-Pd-N(1)	177.90(10)	C(4)-Pd-P(1)	89.93(8)
N(1)-Pd-P(1)	88.11(6)	C(4)-Pd-P(2)	90.20(8)
P(1)-Pd-P(2)	173.76(2)	C(31)-P(1)-C(11)	107.75(12)
C(31)-P(1)-C(21)	105.35(12)	C(11)-P(1)-C(21)	102.01(12)
C(31)-P(1)-Pd	105.48(9)	C(11)-P(1)-Pd	114.19(9)
C(21)-P(1)-Pd	121.22(9)	C(41)-P(2)-C(61)	108.69(12)
C(41)-P(2)-C(51)	101.36(11)	C(61)-P(2)-C(51)	105.76(12)
C(41)-P(2)-Pd	115.55(9)	C(61)-P(2)-Pd	105.01(9)
C(51)-P(2)-Pd	119.84(9)	N(8)-C(9)-C(10)	177.8(4)
C(9)-C(10)-H(10A)	109.5(2)	C(9)-C(10)-H(10B)	109.5(2)
H(10A)-C(10)-H(10B)	109.5	H(10B)C(10)-H(10C)	109.5
C(9)-C(10)-H(10C)	109.5(2)	C(10A)-C(10)-H(10C)	109.5
F(2)-B-F(3)	114.5(4)	F(2)-B-F(4)	111.7(3)
F(3)-B-F(4)	111.0(3)	F(2)-B-F(1)	104.5(4)
F(3)-B-F(1)	108.0(4)	F(4)-B-F(1)	106.7(3)
C(2)-N(1)-Pd	168.0(2)	N(1)-C(2)-C(3)	178.5(3)
C(2)-C(3)-H(3A)	109.5(2)	C(2)-C(3)-C(3B)	109.5(2)
H(3A)-C(3)-H(3B)	109.5	C(2)-C(3)-H(3C)	109.5(2)
H(3A)-C(3)-H(3C)	109.5	H(3B)-C(3)-H(3C)	109.5
O(5)-C(4)-O(6)	123.0(2)	O(5)-C(4)-Pd	125.9(2)
O(6)-C(4)-Pd	111.1(2)	C(4)-O(6)-C(7)	116.5(2)
O(6)-C(7)-H(7A)	109.5(2)	O(6)-C(7)-H(7B)	109.5(2)
H(7A)-C(7)-H(7B)	109.5	O(6)-C(7)-H(7C)	109.9(2)
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(12)-C(11)-C(16)	119.3(2)	C(12)-C(11)-P(1)	119.9(2)
C(16)-C(11)-P(1)	120.8(2)	C(11)-C(12)-C(13)	120.5(3)
C(11)-C(12)-H(12)	119.7(2)	C(13)-C(12)-H(12)	119.7(2)

C(14)-C(13)-C(12)	119.8(3)	C(14)-C(13)-H(13)	120.1(2)
C(12)-C(13)-H(13)	120.1(2)	C(13)-C(14)-C(15)	120.5(3)
C(13)-C(14)-H(14)	119.7(2)	C(15)-C(14)-H(14)	119.7(2)
C(14)-C(15)-C(16)	119.9(3)	C(14)-C(15)-H(15)	120.1(2)
C(16)-C(15)-H(15)	120.1(2)	C(15)-C(16)-C(11)	120.0(2)
C(15)-C(16)-H(16)	120.0(2)	C(11)-C(16)-H(16)	120.0(2)
C(22)-C(21)-C(26)	119.0(2)	C(22)-C(21)-P(1)	117.3(2)
C(26)-C(21)-P(1)	123.7(2)	C(23)-C(22)-C(21)	120.5(3)
C(23)-C(22)-H(22)	119.8(2)	C(21)-C(22)-H(22)	119.8(2)
C(24)-C(23)-C(22)	120.4(3)	C(24)-C(23)-H(23)	119.8(2)
C(22)-C(23)-H(23)	119.8(2)	C(23)-C(24)-C(25)	119.6(3)
C(23)-C(24)-H(24)	120.2(2)	C(25)-C(24)-H(24)	120.2(2)
C(24)-C(25)-C(26)	120.3(3)	C(24)-C(25)-H(25)	119.8(2)
C(26)-C(25)-H(25)	119.8(2)	C(25)-C(26)-C(21)	120.2(3)
C(25)-C(26)-H(26)	119.9(2)	C(21)-C(26)-H(26)	119.9(2)
C(32)-C(31)-C(36)	119.6(2)	C(32)-C(31)-P(1)	123.4(2)
C(36)-C(31)-P(1)	116.9(2)	C(31)-C(32)-C(33)	119.9(3)
C(31)-C(32)-H(32)	120.0(2)	C(33)-C(32)-H(32)	120.0(2)
C(34)-C(33)-C(32)	119.5(3)	C(34)-C(33)-H(33)	120.3(2)
C(32)-C(33)-H(33)	120.3(2)	C(35)-C(34)-C(33)	121.2(3)
C(35)-C(34)-H(34)	119.4(2)	C(33)-C(34)-H(34)	119.4(2)
C(34)-C(35)-C(36)	120.1(3)	C(34)-C(35)-H(35)	120.0(2)
C(36)-C(35)-H(35)	120.0(2)	C(35)-C(36)-C(31)	119.7(3)
C(35)-C(36)-H(36)	120.2(2)	C(31)-C(36)-H(36)	120.2(2)
C(42)-C(41)-C(46)	118.9(2)	C(42)-C(41)-P(2)	120.3(2)
C(46)-C(41)-P(2)	120.7(2)	C(43)-C(42)-C(41)	120.3(3)
C(43)-C(42)-H(42)	119.9(2)	C(41)-C(42)-H(42)	119.9(2)
C(44)-C(43)-C(42)	120.3(2)	C(44)-C(43)-H(43)	119.8(2)
C(42)-C(43)-H(43)	119.8(2)	C(45)-C(44)-C(43)	119.8(3)
C(45)-C(44)-H(44)	120.1(2)	C(43)-C(44)-H(44)	120.1(2)
C(44)-C(45)-C(46)	120.5(3)	C(44)-C(45)-H(45)	119.7(2)

C(46)-C(45)-H(45)	119.7(2)	C(45)-C(46)-C(41)	120.1(3)
C(45)-C(46)-H(46)	119.9(2)	C(41)-C(46)-H(46)	119.9(2)
C(52)-C(51)-C(56)	119.2(2)	C(52)-C(51)-P(2)	123.5(2)
C(56)-C(51)-P(2)	117.2(2)	C(51)-C(52)-C(53)	119.9(3)
C(51)-C(52)-H(52)	120.1(2)	C(53)-C(52)-H(52)	120.0(2)
C(54)-C(53)-C(52)	120.2(3)	C(54)-C(53)-H(53)	119.9(2)
C(52)-H(53)-H(53)	119.9(2)	C(55)-C(54)-C(53)	120.2(3)
C(55)-C(54)-H(54)	119.9(2)	C(53)-C(54)-H(54)	119.9(2)
C(54)-C(55)-C(56)	119.7(3)	C(54)-C(55)-H(55)	120.1(2)
C(56)-C(55)-H(55)	120.1(2)	C(55)-C(56)-C(51)	120.8(3)
C(55)-C(56)-H(56)	119.6(2)	C(51)-C(56)-H(56)	119.6(2)
C(62)-C(61)-C(66)	119.3(3)	C(62)-C(61)-P(2)	123.9(2)
C(66)-C(61)-P(2)	116.8(2)	C(61)-C(62)-C(63)	120.3(3)
C(61)-C(62)-H(62)	119.9(2)	C(63)-C(62)-H(62)	119.9(2)
C(64)-C(63)-C(62)	119.7(3)	C(64)-C(63)-H(63)	120.2(2)
C(62)-C(63)-H(63)	120.2(2)	C(63)-C(64)-C(65)	120.4(3)
C(63)-C(64)-H(64)	119.8(2)	C(65)-C(64)-H(64)	119.8(2)
C(64)-C(65)-C(66)	120.3(3)	C(64)-C(65)-H(65)	119.9(2)
C(66)-C(65)-H(65)	119.9(2)	C(65)-C(66)-C(61)	120.1(3)
C(65)-C(66)-H(66)	120.0(2)	C(61)-C(66)-H(66)	120.0(2)

Figure 3.2 Crystal structure of [Pd(CO_2Me)(MeCN)(PPh_3)$_2$]$^+$



Experiment 3.2.4

Reaction of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with lithium borohydride.

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.1 g, 0.14 mmol) and $LiBH_4$ (0.002 g, 0.14 mmol) were placed in a clean, dry, 2-necked, nitrogen filled flask. To the solid mixture was added acetonitrile (20 ml, dry, degassed). The mixture was stirred at 50°C. After about thirty minutes, a white precipitate had formed. The mixture was stirred for 2 hours in total. The solvent was then removed under reduced pressure before the residue was dried *in vacuo*. Addition of acetonitrile gave an orange solution as well as the white solid. Cannula filtration of the orange liquor was performed before taking the coloured solution to dryness. The orange solid was identified by comparison of the observed $^{31}P\{^1H)$ NMR spectrum with the literature,[1] as being the dimer [Pd_2Cl_4(PPh_3)$_2$]. $^{31}P\{^1H)$ NMR (DMF) $\delta = 31.6$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 7.2 - 7.8$ ppm (**30H**, m, br).

Experiment 3.2.5

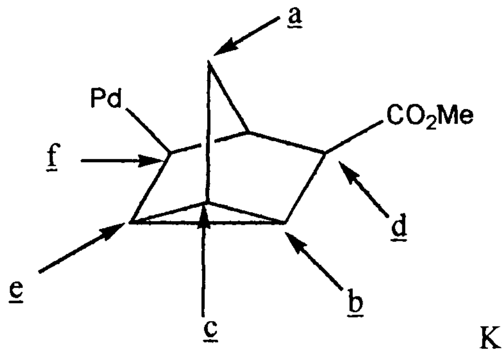
Reaction of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with dppn.

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.1g, 0.14 mmol) was placed in a clean, dry, 2-necked, round bottomed flask. The flask was then evacuated and back-filled with nitrogen three times before dry, degassed tetrahydrofuran (THF) (40 ml) was added to the flask *via* a syringe. The stirring suspension was then heated to 50°C, ensuring all the starting material had dissolved. At this point a slight excess (0.08 g, 0.16 mmol) of 1,8-bis-diphenylphosphinonaphthalene (dppn) was added. The solution was stirred for a total of 1.5 hours and an off-white precipitate was formed. The solvent was removed by cannula filtration before the solid was dried *in vacuo*. The white solid was washed with ether and hexane (10 ml portions of each) before weighing and analysis. Analytical data identified the solid as the palladium dichloride phosphine complex [PdCl$_2$(dppn)]. Found C, 60.52; H, 4.01%. $C_{34}H_{26}Cl_2P_2Pd$ requires C, 60.71; H, 3.90%. $^{31}P\{^1H\}$ NMR (CD$_3$CN) $\delta = 22.0$ ppm (s). ^1H NMR (CD$_3$CN) $\delta = 7.2 - 8.1$ ppm (**26H**, m, br).

Experiment 3.2.6

Reaction of [Pd(Cl)(CO$_2$Me)(PPh$_3$)$_2$] with norbornadiene.

[Pd(Cl)(CO$_2$Me)(PPh$_3$)$_2$] (0.13 g, 0.18 mmol) was placed in a clean, dry, nitrogen filled flask and then dissolved in THF (20 ml, dry, degassed). A slight excess of norbornadiene (0.02g, 0.21 mmol) was then added before the solution was stirred at 50°C for 90 minutes. The solution began to go yellow/ orange after a few minutes. After the solvent was removed, a greyish solid remained. Analysis showed mainly starting material. Extraction into THF gave a solution containing a new species. The solution was examined *in situ* by $^{31}P\ \{^1H\}$ NMR and infra-red spectroscopy and the data obtained were interpreted as arising from a σ-nortricyclene complex [Pd(C$_7$H$_7$CO$_2$Me)(Cl)(PPh$_3$)] (see key over the page). The solvent was removed and the residue remaining was dissolved in CD$_3$CN. $^{31}P\{^1H\}$ NMR (CD$_3$CN) $\delta = 24.0$ ppm (s), 40.0 ppm (s). ^1H NMR (CD$_3$CN) $\delta = 1.7 - 2.3$ ppm (**7H**, m, b-f), 2.51 ppm (**3H**, s, OCH$_3$), 3.6 - 4.2 ppm (**2H**, m, a), 7.2 - 7.8 ppm (**15H**, m, Ph) (See key over page). IR (THF) $\nu_{CO}(max) = 1631 cm^{-1}$.



Key for Experiment 3.2.6

Experiment 3.2.7

Reaction of [Pd(Cl)(CO$_2$Me)(PPh$_3$)$_2$] with SnCl$_2$.

[Pd(Cl)(CO$_2$Me)(PPh$_3$)$_2$] (0.1g, 0.14 mmol) was suspended in THF (20 ml, dry, degassed) and stirred at room temperature. The stirred solution was cooled to 0°C before one equivalent of SnCl$_2$ (0.025g, 0.13 mmol) was added directly. There was a rapid colour change from colourless to red. An aliquot of the solution was removed and its IR spectrum was recorded. The IR spectrum of the reaction mixture revealed a methoxycarbonyl stretching frequency (ν_{CO} = 1664 cm^{-1}) different to that of the starting complex. After stirring for five minutes, solvent was removed under reduced pressure. During this time, there was a formation of a bright yellow precipitate. From the ^{31}P {^{1}H} NMR and from elemental analysis it was found that the yellow solid was [PdCl$_2$(PPh$_3$)$_2$]. An NMR sample taken in the same manner showed no phosphorus signal initially; after a short time period (about 10 minutes) the presence of the dichloride was detected in the same sample (^{31}P{^{1}H} NMR (THF) δ = 23.5 ppm(s)).

Experiment 3.2.8

Reaction of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with lithiumphenylacetylide.

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.1g, 0.14 mmol) was suspended in THF (20 ml, dry, degassed) and stirred at room temperature. The stirring solution was cooled to approximately -15°C before LiC_2Ph (0.017g, 0.16 mmol) in THF was added under a flow of nitrogen. After a few minutes, an aliquot was removed and its IR spectrum was recorded. The IR showed no new methoxycarbonyl stretching frequency. After stirring for five minutes, the solution turned black and palladium metal was precipitated. Solvent was removed under reduced pressure giving a gummy dark solid. No useful analytical data were obtained for this solid

Experiment 3.2.9

Reaction of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with methyl lithium.

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.1g, 0.14 mmol) was suspended in THF (20 ml, dry, degassed) and stirred at room temperature. The stirred solution was cooled to below 0°C before one equivalent of MeLi (0.003g, 0.15 mmol) in THF was added under a flow of nitrogen. An aliquot was removed and its IR spectrum was recorded. The spectrum showed no new peaks in the carbonyl region. After stirring for five minutes, the solution turned colourless and palladium metal was precipitated. Solvent was removed under reduced pressure to give a dark, intractable residue. No useful analytical data were obtained for this residue

Experiment 3.2.10

Reaction of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ in chloroform.

A small amount of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.05g, 0.07 mmol) was placed in a round bottomed flask fitted with restraints on the stoppers. To this was added 5 ml of chloroform. The mixture was stirred at room temperature for 20 minutes. It was thought that decomposition in chloroform led to the formation of MeOH and CO. To test this we attempted to trap the gas released. To this end, a gas cell was evacuated on a vacuum line. The evacuated cell was then connected to the outlet tap on the flask and the tap was opened slowly such that the gas that had evolved was transferred into the evacuated gas cell, but the liquid remained in the flask.

The gas cell was then placed in an infra red spectrometer and the contents analysed. The IR spectrum revealed that the gas was indeed CO, with a strong stretching frequency at 2131 cm^{-1}. The remaining liquor was transferred to a vacuum distillation apparatus and distilled before running the liquid through a gas chromatograph. The liquid showed the presence of methanol as well as the $CHCl_3$ solvent.

3.3 Discussion.

In this chapter, the reactivity of the species $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (**1**) has been examined. Several new compounds have been synthesised and characterised and the nature of the methoxycarbonyl complexes has been investigated by structural and NMR studies.

3.3.1 Reactivity of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with phosphines.

One of the largest problems encountered in studying this system was the extremely insoluble nature of the starting material (**1**). Considerable effort was expended to discover that dissolution of the methoxycarbonyl compound was best achieved at 50 °C in tetrahydrofuran. This higher temperature led to problems when adding phosphines to replace triphenylphosphine. It was found that, at these higher temperatures, for most phosphines the complex was de-stabilised with respect to the palladium dichloride complex of that phosphine. At lower temperatures (ranging from 0°C to -20°C) the same reactions were observed to proceed either slowly or not at all; the lack of reaction is most likely a solubility problem, however. When the system was cooled down further (dry ice/acetone bath) no reaction was observed. Due to the unstable nature of the products in solution, it was decided to monitor the phosphine reactions by NMR. The only phosphine reaction products that were fully isolated were those of dppe (1,2-bis-diphenylphosphinoethane) and dcpe (the cyclohexyl analogue of dppe).

As the dppe product was even less soluble in common solvents than its precursor, it was thought that the isolable nature of this system owed more to its inherent insolubility than to any great increase in true stability. Monitoring was carried out using mainly $^{31}P\{^{1}H\}$ NMR as changes in this were found to be clearer than in the corresponding ^{1}H NMR spectra. It was also found that all of the phosphine systems reacted with chlorinated solvents (including both the dppe complex and(**1**)) to give the palladium dichloride phosphine complex of the phosphine added.

3.3.1.1 Reactions with monophosphines.

Reactions of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] (**1**) with monophosphines were difficult to monitor. The addition of tricyclohexylphosphine to the complex (**1**) gave a mixture of products. The intermediate species were relatively short lived, having a lifetime of minutes. At the end of this time, the only observable species were those of the palladium dichloride phosphine complexes, as well as some starting material and the oxide of the phosphine used.

The PCy_3 methoxycarbonyl [Pd(Cl)(CO_2Me)(PCy_3)$_2$] (**2**) was synthesised by Keim and co-workers[2] by the direct oxidative addition to [Pd(PCy_3)$_2$]. No phosphorus NMR data were published however. This would seem, initially, a much more effective route than to obtain it through ligand exchange. The lack of any other such complexes in the same publication does, however, suggest that it may not be a generally useful method. Additionally, species such as Pd(PR_3)$_n$ (where R is alkyl and n = 2-4) tend to be very air and light sensitive.

A summary of the IR frequencies of the intermediates observed is included at the end of the next chapter (Chapter 4) where all the methoxycarbonyl systems discussed in this work are summarised.

3.3.1.2 Reactions with chelating phosphines.

These reactions were considerably easier to follow by $^{31}P\{^1H\}$ NMR than the monophosphine reactions. The desired product could be unambiguously assigned in each case by the appearance of two doublets indicating two chemically different phosphorus atoms coupling to each other. A typical example of such a phosphorus NMR spectrum (of [Pd(Cl)(CO_2Me)(dcpe)] (**5**)) is shown in Figure 3.3. The phosphines used in this section were dppe, dcpe, dppp and dtbpp, as well as dppn (see chapter 5).

In the case of the dppe reaction, the product was insoluble to such a degree that it precipitated out of solution too rapidly for observation by $^{31}P\{^{1}H\}$ NMR. Other phosphines used did not allow such simple methods of isolation. The other systems tended to decompose in solution. The instability of the Pd-CO_2Me system in solution was to prove the principal reason that more methoxycarbonyl complexes could not be fully isolated.

A summary of the reactions and the data is given in Table 3.3. The format used is that each row represents a reaction and each column represents the passage of the time indicated. The summarised $^{31}P\ \{^{1}H\}$ NMR data clearly show the formation of the dichloride species of the incoming phosphine when the starting material is left in solution for just a few minutes. The dppe reaction with (**1**) proceeded with the formation of a white precipitate.

Table 3.3 Variation of chemical shift with time.

	δ_P after 15 minutes (ppm)	δ_P after 1 hour (ppm)
dcpe	92.0(s), 73.3(d, J_{PP}= 20Hz), 61.5(d, J_{pp}= 20Hz), 19.0(s), -5.2(s)	92.0(s)
dppe	65.2(s), 19.0(s), -5.2(s)	65.2(s), -5.2(s) see text
dppp	21.4(s), 18.9(s), -5.1(s)	21.4(s), -5.1(s)
dtbpp	38.2(s), 19.0(s), -5.3(s)	No change
dppn	34.8(m,br), 32.1(m,br), 21.4(s), 19.0(s), -15.0(s)	21.0(s), -5.1(s), -15.0(s)

The white product [Pd(Cl)(CO_2Me)(dppe)] (**3**) was difficult to characterise due to its very insoluble nature. The only solvent found to dissolve it satisfactorily was dimethylformamide. This meant that a $^{31}P\{^1H\}$ NMR but no ^1H NMR spectrum was obtained, as deuterated dimethylformamide was unavailable. The proton NMR would, at any rate, probably provide little useful data that could not be inferred from phosphorus NMR, IR and elemental analysis. The proton decoupled phosphorus NMR gave two doublets at 33.7 and 48.4 ppm with a phosphorus - phosphorus coupling constant (J_{pp}) of 32.5 Hz. The complex was identified as (**3**). These values are compared with the known ethoxycarbonyl analogue (**4**), the dcpe analogue (**5**) and another palladium dppe complex having two different one electron ligands (**6**), in Table 3.4.

Table 3.4 Comparison of $^{31}P\{^1H\}$ NMR for complexes [Pd(X)(Y)diphos]

Complex	δ_p (ppm)	J_{PP} (Hz)
Pd(dppe)(Cl)(CO_2Me)[3] (**3**)	33.7(d), 48.4(d)	32.5
Pd(dppe)(Cl)(CO_2Et)[4] (**4**)	32.4(d), 46.4(d)	not reported
Pd(dcpe)(CO_2Me)(Cl)[3] (**5**)	63.5(d), 76.3(d)	20.1
Pd(dppe)(Ph)(Cl)[5] (**6**)	31.5(d), 51.7(d)	28.4

The infra red spectrum of the new product (**3**) showed a methoxycarbonyl stretching frequency in the right region at 1653 cm^{-1}, which compared well with the literature value (1652 cm^{-1}) for the analogous ethoxycarbonyl system (**4**). Elemental analysis indicated that the product was obtained in a pure form. The electrospray mass spectrum of this complex was interesting. It appears to show the formation in the spectrometer of a palladium species containing two dppe ligands as well as the chloride and the methoxycarbonyl units (see Figure 3.1).

The suggested decomposition pathway of this species is now discussed. The spectrum showed fragmentation of the methoxycarbonyl complex by loss of Me, O and finally CO in sequence. After the loss of the

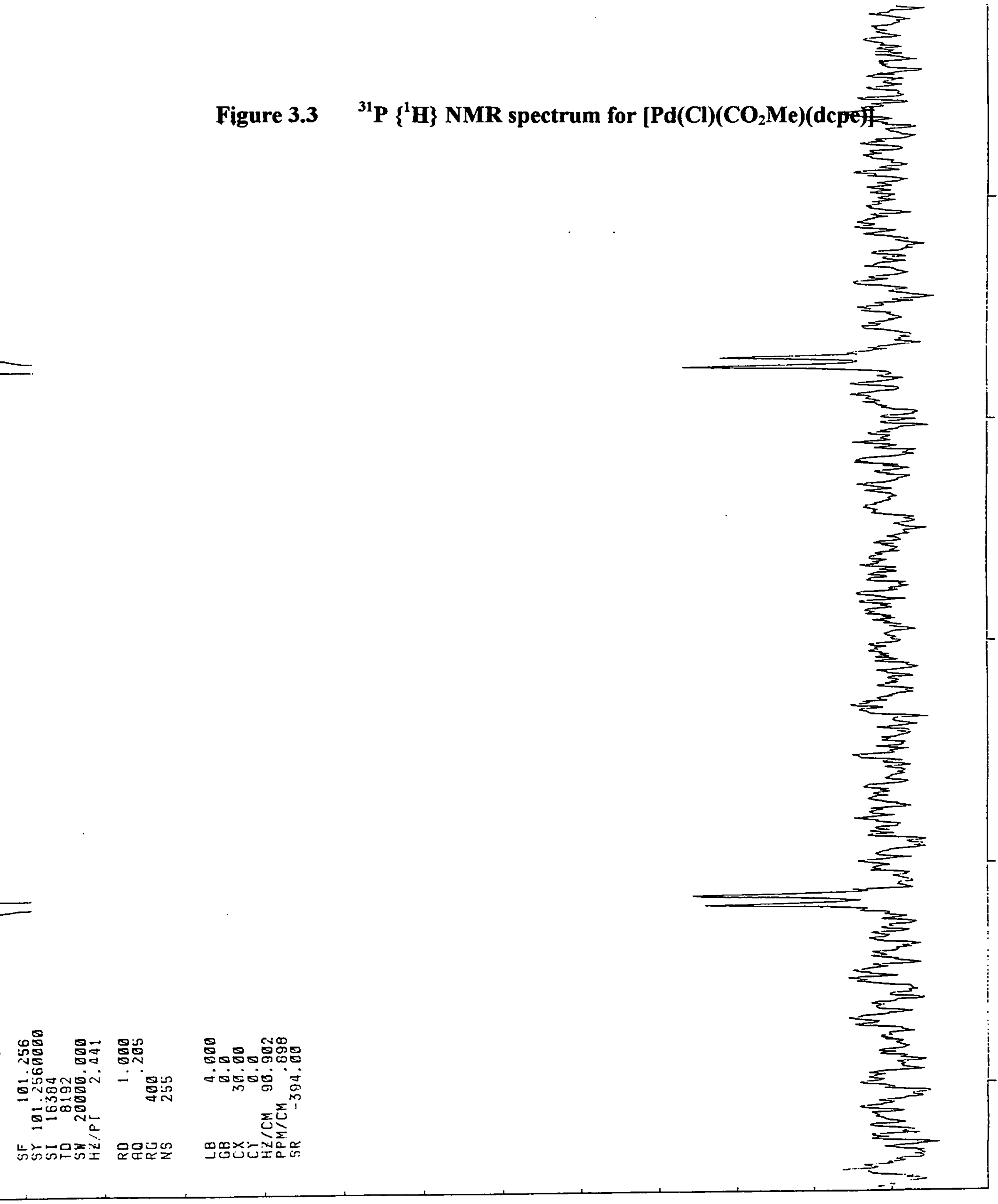


Figure 3.3 $^{31}P\ \{^{1}H\}$ NMR spectrum for [Pd(Cl)(CO_2Me)(dcpe)]

methoxycarbonyl group, the fragmentation proceeded by loss of the Cl ligand before one of the aromatic groups on the phosphine was lost. This species (D in Figure 3.1) seemed to be relatively stable and gave the largest peak in the spectrum. The loss of several aromatic groups followed. After this, many signals appear and a clear pattern of decomposition becomes hard to identify. It is not unreasonable, given the recombination of dppe with starting material exhibited by A in Figure 3.1, to suppose that some of this lower mass material was partly due to recombination in the spectrometer. Interestingly, the mass ion itself was not observed.

In the reactions of (**1**) with most of the other phosphines listed in Table 3.3 another species (presumably the chloromethoxycarbonyl intermediate) was forming, but decomposing very rapidly. This seemed especially true of those ligands with a three carbon backbone. The dppp ligand complex was not observed at all, despite an analogous overall reaction. The dppn (naphthaphos) intermediate was only observed as two low intensity multiplets at high chemical shift. The fact that instability seems to be particularly high for complexes of phosphines with three carbon backbones may have some bearing on the polyketone process, whose effectiveness relies upon the use of such ligands. This may be especially relevant for polyketone initiation at high temperature, for which methoxycarbonyl species have been implicated (see chapter 1).

The dcpe analogue (**5**) has rather different properties. The complex is a white solid, but is very soluble in most common solvents. It was unstable in solution, which meant that it was difficult to isolate. If retained in solution, the complex decomposed fairly rapidly to the dichloride $[Pd(Cl)_2(dcpe)]$. The $^{31}P\{^1H\}$ NMR spectrum of (**5**) is shown in Figure 3.3. This doublet of doublets is a typical pattern for a chelating phosphine where both the coordinated phosphorus atoms are *trans* to different ligands (see Table 3.4).

3.3.1.3 Discussion of NMR results.

The NMR results for the reactions shown above indicate quite clearly that the methoxycarbonyl palladium complexes are unstable with respect to the dichloride species, particularly in the presence of other phosphines. The most easily isolated methoxycarbonyl was the dppe derivative (**3**) whose stability is thought to owe more to its extreme insolubility than to any increased stability of the product.

The analogous reactions of [Pd(Cl)(CO_2Me)(PPh_3)$_2$] with the monophosphines were inconclusive with regards to the assignment of the intermediate methoxycarbonyl species (which were observed by a shift in the IR carbonyl stretching frequency). Complexes of the chelating phosphines with two carbon backbones, however, were relatively easy to observe due to the appearance of two doublets in the phosphorus NMR spectrum. In each case, however, there was a conversion over time of the methoxycarbonyl to the dichloride complexes, which were identified by NMR and, in most cases, by elemental analysis. The presence of Cl was thought to be a contributing factor in the instability (since the product was the dichloride) and so it was decided to try to remove the chloride ligand. This was the aim of the next section.

3.3.2 Reactivity with nucleophiles.

In this section our aim was to remove the chloride from the chloro-methoxycarbonyl adduct (**1**) by nucleophilic attack at the metal. In a system such as this there is always a chance that the nucleophile will attack the wrong site. Consider the following; the addition of hydride was intended to attack the metal centre and displace the Cl^- ligand, effectively giving a methyl formate adduct (see Figure 3.4). A strong nucleophile, such as hydride, could attack at a number of other sites (see Figure 3.5 (i) and (ii)). In the case of R^-, we might expect to see the corresponding ester RCO_2Me.

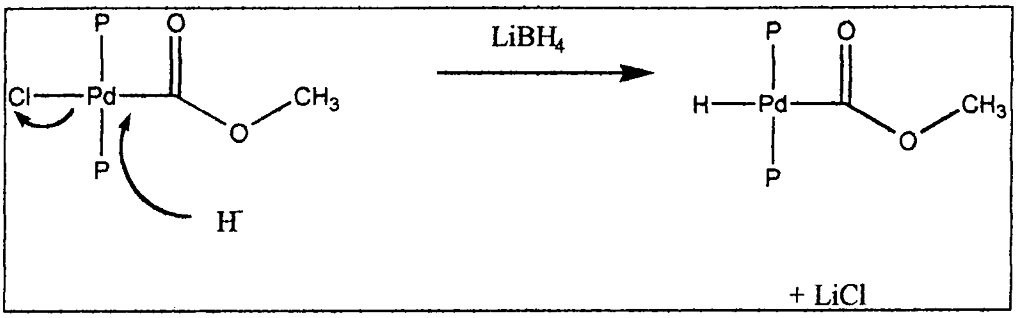


Figure 3.4

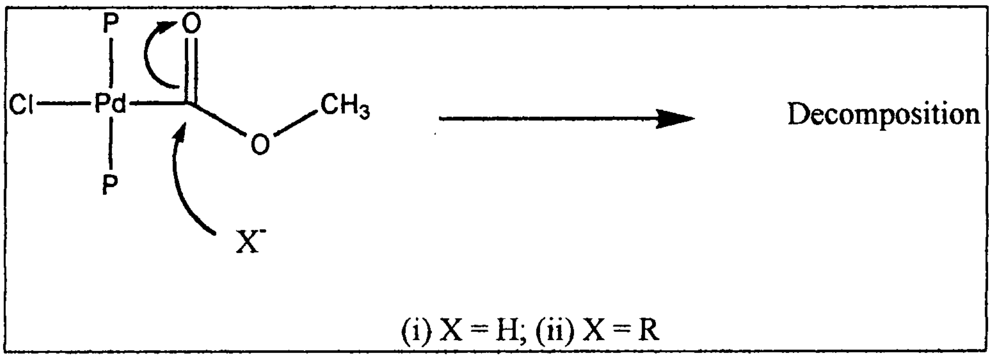
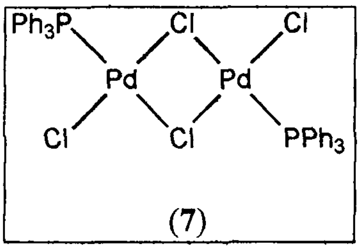


Figure 3.5

3.3.2.1 NMR reaction of (1) with hydride.

The addition of $LiBH_4$ to the chloromethoxycarbonyl adduct (**1**) at zero degrees Celsius resulted in the formation of a strongly coloured residue when the acetonitrile solvent was removed. Extraction of this residue into CD_3CN and subsequent $^{31}P\{^1H\}$NMR analysis gave only a small amount of one signal at 31.5 ppm, and a trace of $O{=}PPh_3$. Comparison with the literature[1] showed that the dimeric species (**7**) shown in Figure 3.6 had probably formed as a minor product of the reaction. The ^1H NMR of the sample showed that there were many impurities throughout the range of the spectrum. IR analysis showed no signal for a methoxycarbonyl ligand. It is believed that the hydride may have attacked the methoxycarbonyl group instead of the metal centre.

The exact nature of the decomposition remains unexplained, but may involve the formation of methyl formate by hydride attack.



(7)

Figure 3.6

3.3.2.2 NMR reaction of (1) with LiMe and with PhC_2Li.

Both of these reactions were carried out at low temperature. It was hoped that by adding an organic nucleophile to (**1**), it might be possible to determine the fate of the ester group on the metal (i.e. by producing an observable organic ester). Unfortunately, in both cases the only product observed was $[PdCl_2(PPh_3)_2]$. An examination of the IR showed no carbonyl stretches, and the fate of the organic groups was not ascertained. The proton NMR showed only the solvent (CD_3CN) and the aromatic groups from the phosphine. Presumably decarbonylation was involved, as no stretches were observed in the carbonyl region of the IR spectrum.

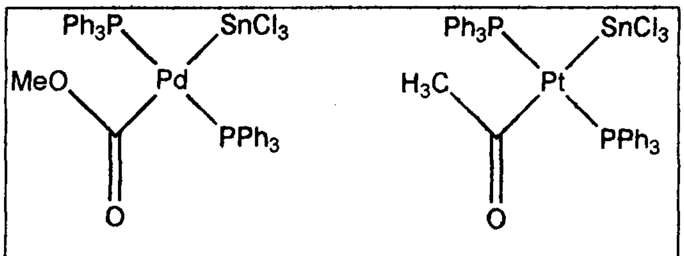
3.3.3 Other reactions of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$.

It was now fairly clear that nucleophilic attack to remove the chloride ligand from (**1**) was proving ineffective. It was decided to try some different approaches.

3.3.3.1 Reaction with $SnCl_2$.

$SnCl_2$ has long been known to insert into metal chloride bonds to give a $SnCl_3^-$ (trichlorostannate) ligand.[6] This approach was tried here as it was thought that the $SnCl_2$ would selectively react with the chloride of (**1**) rather than the methoxycarbonyl ligand. Aside from this, $SnCl_2$ is also a common co-catalyst and it was thought it would be interesting to see if any significant changes occurred in the system.

The $SnCl_3^-$ ligand is known to have a strong *trans* effect (greater than that of chloride).[6] This was not at first perceived as a problem; however it was soon realised that this is probably partly responsible for the very rapid decomposition of the proposed species (**8**), presumably by encouraging decarbonylation of the methoxycarbonyl moiety. Attempts to monitor the reaction by NMR failed utterly. The extremely fluxional nature of the intermediate species ensured that even at reduced temperatures (below -20°C), no $^{31}P\{^1H\}$NMR signal was observed. This observation is not entirely without precedent. In the closely related platinum acyl chloride complex the addition of $SnCl_2$ also produced an extremely fluxional complex (9) (see Figure 3.7).[7] The species only showed $^{31}P\{^1H\}$ NMR resonances at -70°C. Similar experiments with our proposed complex (**8**) gave no such signals.



(**8**) (9)

Figure 3.7

Furthermore, the intermediate product (**8**), in our $SnCl_2$ reaction, was so reactive that within a few minutes of formation, the intermediate complex had gone, leaving only the dichloride. As implied above, one of the main causes could be the strong *trans* effect of the trichlorostannate ligand which may cause rapid dissociation (and thus decomposition) of the methoxycarbonyl group. This may allow more rapid formation of the palladium phosphine dichloride complex. This decomposition could be seen from the IR monitoring which showed the shift in methoxycarbonyl stretching frequencies from the starting material to a value of 1664 cm^{-1}. The band then disappeared as the colour changed from colourless to deep red and then finally to yellow as the dichloride formed. The yellow solution had no methoxycarbonyl signal in either the proton NMR or in the IR spectrum. Work up of the solution gave analytically pure $[PdCl_2(PPh_3)_2]$. An attempt to produce a less soluble intermediate by the addition of dppe to the freshly prepared red solution produced a similar decomposition pattern. No signal was observed in the phosphorus NMR, but a new peak was observed in the IR at 1680 cm^{-1}. This was tentatively assigned to the transient complex $[Pd(SnCl_3)(CO_2Me)$ (dppe)] (**10**), which decomposed rapidly in solution (even at low temperature), to give the palladium dichloride complex of dppe. No further characterisation was achieved.

3.3.3.2 Reaction with $AgBF_4$.

The reaction with silver tetrafluoroborate in acetonitrile proved the key to unlocking the selective reactivity of the Pd-Cl bond. Addition of one equivalent of the silver salt in a flask wrapped in aluminium foil and stirring the mixture at room temperature for an hour yielded a solution with black solid. Upon filtration, the dark colour caused by the black precipitate was removed and an orange/yellow solution was obtained. Upon standing in the flask at -5°C for several days, small colourless crystals formed that were suitable for X-ray analysis. An X-ray structure of the complex $[Pd(CO_2Me)(MeCN)(PPh_3)_2]$ (BF_4) (**11**) was obtained (the analysis was carried out by Dr. C.W. Lehmann) and is shown in Figure 3.2 in the experimental section. Supplementary data can be found in appendix 3

The counter ion, a BF_4^- ion associated with a molecule of CH_3CN, is not shown in the structure. The data for the structure of (**11**) are shown in the experimental section. The angle C(2)-N(1)-Pd is 168°, this is fairly small for such a coordinated molecule. A comparison with other acetonitrile complexes is shown in Table 3.5. As can be seen, there was a difference of around 8°-10° from other coordinated systems.

Table 3.5 Comparison of coordinated acetonitrile bond angles

	(11)	(12)	(13)
C-N-Pd	168.0(2) °	178.6(5)°	176.3(5)°

Key for Table 3.5: (**11**)$[Pd(CH_3CN)(CO_2Me)(PPh_3)_2](BF_4)$[3]; (**12**) $[(P^tBu_3)_2Pd(H)(CH_3CN)](BPh_4)$[8]; (**13**)$[(triphos)Pd(CH_3CN)](BF_4)_2$[9]

In Table 3.6 some selected data for the new complex are compared with those for the other known methoxycarbonyl species. There are, as far as we know, only four other palladium methoxycarbonyl species that have been identified by X-ray diffraction. [10,11,12,13] This crystal structure is doubly significant as it represents the first example, to the best of our knowledge, of a fully isolated cationic palladium methoxycarbonyl species. Since this is the case, it might be expected that the bond lengths would be significantly different from the non-cationic species. It was observed, however, that there were only slight differences in the bond lengths most likely to be affected by the positive charge (see Table 3.6). Interestingly, the Pd-P bond lengths found were the longest of the five species. The charge on the species, reducing the π- basic nature of the metal, should produce less back donation to the P-C σ^* orbital [14] and shorten the overall P-C bonds.

Attempts by previous authors to isolate a cationic palladium methoxycarbonyl complex with a chelating phosphine were frustrated by rapid decomposition, possibly *via* a decarbonylation, to palladium black. [15] By contrast, the monodentate complex, although air and moisture sensitive, is stable if stored under nitrogen at -5°C in dry, degassed solvent.

Table 3.6 Comparison of Bond Lengths for Pd-CO_2Me Complexes

Bond lengths (Å)	(11)	(14)	(15)	(16)	(17)
Pd-CO_2Me	1.984(3)	1.991(10)	1.984(4)	1.989(9)	1.99(2)
Pd-P (1)	2.3418(7)	2.286(2)	2.338(1)	N/A	2.332(4)
Pd-P (2)	2.3470(8)	2.290(3)	2.339(1)	N/A	2.338(4)
C=O (**COO**Me)	1.212(3)	1.20(2)	1.194(5)	1.192(11)	1.21(2)

Key for Table 3.6: **(11)** $[Pd(MeCN)(CO_2Me)(PPh_3)_2](BF_4)$[3];
(**14**) $[Pd(pnp)(CO_2Me)(Cl)]$[4];
(**15**) $[Pd(OAc)(CO_2Me)(PPh_3)_2]$[7]; (**16**) $[Pd(bipy)(CO_2Me)_2]$[10];
(**17**) $[Pd(Cl)(CO_2Me)(PPh_3)_2]$[11].

As can be seen from Table 3.6, the new compound (**11**) has a relatively long carbonyl carbon-oxygen bond and a relatively short palladium-methoxycarbonyl bond. In addition, the perpendicular arrangement of the CO_2Me group relative to the plane of the molecule seemed to be a general trend in these complexes. This fits in with the bonding picture shown below (Figure 3.8). The tendency for the Pd-CO_2Me group to readily decompose is somewhat at odds with this picture which suggests a relatively strong Pd-CO_2Me bond.

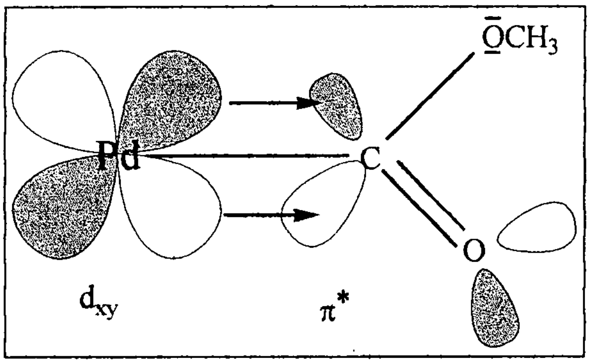


Figure 3.8

The stretch of the carbonyl bond is also lower than the value which might be expected for an ester group (about 1730 cm^{-1}) by a substantial amount (going down to 1673 cm^{-1}). This is observed to be quite general for palladium methoxycarbonyl compounds. The d_{xy} orbital is thought to be involved because of the perpendicular arrangement of the ligand to the plane of the molecule. It is also possible that the large steric bulk of the PPh_3 groups is forcing the methoxycarbonyl ligand to adopt a sterically less demanding conformation. The prevalence of this structural feature in all the known methoxycarbonyl structures casts some doubt on this, however.

The reactivity of this species (**11**) is dealt with in the next chapter.

3.3.4 Reaction with olefins.

It was our intention in the work described in this section to attempt to insert olefins into the $Pd-CO_2Me$ bond in order to mimic the process believed to take place in polyketone synthesis (see chapter 1). This process involves a methoxycarbonyl intermediate.[16] Consider the initiation steps of styrene/CO co-polymerisation in the presence of an oxidant. The methoxycarbonyl species is thought to be directly involved in the catalytic cycle, as shown in Figure 3.9, below.

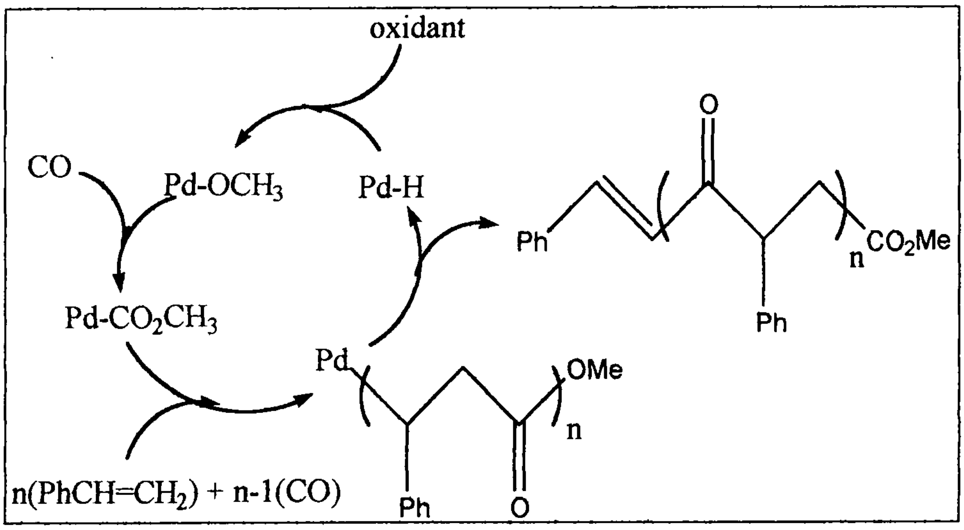
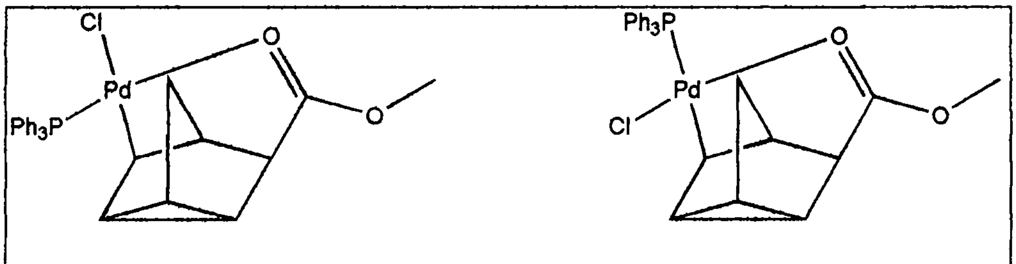


Figure 3.9

The above cycle shows the insertion of styrene into the Pd-CO_2Me bond. Propagation of the chain occurs by similar insertion into a palladium acyl. The main termination step is the β-hydride elimination which gives an unstable Pd-H species. The instability of the Pd-H bond is very great, and the role of the oxidant is to convert this (in the presence of MeOH) to the Pd-OCH_3 species before CO insertion to give the methoxycarbonyl chain end. The importance of the oxidant is underlined by the observation that in the absence of such an oxidant, copolymerisation is entirely repressed. It seems that the difficult step is the formation of the *first acyl* (as opposed to methoxycarbonyl) species, since, from Brookhart's work [17] once the acyl group has formed, the polymerisation proceeds at -80°C. Interestingly this polymerisation does not work using phosphine ligands. Instead, nitrogen or sulphur ligands are required. The reason for this may be the need for harder ligands so that carbonyl coordination can occur, thus blocking off the site required for the hydride elimination that is the termination step. [16]

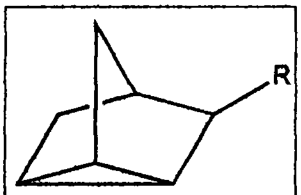
3.3.4.1 Reaction with norbornadiene.

The addition of norbornadiene to the palladium methoxycarbonyl complex (1) was a slow reaction that required heating to about 40°C. Due to rapid decomposition, the olefin insertion products were not isolated. Comparison of our data with the NMR and IR data obtained for the products of alkene insertion into acyl complexes showed that the insertion into the Pd-C bond had probably taken place. Changes in the proton decoupled phosphorus NMR showed the formation of two species (detected as singlets) that were neither the starting material nor the palladium dichloride complex. The peaks were assigned to complexes (**18**) and (**19**) shown in Figure 3.10. The rearrangement to a nortricyclene derivative (**20**) (see Figure 3.11) has precedent in such insertion reactions. [15]



(18) **(19)**

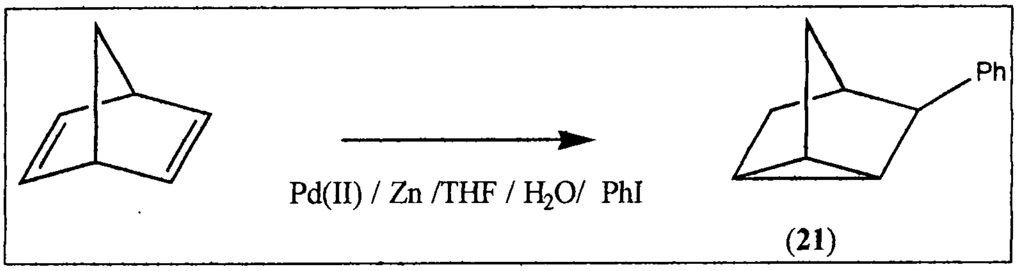
Figure 3.10



(20)

Figure 3.11

The unusual rearrangement of the norbornadiene moiety is also known for some other reactions. In one paper, by Li and co-workers, [18] the alkylation of norbornadiene using Pd(II) and Zn powder gives a substituted nortricyclene, as shown in figure 3.12. This reaction is potentially a useful, general route to substituted nortricyclenes, such as (**21**). Copolymerisation of CO and norbornadiene recently published by Liaw and Tsai [19], on the other hand, showed the presence of a mixture of polymers, but no apparent rearrangement to the nortricyclene derivative.

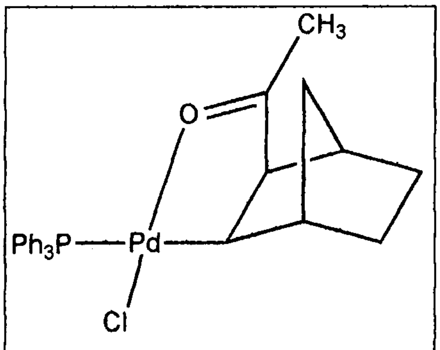


(21)

Figure 3.12

A combination of IR and ^{1}H NMR spectroscopy suggested that the rearrangement had taken place. After a short time, the olefinic protons observed initially were no longer in the reaction mixture. IR data supported the hypothesis. The rest of the proton NMR spectrum was very complex and, like previous workers, who tried low temperature and decoupling experiments[15] with such systems, complete assignment was not achieved.

By contrast, the ${}^{31}P\{{}^{1}H\}$ NMR spectrum was more useful. Two singlet peaks (at 24 ppm and 40 ppm) in roughly 1:1 ratio were observed, and assigned to the two isomers shown in Figure 3.10. After a little time (less than 1 hour) one of the peaks (at 24 ppm) had disappeared, possibly through equilibration to the other product. These values for the chemical shifts were compared with the most similar systems (i.e. acyl complexes) that were reported in literature.[20] The ${}^{31}P\{{}^{1}H\}$ NMR signal assigned to the acyl system (**22**) shown in Figure 3.13 below, was a singlet at 38 ppm. If we assume that the ${}^{31}P\{{}^{1}H\}$ NMR is fairly consistent across methoxycarbonyl and acyl systems, then we can assign the signal at 40 ppm as being due to (**19**) in figure 3.10 above. It is believed that the other signal observed in our spectrum was due to the other isomer (**18**). Since the signals were both singlets, there was clearly no coupling between the phosphorus environments.



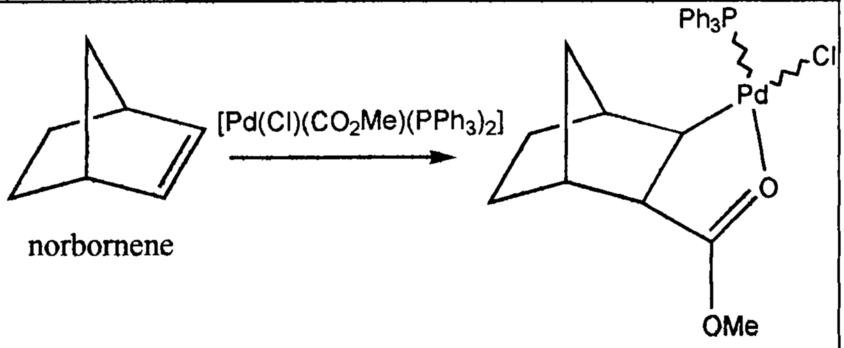
(22)

Figure 3.13

The chelation of the ester carbonyl has other precedent in the literature and is identified by an IR carbonyl stretch that is considerably lower (at about 1620 cm^{-1}) than that for either the methoxycarbonyl (or acyl) complex or the free ester group. Dekker and co-workers noted [15] that the olefin insertion into methoxycarbonyl systems is considerably more difficult than for the corresponding acyl complex, and furthermore that the products were somewhat less stable. Our findings agree with this.

3.3.4.2 Reaction with norbornene.

A similar reaction was attempted with norbornene (see figure 3.14). This olefin was chosen because it had all of the steric properties of norbornadiene, but only one double bond. It was hoped that the proton NMR for (**23**) would be easier to follow, since no such rearrangement could take place.



(23)

Figure 3.14

The following pattern of reactivity was observed in the $^{31}P\{^{1}H\}$ NMR. The spectrum of the starting material (**1**) showed the characteristic singlet at around 19 ppm. Norbornene was added at room temperature and the NMR was recorded after a few minutes. No change was observed, except for the formation of some dichloride species. The solution was then heated to 40 °C for about half an hour. No new changes in the NMR were observed. The IR spectrum remained almost identical to that of the starting material.

3.4 Reaction with chlorinated solvent.

A sample of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ was placed in a flask and stirred at room temperature in chloroform (10 ml). After a few minutes, a gas was evolved which was trapped in a gas cell. An IR spectrum of the trapped gas showed that CO gas had been evolved. The mixture in the flask was distilled before passing through a GC column. A peak corresponding to MeOH was found where a sample of methanol had given a peak on an earlier run of a standard solution of $MeOH/CHCl_3$. It is believed that chlorinated solvents, because of their tendency to form HCl from contact with water, react with the methoxycarbonyl complex as Figure 3.15 below illustrates. It was also possible that decarbonylation occurred first. As palladium methoxy species are known to be unstable, decomposition could occur by β-elimination to give formaldehyde.[21] No formaldehyde was observed, however.

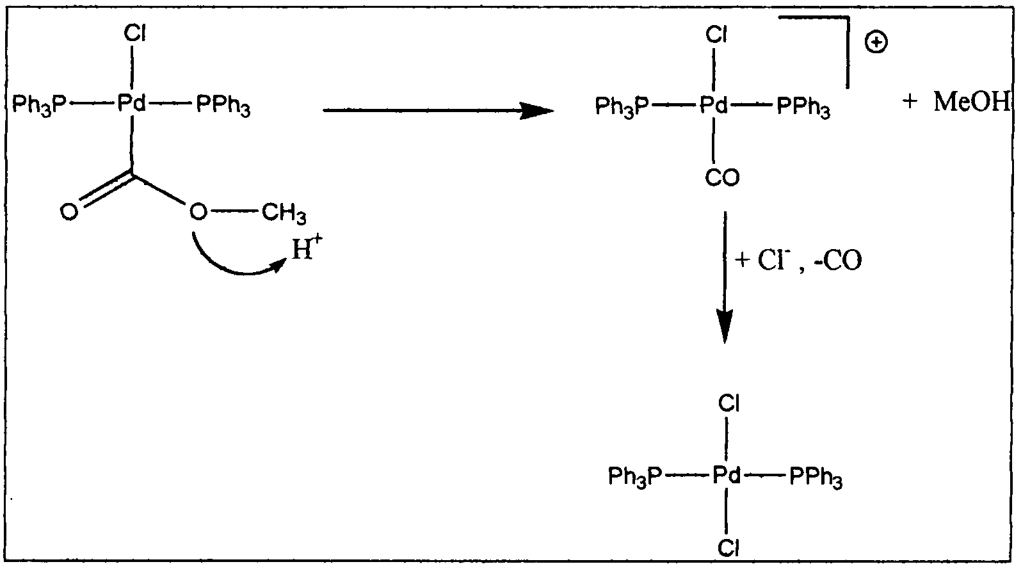


Figure 3.15

3.5 Summary.

In this chapter we have examined the nature of the best known methoxycarbonyl complex of palladium. It has been found that this is one of the most stable of the palladium chloromethoxycarbonyl derivatives, as only a few other examples could be isolated. We have also studied olefin insertion reactions into Pd-CO_2Me bonds analogous to some of the initiation steps of the polyketone process (see chapter 1).

The likely reason that few methoxycarbonyl complexes are known became clear when the instability of these systems in solution was recognised. The observation seemed especially true in the presence of other phosphines. The presence of excess phosphine in a system sets up an equilibrium where phosphines are vying for coordination. When a phosphine dissociates from the metal, there is a finite time before another phosphine can replace it. During this time, a fast intramolecular decarbonylation is possible.

Observation of this behaviour in solution was only possible after strenuous efforts to dissolve the complex initially. Many solvents were tried. The only ones found to work, without direct reaction with the complex, were acetonitrile or tetrahydrofuran at 50°C. Two new types of palladium methoxycarbonyl complex have been synthesised. These are the first examples of chloro-methoxycarbonyl complexes with chelating phosphines (**3**) and (**5**), and the first example of a cationic palladium methoxycarbonyl complex (**11**).

A crystal structure for the latter complex (**11**) was obtained and structural data obtained from it supported the bonding model shown in Figure 3.8.

The new dppe complex [Pd(CO_2Me)(Cl)(dppe)] (**3**), was fully characterised, as was its dcpe analogue [Pd(Cl)(CO_2Me)(dcpe)] (**5**). Most of the other work in the chapter focused on study of *in situ* systems which were too unstable to isolate. NMR studies of the reactivity of the methylchloroformate adduct revealed that there was formation of the palladium dichloride complex of the phosphine added to the starting material. It was thought that the reason that the dppe complex (**3**) was so much more stable than (**5**) was its inherent insolubility in all common solvents except dimethylformamide. This idea was given credence when, in DMF, formation of the dppe dichloride of palladium was observed by $^{31}P\{^{1}H\}$ NMR.

Also in this chapter we have studied the insertion of olefins into the methoxycarbonyl Pd bond. There was a measure of success; the evidence obtained, however was generally qualitative, although it has some precedent in the literature. For the reactions tried, all of the expected observations were made: the phosphorus NMR showed singlets in the expected regions; the proton NMR, although too complex to fully assign, showed that no olefinic protons remained; the IR showed the reduction in frequency of the carbonyl stretch associated with coordination at the metal centre as observed by other workers. [15] Also in common with these workers, none of the compounds were isolated, which emphasised the instability of the methoxycarbonyl moiety compared to the acyl group, whose olefin insertion products are long lived and isolable.

Reactions of nucleophiles seemed only to cause decomposition of the methoxycarbonyl compounds, usually with the concomitant formation of a palladium dichloride species.

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ is a relatively insoluble solid which is moderately stable in solution until some other chemical species is added (such as Lewis bases (or acids) and chlorinated solvents). When this occurs, palladium chloride complexes form readily, or if that is not possible, palladium 'black' separates out of solution. It is clear that solution instability is probably one of the reasons for the relatively small number of known palladium methoxycarbonyl compounds.

Evidence has been presented for olefin insertion into palladium methoxycarbonyl bonds and several methoxycarbonyl derivatives have been observed as transient species.

The chemical behaviour of the species isolated here will be discussed in the next chapter.

3.6 References.

[1] P. S. Pregosin and R.W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, New York,1979, Vol.16, p.129

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Chapter 4

Reactivity of Derivatives of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$

Happy is the man who has been able to learn
the causes of things.

Virgil (BC 70 -19)

4.1 Introduction

The complex $[Pd(MeCN)(CO_2Me)(PPh_3)_2](BF_4)$ (**1**) was synthesised (see chapter three) from the reaction of $AgBF_4$ with the methoxycarbonyl complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (**2**) in acetonitrile. In this chapter we look at the reactivity of (**1**) and consider its properties and the potential it has for catalysis. In particular the work was concerned with the reactivity of species in the presence of halides and in the presence of alkenes.

Also synthesised from (**2**) was the complex $[Pd(dppe)(Cl)(CO_2Me)]$ (**3**). We have examined the chemistry of (**3**) and attempted to perform analogous chemistry to that which was carried out on (**2**), described in the previous chapter.

4.2 Experimental Section

Unless otherwise stated, all experimental work was carried out in a dry, inert atmosphere (N_2) using standard glove box, vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen. All chemicals were bought (from Aldrich, Acros or Lancaster) or synthesised, except for some of the phosphines {e.g.$(^tBu)_2PCH_2CH_2CH_2P(^tBu)_2$, $Cy_2PCH_2CH_2PCy_2$} kindly donated by ICI, and used without further purification. Experimental parameters can be found in Appendix 5.

Experiment 4.2.1

Attempted Synthesis of $[Pd(SCN)(CO_2Me)(PPh_3)_2]$

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.15g, 0.21 mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask wrapped in aluminium foil, before the addition of one equivalent of silver tetrafluoroborate (0.04 g, 0.21 mmol). At this point, dry, degassed acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask to prevent the silver salt reacting with light. After this time, a precipitate (AgCl) had formed in the orange solution. The solution was filtered by transferring the liquid to a filter stick, with a pad of celite, by means of a cannula. To the orange solution, against a counter-flow of nitrogen, was added one equivalent of ammonium thiocyanate (0.015g, 0.20 mmol). There was an immediate precipitation of a solid. The yellow solution was filtered and the solvent was removed under reduced pressure before drying *in vacuo*. The solid was then was recrystallised from acetonitrile. The yellow solid was then washed with ether (2 x 10 ml) before analysis. The air stable solid analysed as $[Pd(SCN)_2(PPh_3)_2]$. Found C, 60.45; H, 4.23; N, 3.12%. $C_{38}H_{30}N_2P_2PdS_2$ requires C, 61.10; H, 4.05; N, 3.75%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 20.3$ ppm (s), ^1H NMR ($CDCl_3$) $\delta = 6.9 - 7.6$ ppm (**30H**, m, br, Ph). IR (nujol/KBr) ν_{SCN} (max.) = 2056 cm^{-1}.

Experiment 4.2.2

Synthesis of [Pd(CO_2Me)(triphos)](BF_4)

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.2g, 0.27 mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask wrapped in foil before the addition of one equivalent of silver tetrafluoroborate (0.050g, 0.26 mmol). At this point, dry, degassed acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask. After this time, a precipitate (AgCl) had formed in the orange solution. The solution was filtered by transferring the liquid to a filter stick, with a pad of celite, by means of a cannula. To the orange solution of [Pd(MeCN)(CO_2Me)(PPh_3)$_2$](BF_4) (0.27 mmol based on 100% conversion) was added one equivalent of triphos ($Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$, 0.13g, 0.28 mmol) in THF (10 ml, dry, degassed) by cannula. There was an immediate colour change to yellow/gold. The yellow solution was stirred overnight at room temperature under an atmosphere of nitrogen. The solvent was removed under reduced pressure and the residue dried *in vacuo*. The pale yellow solid was found to be very soluble in polar solvents and a minimum amount of THF (about 2 ml) was used to wash the solid, giving a white residue. The residue was recrystallised from THF/hexane yielding a white air stable solid which analysed as [Pd(CO_2Me)(Triphos)](BF_4). Found C, 55.19; H, 5.03%. $C_{36}H_{36}BF_4O_2P_3Pd$ requires C, 54.93; H, 4.62%. $^{31}P\{^1H\}$ NMR (THF) $\delta = 97.0$ ppm (t, $J_{pp} = 26$ Hz), $\delta = 43.0$ ppm (d, $J_{PP} = 26$ Hz). $^{13}C\ \{^1H\}$ NMR (THF) $\delta = 30.0$ ppm (s), 33.0 ppm (s) (PCH_2CH_2P), 51 ppm (OMe), 128 ppm (Ph),130 ppm (Ph), 137 ppm (Ph), 157 ppm (CO_2Me). ^1H NMR ($CDCl_3$) $\delta = 2.7$ ppm (**3H**, s, OCH_3), 3.7 ppm (**8H**, m, PCH_2CH_2P), 7.0 - 7.7 ppm (**25H**, m, Ph). IR (nujol/ KBr) ν_{CO} (max.) = 1643 cm $^{-1}$, ν_{BF} (max.) = 1062 cm^{-1}.

Experiment 4.2.3

Reaction of $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ with PPh_3.

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.2g, 0.27 mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask wrapped in foil before the addition of one equivalent of silver tetrafluoroborate (0.054 g, 0.27mmol). At this point, dry, degassed acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask. After this time, a precipitate (AgCl) had formed in the orange solution. The solution was filtered by transferring the liquid to a filter stick, with a pad of celite, by means of a cannula. To the solution was added a slight excess of triphenylphosphine (0.08g, 0.30 mmol). $^{31}P\{^1H\}$NMR showed a variety of species present in solution. The solvent was changed to dichloromethane in order to remove competition for the coordination site with MeCN. The $^{31}P\{^1H\}$ NMR spectrum was only slightly simpler however. $^{31}P\{^1H\}$ NMR (CH_3CN) δ = 34.2 ppm (broad), 33.2 ppm (broad), 14.5 ppm (v. broad) and 10.8 ppm (v. broad). These peaks were not categorically assigned to any species, but the discussion section offers some suggestions as to their possible identities.

Experiment 4.2.4

Attempted Synthesis of $[Pd(Br)(CO_2Me)(PPh_3)_2]$

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.15g, 0.20mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask wrapped in foil, before the addition of one equivalent of silver tetrafluoroborate (0.04 g, 0.20 mmol). At this point, dry, degassed acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask to prevent the silver salt reacting with light. After this time, a precipitate (AgCl) had formed in the orange solution. The solution was filtered by transferring the liquid to a filter stick, with a pad of celite, by means of a cannula. To the coloured solution was added one equivalent of potassium bromide (0.024g, 0.20 mmol). There was a rapid precipitation of KBF_4. The stirring was continued overnight at room temperature before cannula filtration. The orange solution was put under reduced pressure to remove the solvent before drying the residue *in vacuo.* The residue was then extracted into acetonitrile. The acetonitrile was removed under reduced pressure before drying the resulting solid *in vacuo.* The solid $[PdBr_2(PPh_3)_2]$ was then recrystallised from acetonitrile and weighed before analysis. Yield 0.08g, 47%. Found C, 54.34; H, 3.96; Br, 21.34%. $C_{36}H_{30}Br_2P_2Pd$ requires C, 54.68; H, 3.82; Br, 20.21%. $^{31}P\{^1H\}$ NMR (DMF) $\delta = 19.7$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 7.1 - 7.6$ ppm (**30H**, m, Ph). IR (nujol/KBr) ν_{CO}(max.) = 1672 cm^{-1}, 1655 cm^{-1}; ν_{PC} = 1462 cm^{-1}.

Experiment 4.2.5

Attempted Synthesis of $[Pd(I)(CO_2Me)(PPh_3)_2]$

$[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.2g, 0.27 mmol) was placed in a 2-necked, 100ml, nitrogen filled round bottomed flask before the addition of one equivalent of silver tetrafluoroborate (0.53 g, 0.27mmol). At this point, dry, degassed acetonitrile (40 ml) was added to the solid mixture. The suspension was then stirred briskly for two hours at room temperature, keeping aluminium foil around the flask to prevent the silver salt reacting with light. After this time, a black precipitate (AgCl) had formed in the orange solution. To filter the solution, it was transferred by a cannula to a filter stick containing a pad of celite. To the cooled, filtered solution at 0°C was added one equivalent of potassium iodide (0.043g, 0.26 mmol). There was a rapid precipitation of a pale solid. The stirring was continued for an hour before filtration. The solution was reduced in volume before drying *in* vacuo to give an orange solid. The solid was washed with ether then weighed before analysis (yield 0.11g, 46%). The solid was recrystallised from THF. A crystal suitable for X-ray diffraction was found. It was found that the crystal was the di-iodide $[Pd(I)_2(PPh_3)_2]\cdot THF$. Selected data for the crystal structure shown in Figure 4.1 follow in Tables 4.1 and 4.2. Crystal structure analysis was carried out by Dr. A.S. Batsanov. Found C, 49.48; H, 3.35%. $C_{36}H_{30}I_2P_2Pd$ requires C, 48.87; H, 3.42%. $^{31}P\{^1H\}$ NMR (THF) δ = 19.9 ppm (s). ^1H NMR ($CDCl_3$) δ = 7.2 - 7.9 ppm (**30H**, m, Ph).

Table 4.1 Selected Bond Lengths for $[Pd(I)_2(PPh_3)_2](THF)$

Bond	Length Å(error)	Bond	Length Å(error)
Pd-I	2.6081(3)	Pd-P	2.338(1)
P-C(31)	1.820(4)	P-C(21)	1.824(4)
P-C(11)	1.840(4)	C(11)-C(12)	1.387(6)
C(11)-C(16)	1.388(6)	C(12)-C(13)	1.398(6)
C(13)-C(14)	1.380(8)	C(14)-C(15)	1.377(8)
C(15)-C(16)	1.391(6)	C(21)-C(26)	1.396(6)
C(21)-C(22)	1.407(6)	C(22)-C(23)	1.394(6)
C(23)-C(24)	1.386(6)	C(24)-C(25)	1.394(7)
C(25)-C(26)	1.400(6)	C(31)-C(32)	1.393(5)
C(31)-C(36)	1.408(6)	C(32)-C(33)	1.390(6)
C(33)-C(34)	1.385(6)	C(34)-C(35)	1.393(6)
C(35)-C(36)	1.386(6)	O(1)-C(2A)	1.382(10)
O(1)-C(2B)	1.44(2)	O(1)-C(5)	1.446(9)
C(2A)-C(3)	1.497(11)	C(2B)-C(3)	1.52(2)
C(3)-C(4)	1.517(8)	C(4)-C(5)	1.478(9)

Figure 4.1 Crystal Structure of $[Pd(I)_2(PPh_3)_2]\cdot(THF)$

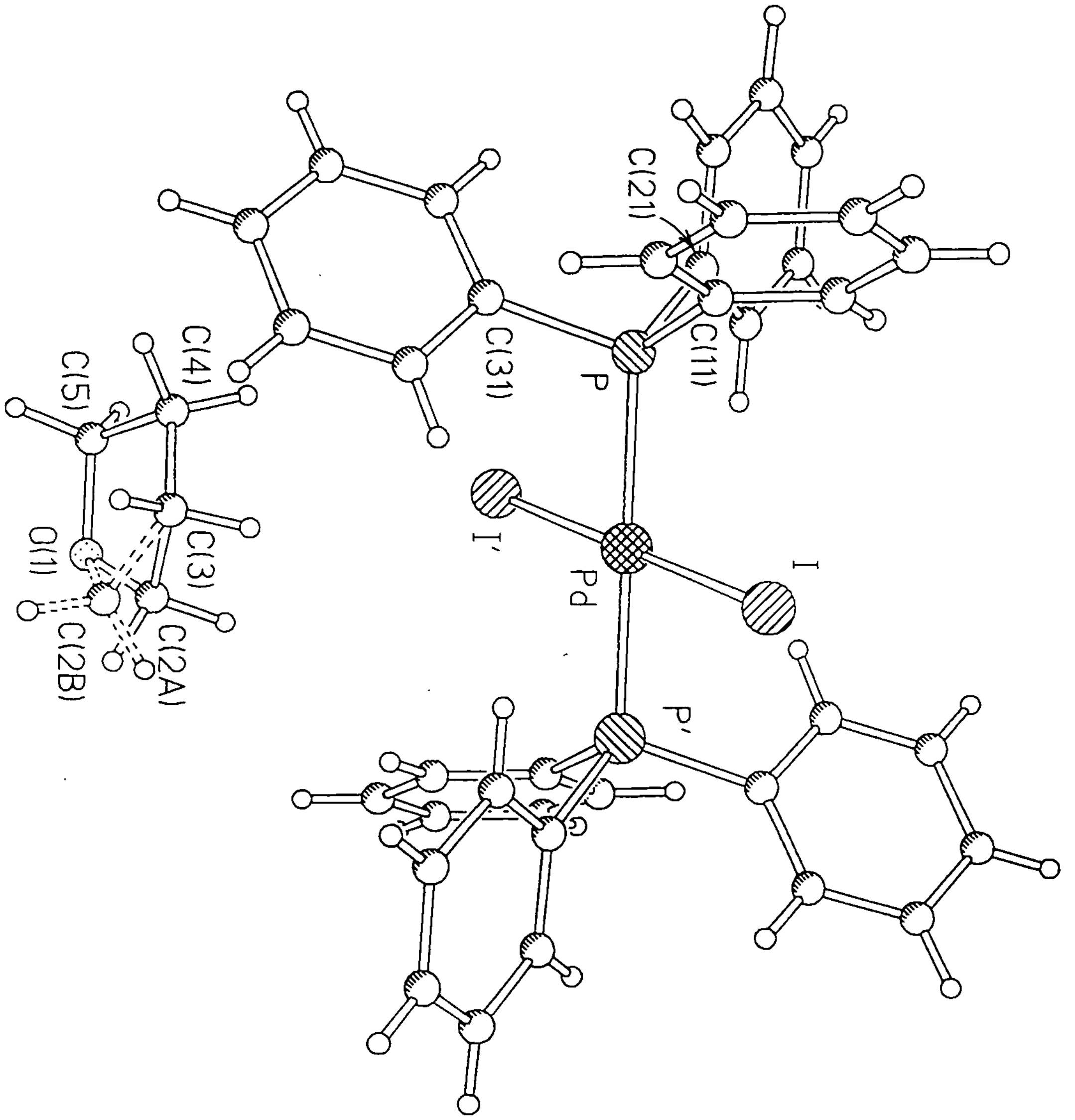


Table 4.2 Selected Bond Angles for $[Pd(I)_2(PPh_3)_2]\cdot(THF)$

Atoms	Angle/° (error)	Atoms	Angle/° (error)
P-Pd-I	92.75(3)	P-Pd-I	87.24(3)
C(31)-P-C(21)	109.5(2)	C(31)-P-C(11)	103.6(2)
C(21)-P-C(11)	100.8(2)	C(31)-P-Pd	108.96(13)
C(21)-P-Pd	114.00(14)	C(11)-P-Pd	119.23(12)
C(12)-C(11)-C(16)	119.2(4)	C(12)-C(11)-P	118.2(3)
C(16)-C(11)-P	122.7(3)	C(11)-C912)-C(13)	120.1(5)
C(14)-C(13)C(12)	120.2(5)	C(15)-C(14)-C(13)	119.8(5)
C(26)-C(21)-C(22)	119.3(4)	C(26)-C(21)-P	120.4(3)
C(22)-C(21)-P	120.2(3)	C(23)-C(22)-C(21)	119.9(4)
C(24)-C(23)-C(22)	120.2(4)	C(23)-C(24)-C(25)	120.5(4)
C(24)-C(25)-C(26)	119.3(4)	C(21)-C(26)-C(25)	120.6(4)
C(32)-C(31)-C(36)	118.4(4)	C(32)-C(31)-P	124.8(3)
C(36)-C(31)-P	116.7(3)	C(33)-C(32)-C(31)	120.8(4)
C(34)-C(33)-C(32)	120.3(4)	C(33)-C(34)-C(35)	119.9(4)
C(36)-C(35)-C(34)	120.0(4)	C(35)-C(36)-C(31)	120.7(4)
C(2A)-O(1)-C(5)	108.5(6)	C(2B)-O(1)-C(5)	109.1(8)
O(1)-C(2A)-C(3)	108.4(7)	O(1)-C(2B)-C(3)	104.2(10)
C(2A)-C(3)-C(4)	99.2(6)	C(4)-C(3)-C(2B)	107.4(7)
C(5)-C(4)-C(3)	104.3(5)	O(1)-C(5)-C(4)	106.0(6)

Experiment 4.2.6

Attempted Synthesis of $[Pd(I)(CO_2Me)(dppe)]$

$[Pd(Cl)(CO_2Me)(dppe)]$ (0.18 g, 0.30 mmol) was placed in a clean, dry 2-necked round bottomed flask wrapped in foil. The flask was flushed with nitrogen before one equivalent of silver tetrafluoroborate was added. Acetonitrile (30 ml, dry, degassed) was then added to the flask by a cannula.

The mixture was stirred at 40 °C for two hours before filtration to remove the silver chloride that had formed. The filtrate was added directly to a flask containing one equivalent of KI (0.31 mmol, 0.050g). The mixture was stirred overnight, after which time a strong orange/yellow colouration had developed and a precipitate (KBF_4) had formed. The solution was filtered and the solvent was removed under reduced pressure before drying *in vacuo*. The orange solid remaining was washed with ether (2 x 10 ml) and hexane (1 x 10 ml). The orange solid was collected and weighed (yield 0.10g, 41%) before analysis. A crystal suitable for diffraction study was obtained. It was found to be the di-iodide complex [Pd(I)$_2$(dppe)]. Found C, 40.64; H, 3.37%. $C_{26}H_{24}I_2P_2Pd$ requires C, 41.16; H, 3.19%. $^{31}P\{^1H\}$NMR (CH_3CN) $\delta = 66.2$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 1.7 - 1.9$ ppm (**4H**, m, PCH_2CH_2P), 7.2 - 7.5 ppm (**20H**, m, Ph). Crystal structure data follows in Tables 4.3 and 4.4. X-ray structural analysis was carried out by Dr. A.S. Batsanov. The crystal structure is shown in Figure 4.2.

Table 4.3 Selected Bond Lengths of [Pd(I)$_2$(dppe)]

Bond	Length, Å(error)	Bond	Length, Å(error)
Pd-P(1)	2.277(1)	Pd-P(2)	2.261(1)
Pd-I(1)	2.6679(5)	Pd-I(2)	2.6515(6)
P(1)-C(11)	1.817(5)	P(1)-C(21)	1.817(5)
P(1)-C(1)	1.850(5)	P(2)-C(41)	1.798(5)
P(2)-C(31)	1.815(5)	P(2)-C(2)	1.833(5)
C(1)-C(2)	1.530(7)	C(11)-C(16)	1.390(7)
C(11)-C(12)	1.394(7)	C(12)-C(13)	1.388(8)
C(13)-C(14)	1.383(9)	C(14)-C(15)	1.374(8)
C(15)-C(16)	1.401(8)	C(21)-C(26)	1.394(7)
C(21)-C(22)	1.410(7)	C(22)-C(23)	1.386(7)
C(23)-C(24)	1.384(8)	C(24)-C(25)	1.381(8)
C(25)-C(26)	1.387(7)	C(31)-C(32)	1.394(8)
C(31)-C(36)	1.402(8)	C(32)-C(33)	1.385(8)

C(33)-C(34)	1.382(9)	C(34)-C(35)	1.391(10)
C(35)-C(36)	1.379(8)	C(41)-C(46)	1.407(7)
C(41)-C(42)	1.409(7)	C(42)-C(43)	1.391(8)
C(43)-C(44)	1.394(9)	C(44)-C(45)	1.377(9)
C(45)-C(46)	1.395(8)		

Table 4.4 Selected Bond Angles of [Pd(I)$_2$(dppe)]

Atoms	Angle/° (error)	Atoms	Angle/° (error)
P(2)-Pd-P(1)	85.08(5)	P(2)-Pd-I(2)	90.31(4)
P(1)-Pd-I(2)	173.71(4)	P(2)-Pd-I(1)	173.80(4)
P(1)-Pd-I(1)	90.10(4)	I(2)-Pd-I(1)	94.79(2)
C(11)-P(1)-C(21)	107.8(2)	C(11)-P(1)-C(1)	105.1(2)
C(21)-P(1)-C(1)	103.6(2)	C(11)-P(1)-Pd	113.4(2)
C(21)-P(1)-Pd	117.5(2)	C(1)-P(1)-Pd	108.4(2)
C(41)-P(2)-C(31)	109.8(2)	C(41)-P(2)-C(2)	103.1(2)
C(31)-P(2)-C(2)	103.4(2)	C(41)-P(2)-Pd	110.9(2)
C(31)-P(2)-Pd	121.4(2)	C(2)-P(2)-Pd	106.2(3)
C(2)-C(1)-P(1)	110.2(4)	C(1)-C(2)-P(2)	107.3(3)
C(16)-C(11)-C(12)	118.7(5)	C(16)-C(11)-P(1)	123.4(4)
C(12)-C(11)-P(1)	117.9(4)	C(13)-C(12)-C(11)	120.9(5)
C(14)-C(13)-C(12)	119.8(5)	C(15)-C(14)-C(13)	120.2(5)
C(14)-C(15-C(16)	120.2(5)	C(11)-C(16)-C(15)	120,2(5)
C(26)-C(21)-C(22)	119.1(5)	C(26)-C(21)-P(1)	122.5(4)
C(22)-C(21)-P(1)	118.4(4)	C(23)-C(22)-C(21)	120.1(5)
C(24)-C(23)-C(22)	120.1(5)	C(25)-C(24)-C(23)	120.0(5)
C(24)-C(25)-C(26)	120.7(5)	C(25)-C(26)-C(21)	119.9(5)
C(32)-C(31)-C(36)	119.0(5)	C(32)-C(31)-P(2)	123.0(4)
C(36)-C(31)-P(2)	118.0(4)	C(33)-C(32)-C(31)	120.1(6)
C(34)-C(33)-C(32)	120.9(6)	C(33)-C(34)-C(35)	119.1(6)

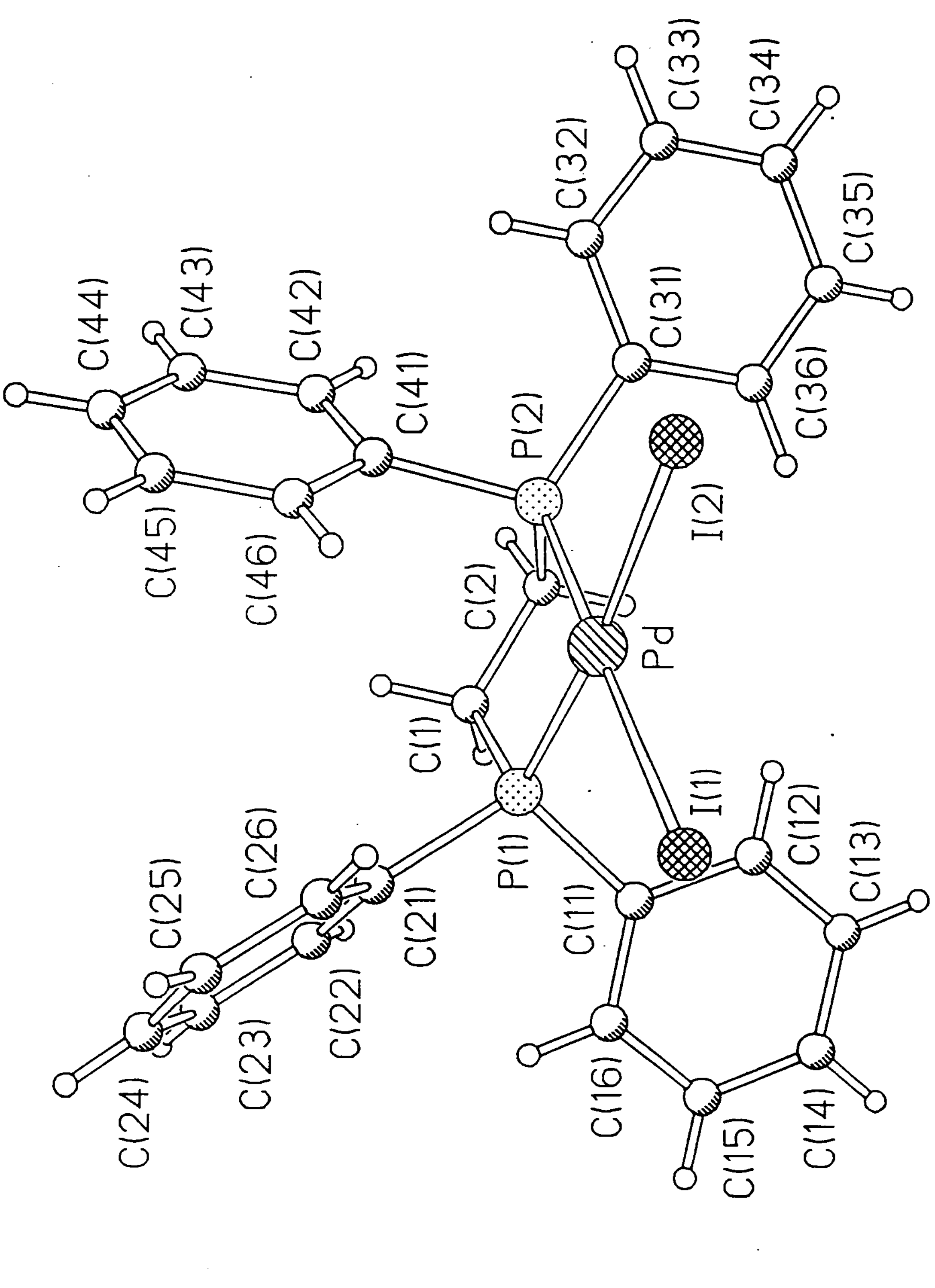
C(36)-C(35)-C(34)	120.7(6)	C(35)-C(36)-C(31)	120.2(6)
C(46)-C(41)-C(42)	118.1(5)	C(46)-C(41)-P(2)	120.2(4)
C(42)-C(41)-P(2)	121.4(4)	C(43)-C(42)-C(41)	120.8(5)
C(42)-C(43)-C(44)	120.0(6)	C(45)-C(44)-C(43)	119.9(6)
C(44)-C(45)-C(46)	120.8(5)	C(45)-C(46)-C(41)	120.4(5)

Experiment 4.2.7

Attempted Synthesis of [Pd(Br)(CO_2Me)(dppe)]

[Pd(Cl)(CO_2Me)(dppe)] (0.18 g, 0.30 mmol) was placed in a clean, dry 2-necked round bottomed flask wrapped in aluminium foil and flushed with nitrogen before one equivalent of silver tetrafluoroborate was added. Acetonitrile (30 ml, dry, degassed) was then added. The mixture was stirred at 40 °C for two hours before filtration to remove the silver chloride formed. The filtrate was added directly to a flask containing one equivalent of KBr (0.035g, 0.29 mmol). The mixture was stirred overnight by which time a yellow colouration had developed and a colourless precipitate (KBF_4) had formed. The mixture was filtered and the solvent was removed under reduced pressure before drying *in vacuo*. The solid remaining was washed with ether (2 x 10 ml) and hexane (1 x 10 ml) before extraction into acetonitrile. The volume of the filtered solution was reduced and the resulting solid was dried *in vacuo*. The solid was collected and weighed before analysis (yield 0.08g, 42 %). Found C, 46.52; H, 3.83%. $C_{26}H_{24}Br_2P_2Pd$ requires C, 46.98; H, 3.64%. $^{31}P\{^1H\}$NMR (CH_3CN) $\delta = 58.3$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 1.8$ (**4H**, m, PCH_2CH_2P), 7.1 - 7.7 ppm (**20H**, m, Ph).

Figure 4.2 Crystal Structure of $[Pd(I)_2(dppe)]$



Experiment 4.2.8

Reaction of [Pd(Cl)(CO_2Me)(dppe)] with norbornene.

To a stirred suspension of [Pd(Cl)(CO_2Me)(dppe)] (0.10g, 0.17 mmol) in acetonitrile (30 ml, dry, degassed) in a 2-necked round bottomed flask was added a slight excess of norbornene (0.019g, 0.20 mmol). The reaction mixture was stirred at 50°C for two to three hours in an oil bath before the formation of a dark solid. The solid was separated by cannula filtration before washing with THF. $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 34.2$ ppm (d, $J_{pp} = 36$ Hz), 58.9 ppm (d, $J_{pp} = 36$ Hz), 65.2 ppm (s). ^1H NMR (CD_3CN) $\delta = 1.2 - 2.9$ ppm (m,br), 7.2 - 7.7 ppm (m, br). IR (nujol/KBr) $\nu_{CO} = 1613$ cm^{-1}. These observations are discussed in section 4.3.

Experiment 4.2.9

NMR Reaction of [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4) with carbon monoxide.

[Pd(Cl)(CO_2Me)(PPh_3)$_2$] (0.18 g, 0.30 mmol) was placed in a clean, dry 2-necked round bottomed flask wrapped in foil. The flask was flushed with nitrogen before one equivalent of silver tetrafluoroborate was added. Acetonitrile (30 ml, dry, degassed) was then added to the flask by a cannula. The mixture was stirred at 40 °C for two hours before filtration to remove the silver chloride that had formed. The freshly prepared solution of [Pd(MeCN)(CO_2Me)(PPh_3)$_2$](BF_4) was transferred under nitrogen into a re-sealable NMR tube. The NMR spectra were taken for later comparison. $^{31}P\{^1H\}$NMR $\delta = 24.9$ ppm (s), ^1H NMR $\delta = 2.0$ ppm (br, CD_3CN), 2.3 ppm (s, CO_2**Me**), 7.5-7.8 (br, Ph). The NMR tube was then filled with CO at atmospheric pressure and agitated frequently over a period of one hour. The NMR spectra of the resulting solution were taken. $^{31}P\{^1H\}$ NMR (CD_3CN), δ

= 25.6 ppm (s), 24.9 ppm (s). ^{1}H NMR(CD_3CN), δ = 2.0 ppm (s, CD_3CN), 2.4 ppm (s, CO_2Me), 7.2 - 7.8 ppm (br, s, Ph). These observations are discussed in section 4.3.

4.3 Discussion

In this chapter we have examined the reactivity of the complexes [Pd(Cl)(CO_2Me)(dppe)] (**3**) and [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4) (**1**). The syntheses of these compounds were discussed in the previous chapter. The overall picture of reactivity for the dppe complex (**3**) was analogous to the chemistry of the triphenylphosphine analogue [Pd(Cl)(CO_2Me)(PPh_3)$_2$] (**2**) covered in the previous chapter. It was found, however, that the addition of $AgBF_4$ to (**3**) produced only a transient species rather than a relatively stable complex similar to (**1**). This transient was assumed to be [Pd(CO_2Me)(MeCN)(dppe)](BF_4) (**4**). Attempts to react the cationic complexes of both the monophosphine (**1**) and the chelating phosphine (**4**) met with similar results. Upon the addition of halide to both (**1**) and (**4**), for example, the di-halide complex of the phosphine in question was formed. When iodide was added to (**1**) and to (**4**), novel crystal structures of the palladium di-iodide complexes were obtained. Also discussed in this chapter are the reactions of (**1**) and (**3**) with alkenes. These reactions are now discussed in detail.

4.3.1 Reaction of [Pd(Cl)(CO_2Me)(dppe)] with $AgBF_4$; subsequent reaction with iodide.

Attempts to synthesise the dppe complex [Pd(CO_2Me)(MeCN)(dppe)](BF_4) (**4**) (as an analogue of the cationic species (**1**) isolated in the previous chapter) from (**3**) by the addition of $AgBF_4$ were fraught with difficulty. The complex (**4**) started to decompose (giving palladium black precipitate) as soon as the orange solution had been separated from the silver chloride. For this reason, no data other than IR were obtained for this complex. It was decided therefore to use (4) *in situ* to attempt to synthesise other dppe methoxycarbonyl systems. The experiment was repeated, and this time the solution of (4) was filtered directly into a flask containing KI (one equivalent based on 100% yield). $^{31}P\ \{^1H\}$ NMR of the resulting solution showed two doublets of equal intensity at 72 and 58 ppm indicating the formation of the methoxycarbonyl iodide complex [Pd(CO_2Me)(I)(dppe)] (**5**). A singlet in the spectrum (at 66.2 ppm) suggested some formation of the di-iodide complex. The presence of the desired product (**5**) was further substantiated by the observation of the methoxycarbonyl stretches in the IR spectrum which came at 1650 and 1632 cm^{-1}. From the solution containing (**5**), orange crystals suitable for X-Ray analysis were obtained. The crystals were, however, those of [PdI_2(dppe)] (**6**). This is a new crystal structure. Selected bond lengths and angles for this crystal structure are compared with known crystal data (and with the structure obtained as described in 4.3.2) in Table 4.5. The structure is shown in Figure 4.2. Supplementary data can be found in Appendix 2. Bond length/angle data can be found in the experimental section

4.3.2 Reaction of [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4) with iodide.

When potassium iodide was added to [Pd(PPh_3)$_2$(MeCN)(CO_2Me)](BF_4) the infrared spectrum of the solution showed the presence of the methoxycarbonyl ligand at 1670 cm^{-1}. The $^{31}P\{^1H\}$ NMR showed two singlets. The singlets were thought to be due to the di-iodide [Pd(I)$_2$(PPh_3)$_2$] (**7**) ($^{31}P\{^1H\}$NMR δ = 19.9 ppm (s)) and the methoxycarbonyl iodide [Pd(I)(CO_2Me)(PPh_3)$_2$] (**8**) ($^{31}P\{^1H\}$NMR δ = 18.6 ppm (s)) complexes. Once again the reactivity of the methoxycarbonyl ligand in the presence of halides was underlined. Attempts to purify the product by recrystallisation from THF gave crystals suitable for diffraction, but unexpectedly, crystals of [Pd(I)$_2$(PPh_3)$_2$]·(THF) (**9**). The crystal structure is shown in Figure 4.1. Two structural analyses of the di-iodide (7) have been previously carried out, and the data of the known compounds are compared with the new structures ((6) and (9)) in Table 4.5 below. Supplementary data for the new species can be found in the appendix 2. Bond length/angle data can be found in the experimental section.

Table 4.5 Comparison of palladium di-iodide crystal structure data

	(6)	(9)	(10)	(11)
Pd-I(1) Å	2.6679(5)	2.6081(3)	2.587(1)	2.6029(5)
Pd-I(2) Å	2.6515(6)	-	-	-
Pd-P(1) Å	2.277(1)	2.338(1)	2.331(2)	2.343(2)
Pd-P(2) Å	2.261(1)	-	-	-
I-Pd-P (1)°	173.71(4)	92.75(3)	87.1(1)	92.32(5)
I-Pd-P (2)°	90.31(4)	87.24(3)	-	87.56(5)
I-Pd-I °	94.79(2)	-	-	-
P-Pd-P °	85.05(5)	-	-	-

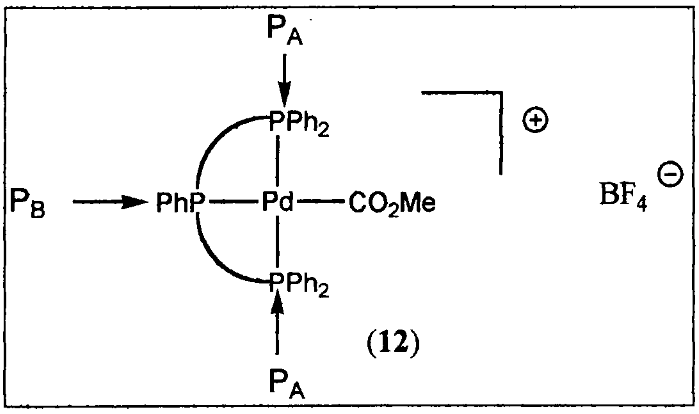
Key to Table 4.5: (6) $[Pd(I)_2(dppe)]^1$; (9) $[Pd(I)_2(PPh_3)_2]·(THF)^1$; (10) $[Pd(I)_2(PPh_3)_2]·2(CH_2Cl_2)^2$; (11) $[Pd(I)_2(PPh_3)_2]·(CHCl_3)^3$.

The structure (6) is the first structure of the $[Pd(I)_2(dppe)]$ complex. The lengths of the Pd-I bonds in the dppe complex were greater than those found in the triphenylphosphine complexes. It can be seen from Table 4.5 that the lengths and angles for the complexes (9) to (11) containing the monodentate PPh_3 ligands were, perhaps unsurprisingly, very similar.

Di-halide formation was also observed upon addition of bromide to $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ and to $[Pd(CO_2Me)(MeCN)(dppe)](BF_4)$. The instability of the palladium methoxycarbonyl with respect to the di-halide, now seemed established beyond reasonable doubt. Despite the absence of halide, the cationic species (1) was still difficult to handle without decomposition. How then could the cationic species be stabilised? It was thought that one of the de-stabilising factors was the presence of a weakly ligated coordination site (i.e. the MeCN ligand). To test this idea out, a tridentate chelating phosphine $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ ('Triphos') was added.

4.3.3 Synthesis of [Pd(CO_2Me)(Triphos)](BF_4)

Upon addition of one equivalent of the triphos ligand to (**1**), there was rapid formation of an off white solid. The solid was obtained by filtration and dried before washing with small aliquots of THF, in which the solid was slightly soluble. The white solid was taken to dryness *in vacuo*, before recrystallisation. The white solid was found to be the expected product (**12**) shown in Figure 4.3 below. The phosphorus NMR of the product showed the expected pattern of a doublet at lower chemical shift (δ = 47.0 ppm) and a triplet at high shift (δ = 97.0 ppm). In addition the IR spectrum showed a methoxycarbonyl stretch at 1643 cm^{-1}. The strong and distinctive BF stretch at 1060 cm^{-1} was also observed.



(**12**)

Figure 4.3

By contrast with the dppe and the PPh_3 cationic methoxycarbonyl compounds (**1**) and (**4**), the complex (**12**) was stable in air at room temperature. However, decomposition did occur when heated in solution above 35 °C, to give an intractable orange oil. The greater stability of the tridentate complex suggests, as proposed above, that the removal of the weakly ligated coordination site greatly stabilises the methoxycarbonyl complex.

Comparison of the phosphorus NMR of the triphos complex (**12**) with similar known compounds shows that the chemical shifts are fairly normal, but that the coupling constant is quite large, although still in the same order of magnitude.

The table below (Table 4.6) summarises some of these comparisons.

Table 4.6 $^{31}P\{^{1}H\}$ **NMR spectra of triphos complexes.**

Complex	triplet δ (ppm)	doublet δ (ppm)	J_{PP} (Hz)
(**12**)	97.0	43.2	25
(**13**)	99.5	52.0	3
(**14**)	104.0	36.1	9
(**15**)	109.5	45.7	10

Key to Table 4.6: (**12**) $[Pd(CO_2Me)(Triphos)](BF_4)$[1];
(**13**) $[Pd(MesP(CH_2CH_2PPh_2)_2)(MeCN)](BF_4)_2$ [4];
(**14**) $[Pd(Cl)(MeP(CH_2CH_2PMe_2)_2)](Cl)$ [5];
(**15**) $[Pd(Cl)(Triphos)](PF_6)$ [5]

The chemical shift values of the doublets were observed between 36 and 52 ppm, with the triplets coming between 97 and 110 ppm. Consider the complex (**12**) in Figure 4.3. The doublet is due to the two identical phosphorus atoms (P_A) which are *trans* to each other, coupling with the third phosphorus atom. The triplet comes from the phosphorus (P_B), *trans* to the methoxycarbonyl group, by coupling to the two identical phosphorus atoms (P_A) which are mutually *trans*. The intensities of the phosphorus signals are as expected with the intensity of the doublet twice that of the triplet.

4.3.4 Reaction of $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ with alkenes.

The attempt to insert alkenes into the Pd-CO_2Me bond of the cationic species (**1**) follows from the mechanism proposed by Drent for polyketone synthesis.[6] The cationic nature of (**1**) made it particularly interesting, as the catalyst systems used by Drent[6] and Sen[7] both involve cationic palladium complexes. Elsevier and co-workers have performed stepwise insertion into neutral and cationic palladium acyl complexes with bidentate nitrogen ligands to mimic the propagation step of the process (see Figure 4.4).[8]

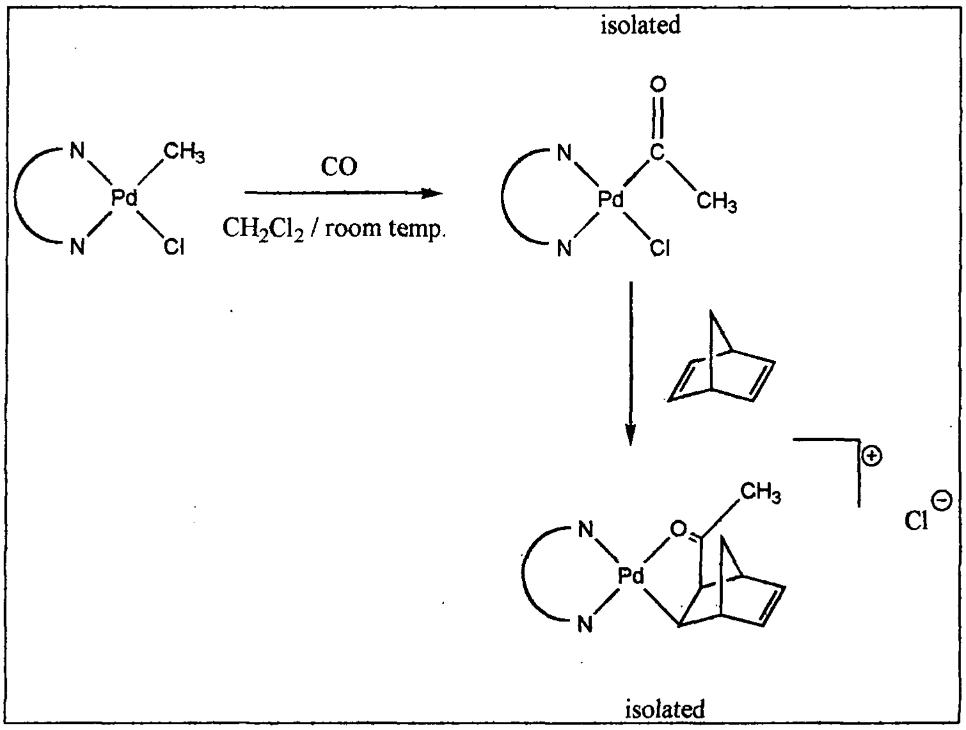


Figure 4.4

In some respects the next step carried out was even more remarkable. The same workers added another CO and another norbornadiene sequentially to get the complex shown below (Figure 4.5).

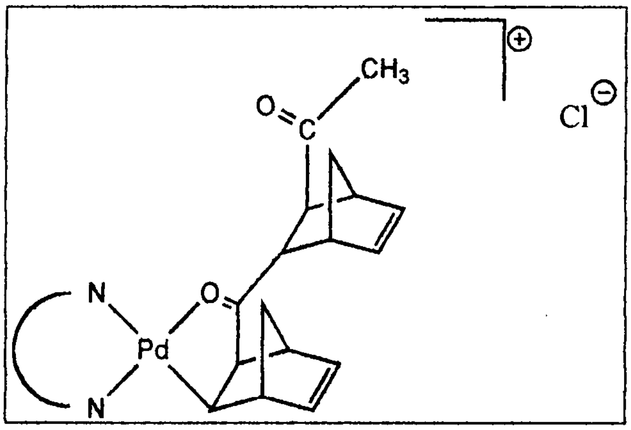


Figure 4.5

This series of reactions was put forward as (fairly convincing) evidence for the alkene insertion step of the proposed polyketone mechanism outlined by Drent.[6] This mechanism is summarised in Figure 4.6 below. As can be seen, the proposed mechanism involves two cycles. The cycles operate independently, both cycles being capable of producing the 'keto-ester' polyketone. Also found in the product mixture are the other two products (i.e. di-ester and di-ketone polyketone). The left hand initiation cycle operates through a palladium methoxycarbonyl intermediate which can be formed either by CO insertion into Pd-OMe or by direct attack of MeOH on the coordinated CO; this leads to the ester end group. The other cycle starts a chain by insertion of ethene into a palladium hydride species; this leads to the ketone end group. It is thought that at lower temperatures, the right hand hydride cycle predominates. At higher temperatures, a significant amount of the crossover products (i.e. the di-ester and the di-ketone) were found, indicating that both cycles operated at comparable rates. This observation stresses the importance of methoxycarbonyl complexes at higher temperatures in this reaction. At lower temperatures, the proportion of ester end groups may be increased by adding an oxidant such as quinone in the presence of MeOH. This was thought to convert the Pd-H species into a Pd-CO_2Me species as shown in Figure 4.7

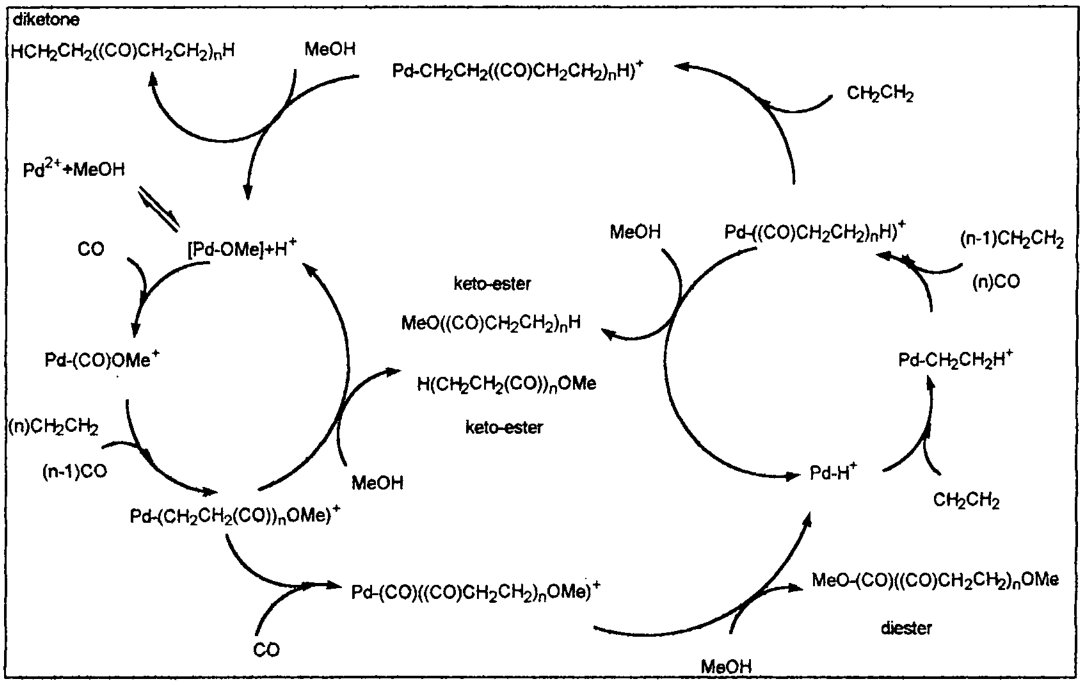


Figure 4.6

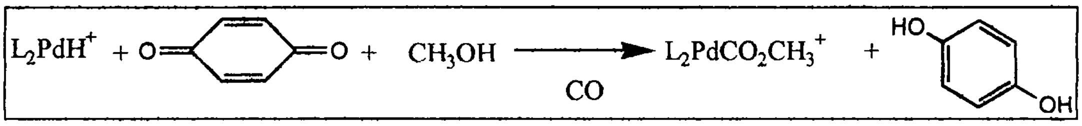


Figure 4.7

The same workers also investigated the insertion of alkenes into methoxycarbonyl-palladium bonds.[6] They observed the insertion of norbornene into the Pd-CO_2Me bond of a chelating cationic palladium methoxycarbonyl species (which was not fully characterised) *in situ*. There seems to have been no attempt to carry out the reaction for a monodentate phosphine complex such as (1) synthesised in this project. The cationic complex (1) is the first complex of this type to be isolated and structurally characterised. Consequently, it is thought that the alkene insertion properties of (1) have never been examined.

The complex $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ (1) was reacted with norbornene and with norbornadiene. Upon addition of the alkenes to (1) in solution, palladium black was precipitated in both cases, and no alkene insertion or coordination was observed for either reaction. The proton NMR showed free alkene at 5.8 ppm and no carbonyl signal was observed in the IR. It was thought that this was partly to do with the solvent (i.e. acetonitrile) which was occupying the most accessible coordination site. CH_3CN is quite a strong Lewis base and so it might provide competition to the incoming alkene. Repetition of the reaction in CH_2Cl_2 also caused decomposition to palladium black, however. Attempts to re-synthesise the cationic complex using a different solvent to act as a ligand (e.g. ether, pyridine, methanol) failed to produce any useful material.

4.3.5 Reaction of $[Pd(CO_2Me)(MeCN)(dppe)](BF_4)$ with alkenes.

As for the insertion reactions with (**1**), no insertion products were observed when norbornene and norbornadiene were added separately to (**4**). In both cases, the palladium complex decomposed rapidly giving a black precipitate. This was perhaps not very surprising since the reactivity of the *cis* methoxycarbonyl cationic complex is known to be very great, greater even that the monodentate species, and previous workers[9] also failed to isolate the complex.

4.3.6 Reaction of $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ with CO.

In order to assess the strength of the interaction between the MeCN ligand and the Pd centre, CO gas was added to the cationic solution in a re-sealable air-tight NMR tube. The reaction was monitored by $^{31}P\{^1H\}$ NMR. CO gas was added to (**1**) at atmospheric pressure. After agitation, a colour change from orange to yellow was observed. The phosphorus NMR was recorded and compared with that of the starting material. It was found that the starting material peak (at 24.9 ppm) was present, but was the minor peak. A new peak appeared at 25.6 ppm. It was proposed that the new peak was due to the complex (**16**) shown on the left hand side of the equation shown in Figure 4.8, below.

Attempts to obtain the IR spectrum for this complex (**16**) were fruitless. The presence of free CO was not observed, because, it is believed, of the equilibrium shown in Figure 4.8. When the NMR tube was opened in order to obtain an IR sample of (**16**) decomposition was observed. It is believed the equilibrium shifts almost entirely to the right hand side to give the unstable complex (**17**) which decomposes at room temperature.

$$\underset{\mathbf{(16)}}{[Pd(CO)(CO_2Me)(PPh_3)_2](BF_4)} \underset{+\,CO\,/\,-MeCN}{\overset{-\,CO\,/\,+\,MeCN}{\rightleftharpoons}} \underset{\mathbf{(17)}}{[Pd(MeCN)(CO_2Me)(PPh_3)_2](BF_4)}$$

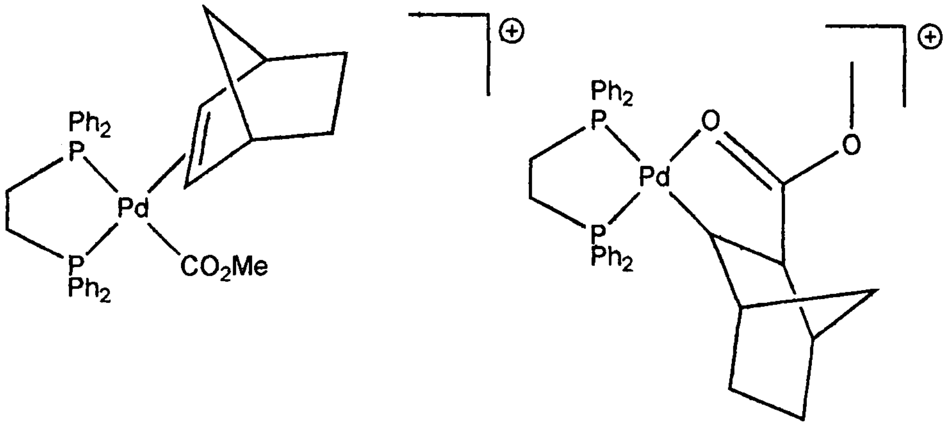
Figure 4.8

4.3.7 Reaction of [Pd(Cl)(CO$_2$Me)(dppe)] with norbornene

The addition of norbornene to a suspension of the dppe complex (**3**) in THF was monitored by $^{31}P\{^1H\}$ NMR and ^1H NMR as well as IR spectroscopy. The changes observed in the various spectra are described below.

The ^1H NMR spectra for the free alkene as well as for the resulting product were very complex in the alkyl region and no useful data could be gleaned from a comparison of the two. In the -CH=CH- region, however, it was observed that the signals due to the alkene proton in the norbornene (at 5.7 ppm) disappeared with time upon addition to the palladium complex (**1**). This was taken as an indication that the predicted insertion reaction had taken place to give (**19**) (Figure 4.9). It was possible, though, that the alkene could simply have coordinated giving (**18**), and it was important to gain some evidence to ascertain which of these things had occurred. The other two spectroscopic probes helped in this respect.

The $^{31}P\{^{1}H\}$ NMR showed two doublets (at 34.2 and 58.9 ppm) which were in a substantially different position to the peaks observed for the chloromethoxycarbonyl species (found at 33.6 and 48.3 ppm). It was inferred from this that the alkene had reacted with the system, but the nature of the reaction was not so clear, as either of the two structures (**18**) or (**19**) (with chloride as the counter-ion) in Figure 4.9 could give two doublets in the $^{31}P\{^{1}H\}$ NMR spectrum.



(**18**) (**19**)

Figure 4.9

The problem was resolved, however, when the IR spectrum of the product was examined. We could not readily ascertain whether or not the alkene stretching frequency had been reduced by coordination or simply removed by insertion. This is a general problem for palladium and platinum compounds. According to Hartley [10]- "the carbon-carbon double bond stretching frequency is lowered upon coordination to Pt(II) and Pd(II). It is not possible....to put a quantitative value on this lowering." We therefore turned to the carbonyl group. The IR showed a peak in the carbonyl region. The peak was different from the starting material which had a signal at 1672 cm^{-1}. The new peak was found at 1613 cm^{-1} and was attributed to the oxygen coordinated ester group shown in complex (**19**). This lowering of CO stretching frequency upon coordination has been observed by previous workers [11]. The insertion of olefins into acyl complexes, for example[8] caused the observed IR stretching frequency to drop from 1705 cm^{-1} to 1600 cm^{-1} upon coordination of the carbonyl oxygen.

Isolation of this product (**19**) was not achieved. It is thought, however, that along with the insertion described in the previous chapter, this is the first observation of alkene insertion into Pd-CO_2Me bonds for the chloromethoxycarbonyl species. The work by Dekker and co-workers[9] showed that insertion into cationic methoxycarbonyl palladium species was feasible, however. All of these reactions may have implications for the higher energy initiation pathway observed for the polyketone synthesis.[6]

4.3.8 Reaction of [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4) with thiocyanate.

The addition of SCN^- to the *in situ* reaction mixture of (**1**) resulted in fast formation of solid KBF_4. $^{31}P\{^1H\}$ NMR monitoring of the remaining solution did not show any signals. An IR spectrum of an aliquot of the solution showed that the methoxycarbonyl thiocyanate may have formed (since the methoxycarbonyl frequency had changed from the starting material) but such a product was not isolated. Leaving the sample in solution gave [Pd(SCN)$_2$(PPh_3)$_2$] over time.

4.3.9 Reaction of $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ with PPh_3 and dppe.

Upon addition of triphenylphosphine to the cationic species (**1**) (used *in situ*) there was a deepening of the initial orange colour to red. $^{31}P\{^1H\}$ NMR analysis of the mixture showed an extremely complex, broad spectrum which was not assigned. An even more complex NMR spectrum was obtained when dppe was added to the *in situ* solution of (**1**). It was thought that the reason for this was that many species with different numbers of phosphine groups were being formed at once. Examples of such species may include $[Pd(CO_2Me)(dppe)(PPh_3)](BF_4)$; $[Pd_2(PPh_3)_2(CO_2Me)_2(dppe)_2](BF_4)_2$; $[Pd(MeCN)(PPh_3)(dppe)](BF_4)$ and so on. The $^{31}P\{^1H\}$NMR spectrum contained several doublets, triplets and more complex splitting patterns, as well as broad signals indicating exchange processes. The spectrum was not assigned. By changing solvent from acetonitrile to dichloromethane it was thought that the phosphorus spectrum may be simplified. Surprisingly, this did not affect the overall complexity of the spectrum, but did reduce the broadness of some peaks observed in acetonitrile (at 27.7 ppm and 2.3 ppm) suggesting that the parent species were solvated. The addition of PR_3 to (**1**) produced signals too broad for splitting to be observed.

4.3.10 Comparison of carbonyl stretching frequencies for known palladium methoxycarbonyl complexes.

There have been comparatively little data published on the carbonyl stretching frequencies of the methoxycarbonyl groups on a metal centre. The stretching frequencies for palladium methoxycarbonyl compounds given below (Table 4.7) are for previously known, and our own, methoxycarbonyl complexes.

Table 4.7 A comparison of Pd-CO_2Me carbonyl stretching frequencies

Complex	Notes	CO stretching frequency
$[Pd(Cl)(CO_2Me)(PPh_3)_2]$[12]	(a)	1673, 1651 cm^{-1}
$[Pd(bipy)(CO_2Me)_2]$[13]	(b)	1633 cm^{-1}
$[Pd(PPh_3)_2(CO_2Me)_2]$[14]	(d)	1655 cm^{-1}
$[Pd(OAc)(CO_2Me)(PPh_3)_2]$[9]	(c)	1630 cm^{-1}
$[Pd(pnp)(CO_2Me)(Cl)]$[15]	(b)	1665, 1600 cm^{-1}
$[Pd(pnp)(CO_2Me)(ClO_4)]$[10]	(a)	1663, 1601 cm^{-1}
$[Pd(CO_2Me)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)C_5H_3N\}]$[10]	(a)	1638, 1603 cm^{-1}
$Pd(PCy_3)_2(Cl)(CO_2Me)$[16]	(d)	1665 cm^{-1}
$[Pd(pnp)(CO_2Me)_2]$[17]	(a)	1648, 1610 cm^{-1}
$[Pd(Cl)(CO_2Me)(^tBuNC)_2]$[18]	(b)	1680 cm^{-1}
$[Pd(dppe)(Cl)(CO_2Me)]$[1]	(a)	1653cm^{-1}
$[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$[1]	(c)	1640 cm^{-1}
$[Pd(triphos)(CO_2Me)](BF_4)$[1]	(a)	1643 cm^{-1}
$[Pd(Cl)(dcpe)(CO_2Me)]$[1]	(d)	1652, 1636 cm^{-1}
$[Pd(Br)(CO_2Me)(PPh_3)_2]$[1]	(d)	1672, 1655 cm^{-1}
$[Pd(I)(CO_2Me)(PPh_3)_2]$[1]	(d)	1670 cm^{-1}
$[Pd(I)(dppe)(CO_2Me)]$[1]	(d)	1650, 1632 cm^{-1}
$[Pd(Br)(dppe)(CO_2Me)]$[1]	(c)	1656 cm^{-1}
$[Pd(SnCl_3)(CO_2Me)(PPh_3)_2]$[1]	(a)	1670 cm^{-1}
$[Pd(SnCl_3)(CO_2Me)(dppe)]$[1]	(d)	1680 cm^{-1}

Table 4.7

Key to Notes for Table 4.7: (a) nujol mull; (b) KBr Disk; (c) CH_3CN; (d) thf.

As can be seen from Table 4.7, there is a fairly wide range for methoxycarbonyl stretches in the IR spectrum. There are normally one or two stretches. Where there are two stretches (normally obtained from a sample run in a solid matrix), the lower of the two seems to come at about 1600 - 1655 cm^{-1}. The higher stretches tend to come at around 1650 - 1680 cm^{-1}.

When only one stretch is present, it is usually observed in the higher range. There seems no clear pattern linking the observed frequency and the metal environment, although the presence of a nitrogen ligand seems to lower the observed frequencies (particularly that of the lower frequency stretch).

Studies of other metal systems with methoxycarbonyls (see Chapter 1) have shown little variation of the stretching frequency of the CO_2Me group. Thus IR is one of the best methods of detection for methoxycarbonyl groups.

4.4 Conclusions.

Of the compounds made in this chapter (most of which are new) few were found to be sufficiently stable to be isolated. This instability reinforces the conclusions drawn at the end of the last chapter where it was observed that the only examples of palladium methoxycarbonyls that have been fully isolated and relatively stable have been those which have been very insoluble, or those where there are no free halides present in solution or on the metal. It was, therefore, perhaps not entirely surprising that addition of bromide and iodide gave the di-halide species. This is particularly emphasised by the determination of two new palladium di-iodide phosphine complex crystal structures.

The isolation of the triphos complex, which is only the second example of a cationic palladium methoxycarbonyl species, and the first example of an isolated chelating ligand complex of a cationic methoxycarbonyl of palladium, highlights another factor thought to affect stability. Blocking of the weakly ligated coordination site is probably a large contributory factor in the stability of the complex. The triphos complex is markedly more stable than the cationic species isolated in the previous chapter, so much so that handling in air produces no discernible decomposition.

Attempts to displace the acetonitrile ligand of the cationic species (**1**) with a phosphine to produce complexes of the type $[Pd(CO_2Me)(diphos)(PR_3)]^+$ employed by Vrieze and co-workers,[8] were frustrated by the development of very complex equilibria in solution. Monitoring by $^{31}P\{^1H\}$ NMR of the reaction showed the formation of some twenty new peaks, with a narrow range of coupling constants arising from a mixture of species. Changing the incoming phosphine from PPh_3 to other phosphines such as PBu_3 made no difference to the complexity of the resulting spectra. The addition of dppe to the cationic complex (**1**) produced equally complex mixtures.

The decomposition of the species (**1**) and (**4**) in the presence of halide remains something of a puzzle. One possible explanation could be as follows. When the halide ion attacks the metal, it displaces the coordinated acetonitrile complex to give observed halo-methoxycarbonyl intermediates (**5**) and (**8**). Once formed (**5**) and (**8**) are thought to undergo ligand exchange reactions, such that a di-halide complex and a di-methoxycarbonyl complex may form (see Figure 4.10). The di-methoxycarbonyl complex may then reductively eliminate to give dimethyl oxalate (MeOC(O)C(O)OMe) and Pd(0), observed as palladium black. The chloromethoxycarbonyl complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ may decompose in an analogous manner.

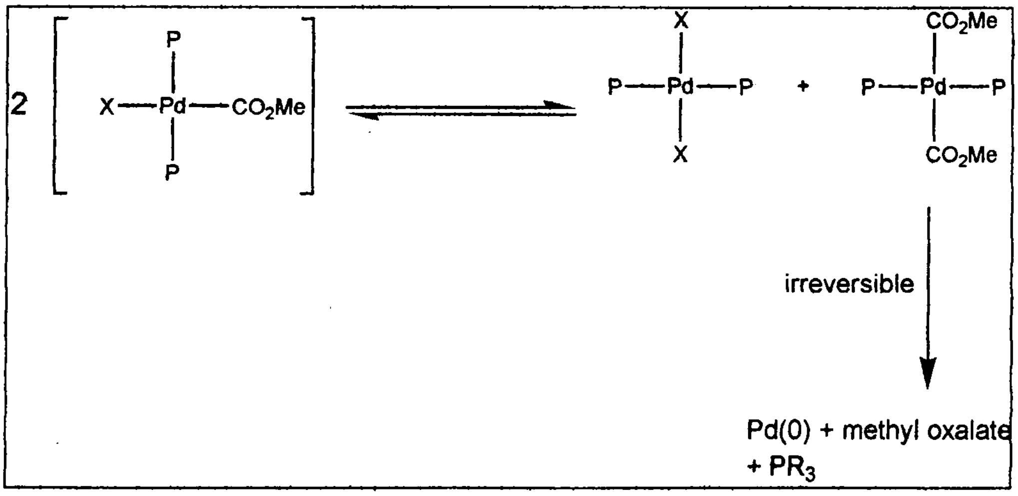


Figure 4.10

The presence of dimethyl oxalate was not entirely proven, but weak stretches observed in the IR spectra (of the decomposition products) at 1710 cm^{-1} were thought to be due to this compound.

4.5 References

[1] This work

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Chapter 5

1, 8-Bis(diphenylphosphino) naphthalene and related chemistry.

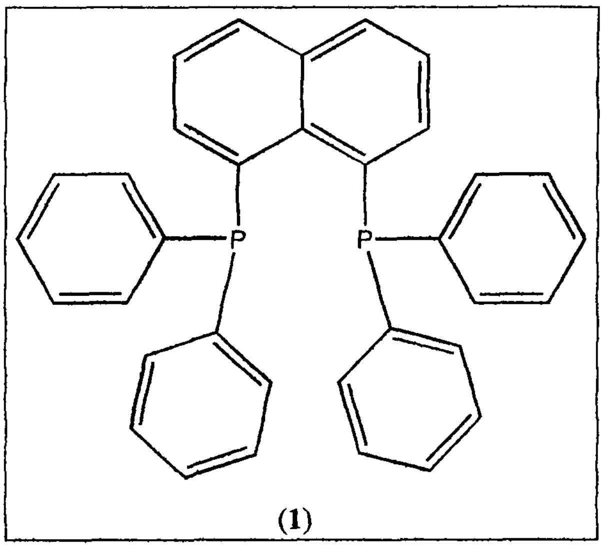
Do not do what is already done

Terence (BC. 185-159)

5.1 Introduction

This chapter deals with the synthesis of an unusual ligand (and its analogues) and the coordination of the ligand to metal centres. The ligand under investigation was 1,8-bis-(diphenylphosphino)naphthalene (dppn) (**1**), or naphthaphos (see Figure 5.1). The aromatic backbone and the stringent steric requirements of this bulky ligand made it an interesting and unusual ligand. Bidentate phosphines with aromatic backbones have already been shown to be useful ligands for palladium in the context of ethene carbonylation. [1] This ICI patent deals with ligands which have a separating unit between the phosphorus moiety and the aromatic backbone {for example the ligand $[(^tBu)_2P\text{-}CH_2\text{-}Ar\text{-}CH_2\text{-}P(^tBu)_2]$}. Our system has no such separating units, however. Note also that ^{t}Bu groups are very bulky, this is similar to the bulky PPh_2 substituents on dppn. The fact that the ligand (**1**) has a rigid aromatic backbone made it of interest to our own carbonylation studies.

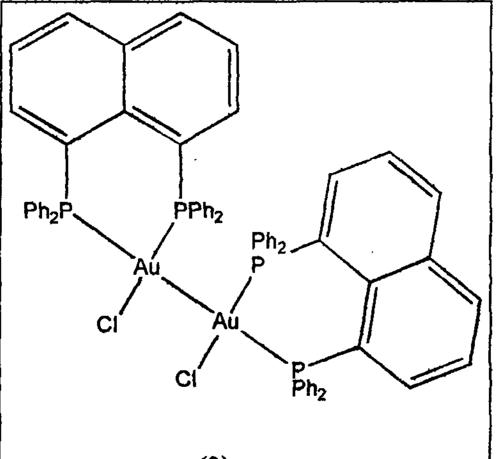
The ligand (**1**) was made originally by Jackson and co-workers who released a preliminary communication in 1993.[2a] Little other work has appeared in literature except for an improved synthesis in 1995,[2b] and a crystal structure of a palladium allyl complex. [3]



(1)

Figure 5.1

Recently, there has been a communication[4] with the structure of the gold dimer (**2**) shown in Figure 5.2 below.



(2)

Figure 5.2

The Au is in a nearly square planar arrangement, with a P-Au-P bite angle of 86°. This angle, as demonstrated later in this chapter, is close to what is thought to be the preferred bite angle for the ligand.

5.2 Experimental

Unless otherwise stated, all experimental work was carried out in a dry, inert atmosphere (N_2) using standard glove box, vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen. All chemicals were bought (from Aldrich, Acros or Lancaster) or synthesised and used without further purification. Experimental parameters can be found in Appendix 5

Experiment 5.2.1

Synthesis of 1, 8-bis-(diphenylphosphino)naphthalene (dppn).[2]

A 250 ml, 3-necked, round bottomed flask was fitted with a gas inlet and flushed with N_2. To the flask was added diethylether (20 ml, dry, degassed) and a solution of n-BuLi (1.6 M, 15 ml, 0.24 mol). The flask was cooled in an acetone/dry ice bath to -40°C before the addition of 1-bromonaphthalene (4.1 g, 0.02 mol) in one portion. The mixture was stirred and allowed to warm up to about 15 °C over about fifteen minutes. The white suspension was then cooled to below 0°C before cannula filtration. The solid left behind was washed three times with hexane (20 ml portions) and the liquid was carefully decanted under a counterflow of N_2. At this point a second equivalent of n-BuLi in (20ml hexane) was added. Immediately, one equivalent of TMEDA (N,N,N',N', -tetramethylethylenediamine) was added. The solution immediately darkened. The flask was fitted with a condenser with a nitrogen bubbler outlet. The mixture was refluxed for three and a half hours until the evolution of butane gas had stopped. The solution was then cooled before dry, degassed THF (20 ml) was added at -5°C. The flask was placed in an acetone/dry ice bath before the slow addition (over 5 min) of chlorodiphenylphosphine ($ClPPh_2$) (8.84g, 0.04 mol) and 10 ml THF, (dry, degassed) ensuring that the temperature remained at about -60°C. The dry ice bath was removed and the reaction was allowed to warm up to room temperature over 2 hours. The solution was poured into water (30 ml) and shaken vigorously before addition of dichloromethane to dissolve the yellow solid which had started to form. The layers were then separated and the dichloromethane layer was dried over $MgSO_4$. The organic layer was placed under reduced pressure to remove all the solvent before washing the resulting residue with ether. The yellow solid was separated from the solution by removing the liquid with a cannula filter. The solid was extracted into CH_2Cl_2 before being dried *in vacuo*. Yield, 42%, 4.2g. Found C, 75.21; H, 4.74%. $C_{34.5}H_{27}P_2Cl$ {dppn·[0.5(CH_2Cl_2)]} requires C, 76.88; H, 5.05%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -14.9$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 5.4$ (**1H**, s, CH_2Cl_2), 7.2 - 8.2 ppm (**26H**, m, Ph, naphthalene). Published data agrees with the NMR observations, but no elemental analyses were given in either of the original references. [2a, 2b]

Experiment 5.2.2

Improved route to dppn.

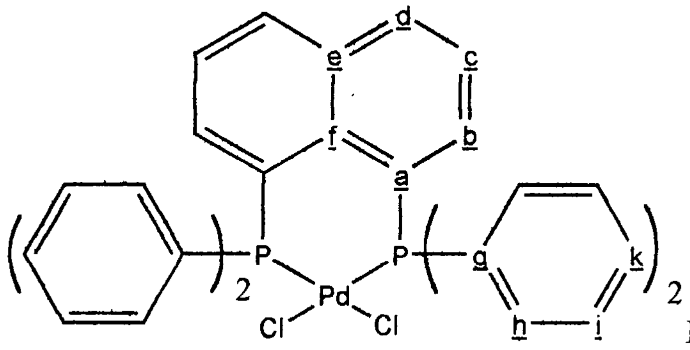
A 250 ml, 3-necked, round bottomed flask was fitted with a gas inlet and flushed with N_2. To the flask was added diethylether (20 ml, dry, degassed) and a solution of n-BuLi (1.6 M, 15 ml). The flask was cooled in an acetone/dry ice bath before the addition of 1-bromonaphthalene (4.1 g, 0.02 mol) in one portion. The mixture was stirred and allowed to warm up to about 15 °C over fifteen minutes. The white suspension was then cooled to below 0°C before cannula filtration. The resulting solid was washed three times with hexane (20 ml portions) and the washings were carefully decanted under a counterflow of N_2. At this point, 20 ml hexane (dry, degassed) was added before a second equivalent of n-BuLi was added. Immediately, one equivalent of N,N,N',N',-tetramethylethylenediamine (TMEDA) was added. The solution darkened. The flask was fitted with a condenser with a nitrogen bubbler outlet. The mixture was refluxed for three and a half hours until the evolution of butane gas had stopped. The solution was then cooled before tetrahydrofuran (20 ml) was added at -5°C. The flask was placed in an acetone /

dry ice bath before the slow addition (over 5 min) of chlorodiphenylphosphine ($ClPPh_2$) (8.82 g, 0.04 mol) and 10 ml diethyl ether, ensuring that the temperature remained at about -60°C. The dry ice bath was removed and the reaction was allowed to warm up to room temperature over 2 hours. The solution was taken to dryness under reduced pressure, before soxhlet extraction with first dichloromethane and then, after removing the dichloromethane under reduced pressure, extraction into toluene. The resulting yellow solution was then taken to dryness under reduced pressure. The yellow solid that remained was then analysed. Yield 6.26 g, 63%. Found C, 81.85 H, 5.11%. $C_{34}H_{26}P_2$ requires C, 82.25; H, 5.20%. ^1H NMR ($CDCl_3$) $\delta = 7.2 - 8.2$ ppm (**26H**, m, Ph, naphthalene). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -14.8$ ppm.

Experiment 5.2.3

Reaction of $[PdCl_2(PhCN)_2]$ with dppn.

$[PdCl_2(PhCN)_2]$ (0.1 g, 0.29 mmol) and $C_{34}H_{26}P_2$ (dppn) (0.14 g, 0.30 mmol) were placed in a clean, dry, 2-necked 100 ml nitrogen filled flask before toluene (30 ml, dry, degassed) was added. The reaction mixture was heated in an oil bath to 50°C and stirred for 2 hours at that temperature. There was formation of a yellow precipitate. The solution was filtered and the solid was washed with a portion of ether and a portion of hexane (10 ml each). The solid was dried *in vacuo*. Yield 0.16g, 82%. Found C, 61.02; H, 4.34%. $C_{34}H_{26}Cl_2P_2Pd$ requires C, 60.60; H, 3.90%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 21.0$ ppm (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 125.7$ ppm ($\underline{c}$, s), 127.6 ppm ($\underline{k}$, s) 128.3 ppm ($\underline{i}$, s), 131.1 ppm ($\underline{d}$, s), 133.9 ppm ($\underline{h}$, s), 134.5 ppm ($\underline{e}$, s), 137.7 ppm ($\underline{b}$, s) 138.4 ppm ($\underline{f}$, s). See key for assignments. ^{13}C $\{^1H\}$NMR assignments based on literature values[2] for free ligand. ^1H NMR ($CDCl_3$) $\delta = 7.1 - 7.5$ ppm (**26H**, m, Ph, naphthalene).



Key for ^{13}C assignments

Experiment 5.2.4

Reaction of dppn with $CoCl_2{\cdot}6(H_2O)$

Dppn (0.2 g, 0.43 mmol) and $CoCl_2{\cdot}6(H_2O)$ (0.1g, 0.42 mmol) were placed in a 2-necked nitrogen filled round bottomed flask. To this mixture was added ethanol (30 ml, dry, degassed). The mixture was stirred at room temperature for 2 hours. The solution turned from blue to purple. After the 2 hours had elapsed it was observed that a purple precipitate had formed in the blue solution. The blue solution was removed by means of a cannula filter and the purple solid was washed with ethanol. The blue solution was the minor product. The dark purple solid was found to be insoluble in all solvents tried and was thought to be a polymeric octahedral species (see Figure 5.3). The elemental analysis, however was not very satisfactory for the proposed polymeric complex. Found C, 70.02; H, 4.34%. $(C_{34}H_{26}Cl_2P_2Co)_n$ requires C, 65.20; H, 4.18%. Suspension of the purple solid in dichloromethane (especially in the presence of small quantities of oxygen) however, caused a gradual transformation into a blue oxo species. Crystals grown from this blue solution were analysed as $[CoCl_2(Ph_2P(O)\text{-}C_{10}H_6\text{-}PPh_2)]{\cdot}(CH_2Cl_2)_2$. Found C, 53.48; H, 4.08%. $C_{36}H_{30}Cl_6CoOP_2$ requires C, 53.24; H, 3.72%. IR $\nu_{PO} = 1272\ cm^{-1}$. The crystals grown were found to be suitable for X-Ray analysis. The crystal structure (shown in Figure 5.4) was solved by Dr. C.W. Lehmann. Selected bond length and angle data for the structure follow in Tables 5.1 and 5.2 respectively.

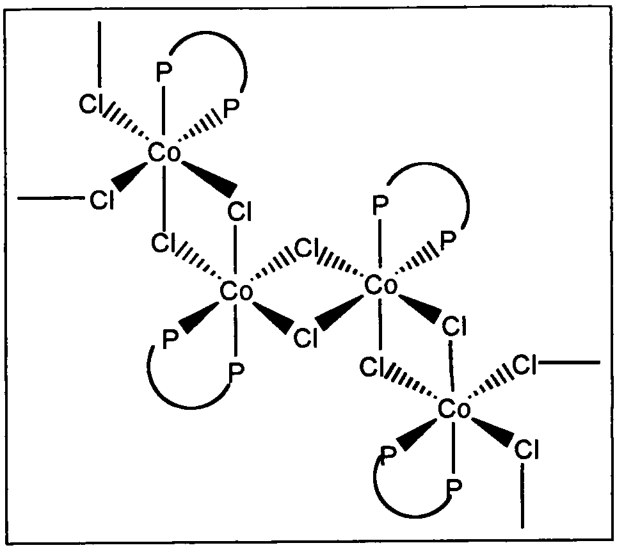


Figure 5.3

Table 5.1 Selected bond lengths for $[CoCl_2(Ph_2P(O)\text{-}C_{10}H_6\text{-}PPh_2)]\cdot(CH_2Cl_2)_2$

Bond	Length/Å(error)	Bond	Length/Å(error)
Co(1)-O(1)	1.958(2)	Co(1)-Cl(2)	2.2285(10)
Co(1)-Cl(1)	2.2396(11)	Co(1)-P(1)	2.4067(11)
P(1)-C(21)	1.825(4)	P(1)-C(11)	1.832(4)
P(1)-C(1)	1.858(4)	P(2)-O(1)	1.516(2)
P(2)-C(8)	1.819(4)	C(1)-C(2)	1.383(5)
C(1)-C(8A)	1.448(5)	C(2)-C(3)	1.405(5)
C(3)-C(4)	1.354(6)	C(4)-C(4A)	1.419(5)
C(4A)-C(5)	1.415(5)	C(4A)-C(8A)	1.446(5)
C(5)-C(6)	1.353(6)	C(6)-C(7)	1.417(5)
C(7)-C(8)	1.389(5)	C(8)-C(8A)	1.446(5)

Figure 5.4 Crystal Structure of $[CoCl_2(Ph_2P(O)\text{-}C_{10}H_6\text{-}PPh_2)]\cdot(CH_2Cl_2)_2$

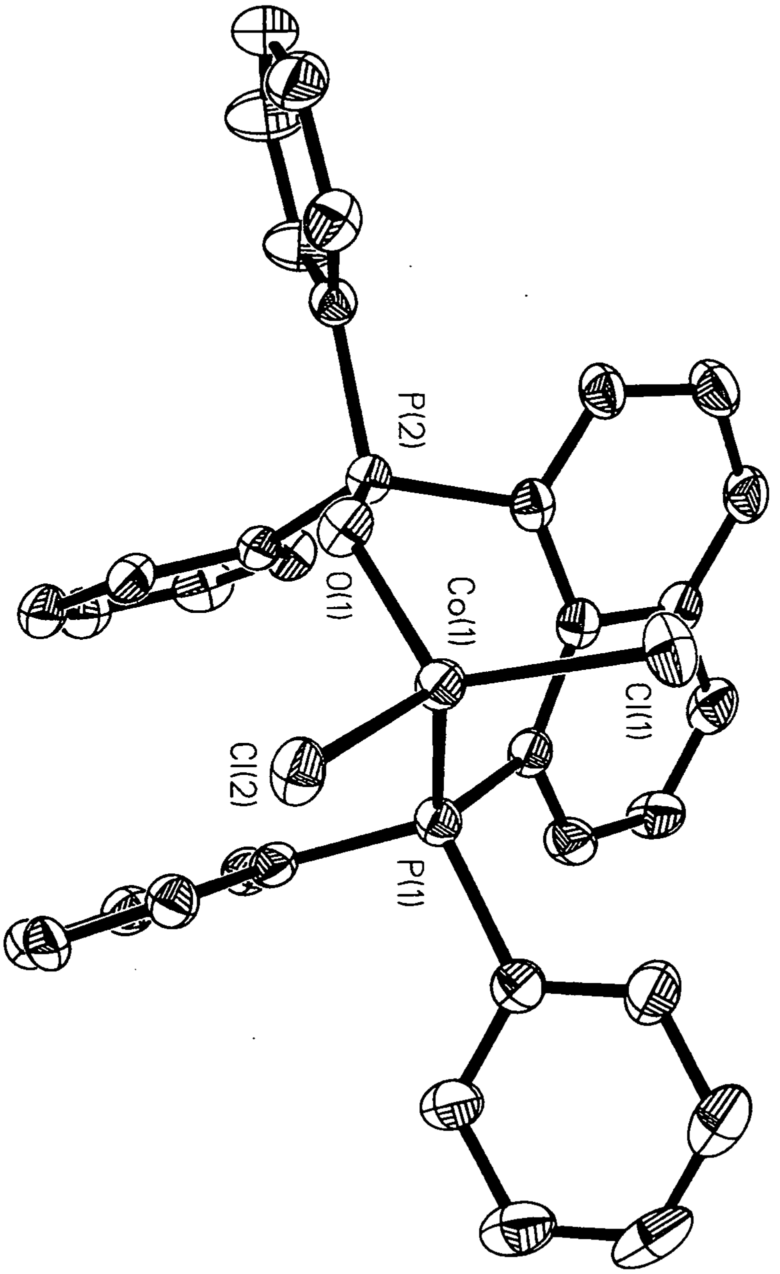


Table 5.2 Selected bond angles for $[CoCl_2(Ph_2P(O)\text{-}C_{10}H_6\text{-}PPh_2)]\cdot(CH_2Cl_2)_2$

Atoms	Angle/° (error)	Atoms	Angle/° (error)
O(1)-Co(1)-Cl(2)	108.59(7)	O(1)-Co(1)-Cl(1)	116.70(8)
Cl(1)-Co(1)-Cl(2)	112.44(4)	O(1)-Co(1)-P(1)	95.28(8)
Cl(2)-Co(1)-P(1)	114.40(4)	Cl(1)-Co(1)-P(1)	108.46(4)
C(21)-P(1)-C(11)	102.3(2)	C(21)-P(1)-C(1)	108.5(2)
C(11)-P(1)-C(1)	102.3(2)	C(21)-P(1)-Co(1)	114.64(12)
C(11)-P(1)Co(1)	112.02(13)	C(1)-P(1)-Co(1)	115.59(12)
O(1)-P(2)-C(41)	113.5(2)	O(1)-P(2)-C(31)	106.7(2)
C(41)-P(2)-C(31)	104.8(2)	O(1)-P(2)-C(8)	115.1(2)
C(41)-P(2)-C(8)	107.6(2)	C(31)-P(2)-C(8)	108.6(2)
P(2)-O(1)-Co(1)	127.5(2)	C(2)-C(1)-C((8A)	119.3(3)
C(2)-C(1)-P(1)	114.4(3)	C(8A)-C(1)-P(1)	125.0(3)
C(1)-C(2)-C(3)	122.9(4)	C(4)-C(3)-C(2)	118.9(4)
C(3)-C(4)-C(4A)	121.2(4)	C(5)-C(4A)-C(4)	118.9(3)
C(5)-C(4A)-C(bA)	120.6(3)	C(4)-C(4A)-C(8A)	120.5(3)
C(6)-C(5)-C(4A)	122.0(3)	C(5)-C(6)-C(7)	118.2(4)
C(8)-C(7)-C(6)	122.3(4)	C(7)-C(8)-C(8A)	120.1(3)
C(7)-C(8)-P(2)	113.5(3)	C(8A)-C(8)-P(2)	125.8(3)
C(8)-C(8A)-C(4A)	115.5(3)	C(8)-C(8A)-C(1)	128.4(3)
C(4A)-C(8A)-C(1)	116.1(3)		

Experiment 5.2.5

Reaction of dppn with anhydrous $NiCl_2$

Yellow, anhydrous $NiCl_2$ (0.2 g, 1.5 mmol) and dppn (0.8 g, 1.6 mmol) were placed in a 2-necked round bottomed, nitrogen filled flask. To the flask was added ethanol (25 ml, dry, degassed). The mixture was stirred at 40°C for 2 hours. After this time, the solution had turned orange and there was formation of an orange precipitate. The volume of solvent was taken down under reduced pressure to about 5 ml. The orange solid was then removed by filtration and washed with ethanol before analysis. Found C, 65.64; H, 4.43%. $C_{34}H_{26}Cl_2P_2Ni$ requires C, 65.22; H, 4.19%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 34.2$ ppm (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 125.9$ ppm (s), 128.1 ppm (s), 131.2 ppm (s), 134.0 ppm (s), 135.3 ppm (s), 140.4 ppm (s). ^1H NMR ($CDCl_3$) $\delta = 7.2$- 8.0 ppm (**26H**, m, Ph, naphthalene). A crystal suitable for X-Ray diffraction was grown from $CHCl_3$ and structurally analysed by Dr. C.W. Lehmann. The crystal structure is shown in Figure 5.5. A selection of the bond lengths and angles follows (Tables 5.3 and 5.4 respectively). Mass spectrum m/z (+ve ions): 591 (100%, M^+- Cl), 514 (40%, M^+ - Cl, -Ph), 441, (10%, M^+ - PPh_2)

Table 5.3 Selected bond lengths for $[NiCl_2(Ph_2P\text{-}C_{10}H_6\text{-}PPh_2)]\cdot(CHCl_3)$

Bond	Length (Å)	Bond	Length (Å)
Ni(1)-P(2)	2.1627(11)	Ni(1)-P(1)	2.1641(11)
Ni(1)-Cl(2)	2.1986(11)	Ni(1)-Cl(1)	2.2033(11)
P(1)-C(11)	1.824(4)	P(1)-C(21)	1.824(4)
P(1)-C(1)	1.835(4)	P(2)-C(41)	1.825(4)
P(2)-C(8)	1.827(4)	P(2)-C(31)	1.829(4)
C(1)-C(2)	1.378(6)	C(1)-C(8A)	1.439(5)
C(2)-C(3)	1.409(6)	C(3)-C(4)	1.336(7)
C(4)-C(4A)	1.413(6)	C(4A)-C(5)	1.414(6)
C(4A)-C(8A)	1.444(5)	C(5)-C(6)	1.358(6)
C(6)-C(7)	1.405(6)	C(7)-C(8)	1.385(5)
C(8)-C(8A)	1.433(5)		

Figure 5.5 Crystal Structure of [$NiCl_2(Ph_2P-C_{10}H_6-PPh_2)$]·($CHCl_3$)

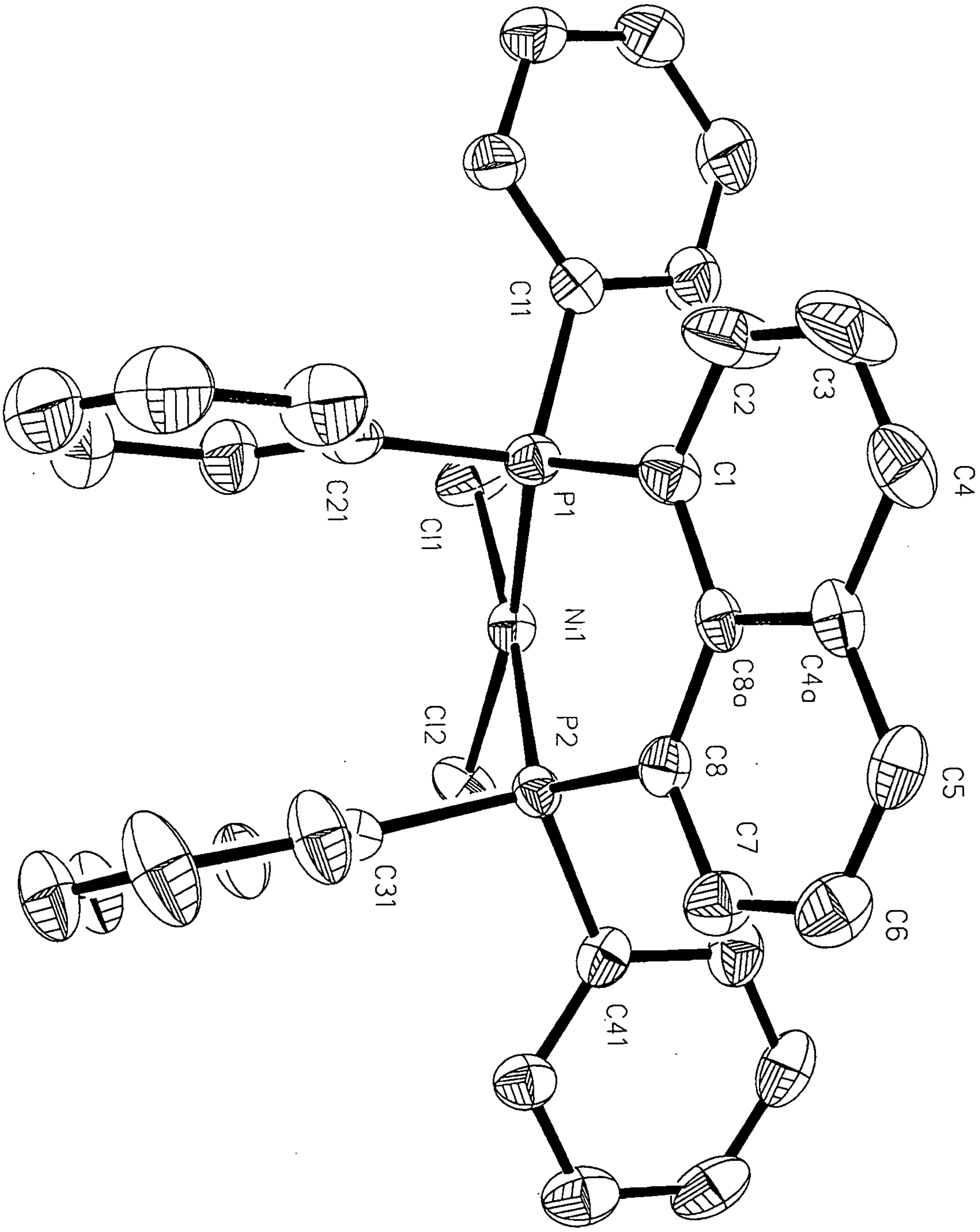


Table 5.4 Selected bond angles for $[NiCl_2(Ph_2P\text{-}C_{10}H_6\text{-}PPh_2)]\cdot(CHCl_3)$

Atoms	Angle/° (error)	Atoms	Angle/° (error)
P(2)-Ni(1)-P(1)	89.47(4)	P(2)-Ni(1)-Cl(2)	88.74(4)
P(1)-Ni(1)-Cl(2)	172.17(5)	P(2)-Ni(1)-Cl(1)	176.13(5)
P(1)-Ni(1)-Cl(1)	91.22(4)	Cl(2)-Ni(1)-Cl(1)	90.06(4)
C(11)-P(1)-C(21)	106.2(2)	C(11)-P(1)-C(21)	102.0(2)
C(21)-P(1)-C(1)	105.1(2)	C(11)-P(1)-Ni(1)	115.25(13)
C(21)-P(1)-Ni(1)	106.95(14)	C(1)-P(1)-Ni(1)	120.17(13)
C(41)-P(2)-C(8)	101.5(2)	C(41)-P(2)-C(31)	106.8(2)
C(8)-P(2)-C(31)	105.1(2)	C(41)-P(2)-Ni(1)	113.28(13)
C(8)-P(2)-Ni(1)	120.35(13)	C(31)-P(2)-Ni(1)	108.82(12)
C(2)-C(1)-C(8A)	119.2(4)	C(2)-C(1)-P(1)	116.8(3)
C(8A)-C(1)-P(1)	124.0(3)	C(1)-C(2)-C(3)	122.5(4)
C(4)-C(3)-C(2)	119.7(4)	C(3)-C(4)-C(4A)	121.3(4)
C(4)-C(4A)-C(5)	119.3(4)	C(4)-C(4A)-C(8A)	120.3(4)
C(5)-C(4A)-C(8A)	120.4(4)	C(6)-C(5)-C(4A)	120.8(4)
C(5)-C(6)-C(7)	119.5(4)	C(8)-C(7)-C(6)	122.7(4)
C(7)-C(8)-C(8A)	119.0(3)	C(7)-C(8)-P(2)	115.1(3)
C(8A)-C(8)-P(2)	125.9(3)	C(8)-C(8A)-C(1)	125.5(3)
C(8)-C(8A)-C(4A)	117.5(3)	C(1)-C(8A)-C(4A)	117.0(3)

Experiment 5.2.6

Reaction of $[PtCl_2(PhCN)_2]$ with dppn.

$[PtCl_2(PhCN)_2]$ (0.1g, 0.21 mmol) and $C_{34}H_{26}P_2$ (dppn) (0.11g, 0.21 mmol) were placed in a clean, dry, 2-necked 100 ml nitrogen filled flask before toluene (30 ml, dry, degassed) was added. The reaction was heated in an oil bath to 50°C and stirred for 2 hours at that temperature. There was formation of a yellow precipitate. Solvent was removed by filtration and the remaining solid was washed with a portion of ether and a portion of methanol (10 ml each). The solid was dried *in vacuo*. Found C, 52.32; H, 3.04%. $C_{34}H_{26}Cl_2P_2Pt$ requires C, 53.56; H, 3.44%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 1.6$ ppm (s & d, $J_{Pt-P} = 3312$ Hz). ^1H NMR ($CDCl_3$) $\delta =$ 7.2 - 8.2 ppm (**26H**, m, Ph).

Experiment 5.2.7

Reaction of $Pd(OAc)_2$ with dppn

Brown palladium acetate (0.1g, 0.5 mmol) was placed in a 2-necked round bottomed flask flushed with nitrogen before being dissolved in 5 ml of dry degassed toluene. In a separate flask the dppn ligand (0.25g, 0.5 mmol) was dissolved in 10 ml toluene (dry and degassed). Upon stirring, the mixture rapidly developed a light coloured precipitate. The mixture was stirred at room temperature for a total of three hours. After this time, the dark coloured solution was filtered leaving an off white solid. The solid was washed three times with diethyl ether (3 x 5 ml portions) before analysis. Found C, 63.77; H, 4.77%. $C_{38}H_{32}O_4P_2Pd$ requires C, 63.33; H 4.40%. $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 26.1$ ppm (s). ^1H NMR (CD_3CN) $\delta =$ 2.4 ppm (**6H**, s, OAc), 7.1-7.7 ppm (**24H**, m, aromatic), 8.4 ppm (**2H**, m, aromatic). Mass spectrum m/z (+ve ions): 661 (100%, M^+ - OAc), 601 (45%, M^+ - 2 (OAc)), 524 (10%, M^+ - 2(OAc) - Ph), 418 (70%, M^+ - 2(OAc) -Ph -Pd).

Experiment 5.2.8

Reaction of $[Pd(MeCN)_4](BF_4)_2$ with dppn

Dppn (0.13g, 0.26 mmol) was dissolved in toluene (20 ml, dry, degassed) in a clean dry nitrogen flushed, round bottomed flask. In a separate similarly prepared flask, $[Pd(MeCN)_4](BF_4)_2$ (0.1g, 0.23 mmol) was dissolved in 5 ml of dry degassed acetonitrile. Both flasks were cooled in a dry ice/acetone bath before the phosphine solution was transferred by cannula to the flask containing the acetonitrile complex, over a period of about five minutes. During this time, the solution started to change colour from yellow to orange/red. The mixture was stirred at between -10°C and -20 °C for 2 hours and then allowed to warm slowly to room temperature. At the end of this period, a small amount of red precipitate was observed. Solvent was removed under reduced pressure to about one third volume. It was observed that no red colouration remained in solution and the solvent was removed by syringe under a counterflow of nitrogen. The gummy red solid which remained was washed with diethylether, hexane and dried *in vacuo* before re-dissolving in acetonitrile. The acetonitrile was removed under reduced pressure, before drying *in vacuo*. The resulting product $[Pd(MeCN)_2(dppn)](BF_4)_2$ was an orange/red crystalline solid. Found C, 53.66; H, 3.56%. $C_{38}H_{32}B_2F_8N_2P_2Pd$ requires C, 53.15; H, 3.76%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 21.7$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 2.3$ ppm (**6H**, s, MeCN), 7.2 - 8.2 ppm (**26H**, m, Ph, naphthalene).

Experiment 5.2.9

Reaction of $[Pd(MeCN)_2(dppn)](BF_4)_2$ with dppe.

$[Pd(MeCN)_2(dppn)](BF_4)_2$ (0.1g, 0.13 mmol) was placed in a clean, dry 2-necked round bottomed nitrogen flushed flask and then dissolved in 2ml of MeCN (dry, degassed) before the addition of a pre-prepared solution of dppe (0.11g, 0.28 mmol) in CH_2Cl_2 (10 ml, dry, degassed). The mixture was stirred briskly at room temperature. After twenty minutes a precipitate was observed. The solution was stirred for a total of two hours after which time more of the off-white precipitate had formed. The liquor was removed by cannula filtration before the grey solid was washed with two portions of dichloromethane. The grey solid was dried *in vacuo* then weighed and analysed. The solid was found to be the complex $[Pd(dppe)_2](BF_4)_2$. Found C, 57.82; H, 4.68%. $C_{52}H_{48}B_2F_8P_4Pd$ requires C, 58.00; H, 4.49%. $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 58.4$ ppm (s). ^1H NMR (CD_3CN) $\delta = 2.5$ ppm (**8H**, d, $^2J_{PH}$= 15 Hz, PCH_2), 7.1 - 7.8 ppm (**40H**, m, Ph).

Experiment 5.2.10

Reaction of $[Pd(MeCN)_2(dppn)](BF_4)_2$ with dppm

$[Pd(MeCN)_2(dppn)](BF_4)_2$ (0.15g, 0.17 mmol) was placed in a clean, dry 2-necked round bottomed nitrogen flushed flask and then dissolved in 2ml of MeCN (dry, degassed) before the addition of a pre-prepared solution of dppm (0.08g, 0.21mmol) in CH_2Cl_2 (10 ml, dry, degassed). The mixture was stirred briskly at room temperature. The red mixture was taken to dryness under reduced pressure and then washed with ether and toluene before the remaining solid was analysed. The white solid was found to be $[Pd(dppm)_2](BF_4)_2$. Found C, 56.54; H, 4.04%. $C_{50}H_{44}B_2F_8P_4Pd$ requires C, 57.26; H, 4.23%. ^{31}P $\{^1H\}$ NMR (CD_3CN) $\delta = -32.4$ ppm.[5b] ^1H NMR (CD_3CN) $\delta = 2.7$ ppm (**4H**, d, $^2J_{PH} = 13$ Hz, PCH_2), $\delta = 7.3 - 7.7$ ppm (**40H**, m, Ph).

Experiment 5.2.11

Reaction of $[Pd(MeCN)_2(dppn)](BF_4)_2$ with PPh_3.

$[Pd(MeCN)_2(dppn)](BF_4)_2$ (0.15g, 0.17 mmol) was placed in a clean, dry 2-necked round bottomed, nitrogen flushed flask and then dissolved in 2ml of MeCN (dry, degassed) before the addition of a pre-prepared solution of 2 equivalents of PPh_3 (0.08g, 0.3 mmol) in CH_2Cl_2 (10 ml, dry, degassed). The mixture was stirred briskly at room temperature. After twenty minutes a colour change was observed from red to orange. The solution was stirred for a total of two hours. The orange solution was taken to dryness under reduced pressure and then a sample was dissolved in $CDCl_3$ before placing the sample in an NMR tube. The resulting $^{31}P\{^1H\}$ NMR spectrum gave a mixture of signals including doublets at 35.6 ppm and 28.5 ppm. This system is further discussed in section 5.3.

Experiment 5.2.12

NMR scale reaction of $[Ni(Cl)_2(dppn)]$ with dppe

A sample of $[NiCl_2(dppn)]$ (0.01g, 0.02 mmol) was placed in an NMR tube, and dissolved in chloroform. The $^{31}P\{^1H\}$ NMR phosphorus spectrum was taken at this point and showed the expected signal at 33 ppm. To the tube was added one equivalent of dppe (0.007g, 0.02 mmol). The mixture was agitated frequently at 60°C over two hours before its phosphorus NMR was taken. The sample showed several peaks. Peaks were observed for free dppn (-15 ppm), free dppe (-12 ppm), $[Ni(Cl)_2(dppn)]$ (33 ppm) and $[Ni(Cl)_2(dppe)]$ (57 ppm). The reaction was heated in an oil bath for another hour. The peaks at 57 ppm and 33 ppm were now of equal intensity. The solution was refluxed for several more hours, but no more change was observed. Upon addition of a large excess of dppe (0.05g, 0.12 mmol), a new peak appeared at 49 ppm, to the detriment of the peaks at 57 ppm and 33 ppm. Finally, with further heating, most of the peak at 33 ppm, and all of the peak at 57 ppm disappeared, giving a strong signal at 49 ppm (attributed to $[Ni(dppe)_2]^{2+}$) as well as signals for the free phosphines at -12 ppm (dppe) and -15 ppm (dppn). These observations are considered in the discussion section (section 5.3)

Experiment 5.2.13

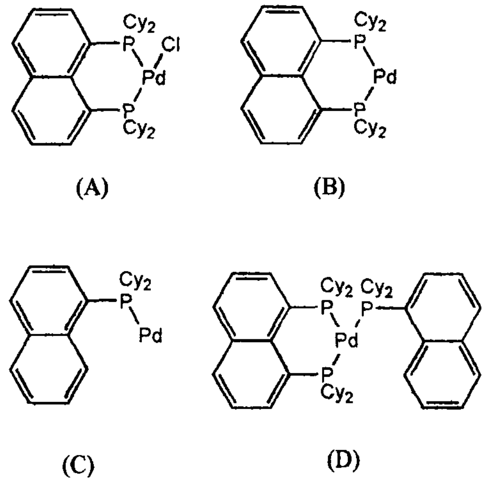
Synthesis of 1,8-bis-dicyclohexylphosphinonaphthalene (dcpn)

A 250 ml, 3-necked, round bottomed flask was fitted with a gas inlet and flushed with N_2. To the flask was added diethylether (20 ml, dry, degassed) and a solution of n-BuLi (1.6 M, 15 ml). The flask was cooled in an acetone/dry ice bath before the addition of 1-bromonaphthalene (4.1g, 0.02 mol) in one portion. The mixture was stirred and allowed to warm up to about 15 °C over about fifteen minutes. The white suspension was then cooled to below 0°C before cannula filtration. The solid was washed three times with hexane (20 ml portions) and the liquid was carefully decanted under a counterflow of N_2. At this point a second equivalent of n-BuLi in 20 ml hexane was added. Immediately, one equivalent of N,N,N',N',-tetramethylethylenediamine (TMEDA) was added, causing the solution to darken. The flask was fitted with a condenser with a nitrogen bubbler outlet. The mixture was refluxed for three and a half hours until the evolution of butane gas had stopped. The solution was then cooled before tetrahydrofuran (20 ml, dry, degassed) was added at -5°C. The flask was placed in an acetone/dry ice bath before the slow addition (over 5 min) of one equivalent of chloro-dicyclohexylphosphine ($ClPCy_2$) (9.3g, 0.04 mol) and 10 ml diethyl ether (dry, degassed), ensuring that the temperature remained at about -60°C. The dry ice bath was removed and the reaction mixture was allowed to warm up to room temperature over 2 hours. The solution was taken to dryness under reduced pressure, before soxhlet extraction with toluene. The resulting yellow solution was then taken to dryness under reduced pressure. The air sensitive yellow solid that remained was then analysed. Found C, 77.62; H, 9.76%. $C_{34}H_{50}P_2$ requires C, 78.41; H, 9.68%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -15.1$ ppm (s). ^1H NMR ($CDCl_3$) $\delta =$ 7.2 - 8.2 ppm (**6H**, m, naphthalene), 1.3 - 2.0 ppm (**44H**, m, Cy).

Experiment 5.2.14

Synthesis of [$PdCl_2$(dcpn)]

[$PdCl_2(PhCN)_2$] (0.1 g, 0.29 mmol) and dcpn (0.14 g, 0.30 mmol) were placed in a clean, dry, 2-necked 100 ml nitrogen filled flask before toluene (30 ml, dry, degassed) was added. The reaction was stirred for 2 hours at room temperature. Solvent was then removed under reduced pressure, before drying *in vacuo*. The yellow solid was then washed repeatedly with diethyl ether. The solid was again dried *in vacuo*. Found C, 58.61; H, 7.52%. $C_{34}H_{50}Cl_2P_2Pd$ requires C, 58.50; H, 7.23%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 36.6$ ppm (s). $^{13}C\ \{^1H\}$ NMR $\delta = 25.7$ ppm (s, Cy), 27.1 ppm (d, Cy), 30.1 ppm (s, Cy), 29.7 ppm (s, Cy), 39.8 ppm (s, Cy). 40.0 ppm (s, Cy), 124.3 ppm (s, naphthalene), 133.5 ppm (s, naphthalene), 133.8 ppm (s, naphthalene). ^1H NMR ($CDCl_3$) $\delta = 7.1$ -7.5 ppm (**6H** m, naphthalene), 1.3 - 2.0 ppm (**44H**, m, Cy). Mass spectrum m/z (+ve ions): 661 (35%, A), 626 (10%, B), 429 (35% ,C) - see following key for assignments. A peak at 949 mass units was also observed and was assigned to a recombination product (D in the key below)



Key for assignments of mass spectrum from experiment 5.2.14

Experiment 5.2.15

Synthesis of $[Pd(MeCN)_2(dcpn)](BF_4)_2$

$[Pd(MeCN)_4](BF_4)_2$ (0.1g, 0.23 mmol) was placed in a dry flask and to it was added 20 ml dichloromethane (dry, degassed). The flask was cooled to - 20°C. To the flask was added a pre-cooled solution of dcpn (0.11g, 0.21 mmol) in dichloromethane (10 ml). The mixture was stirred at -20°C for half an hour before being allowed to warm up to room temperature. Once at room temperature, the resulting yellow solution was placed under reduced pressure before drying *in vacuo*. The resulting yellow solid was washed several times with ether. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 43.9$ ppm(s). ^1H NMR ($CDCl_3$) $\delta = 1.3 - 2.5$ ppm (**44H**, br, m, Cy), 7.7 - 8.4 ppm (**6H**, m, naphthalene).

Experiment 5.2.16

NMR Reaction of $[Pd(MeCN)_2(dcpn)](BF_4)_2$ with dppe

$[Pd(MeCN)_2(dcpn)](BF_4)_2$ (0.02 g, 0.05 mmol) was placed in a small flask. To the flask was added a slight excess of dppe (0.03 g, 0.07 mmol). The mixture was then dissolved in dichloromethane (10 ml, dry, degassed) before monitoring with $^{31}P\{^1H\}$ NMR. The starting material showed a $^{31}P\{^1H\}$ signal at 43.9 ppm. The first $^{31}P\{^1H\}$NMR spectrum after adding the dppe showed the presence of dppe (-12 ppm), dcpn (-15 ppm) and a small quantity of the phosphine oxide dcpo (44.7 ppm) as well as the starting material at 43.9 ppm. There was formation of an off-white precipitate. The solution was decanted and the remaining white precipitate of $[Pd(dppe)_2](BF_4)_2$ was washed with dichloromethane before it was analysed. Found C, 58.55; H, 4.36%. $C_{52}H_{48}B_2F_8P_2Pd$ requires C, 58.00; H, 4.49%. $^{31}P\{^1H\}$NMR (CD_3CN) $\delta = 57.1$ ppm. ^1H NMR (CD_3CN) $\delta = 2.4$ ppm (**8H**, d, $J_{PH} = 17$ Hz, PCH_2), $\delta = 7.2 - 7.8$ ppm (**40H**, m, Ph).

Experiment 5.2.17

NMR Reaction of $[Pd(MeCN)_2(dcpn)](BF_4)_2$ with dppm

$[Pd(MeCN)_2(dcpn)](BF_4)_2$ (0.02 g, 0.023 mmol) was placed in an NMR tube and to the tube was added a small portion of dppm. The mixture was then dissolved in dichloromethane before monitoring with $^{31}P\{^1H\}$ NMR. The initial spectrum showed signals at 44.7 ppm (dcpo - the phosphine oxide of dcpn), -23 ppm (free dppm) and -32.5 ppm $\{[Pd(dppm)_2]^{2+}\}$.[5b]

Experiment 5.2.18

Synthesis of dppn dioxide (dpno)

1,8-bis(diphenylphosphino)naphthalene (dppn) (0.2g, 0.5 mmol) was weighed into a clean, dry two necked round bottomed flask before being dissolved in 20 ml toluene (dry, not de-oxygenated). The mixture was allowed to stand in air for approximately one week. During this time there was a colour change from yellow to colourless accompanied by the precipitation of a colourless crystalline solid. Some of these crystals were suitable for X-ray analysis. Structural analysis was carried out by Dr. C.W. Lehmann. The crystal structure is shown in Figure 5.6. Selected crystal structure data follows in Tables 5.5 and 5.6. The remainder of the solution was taken to dryness, washed with toluene and ether (twice, until all yellow colouration had gone) and analysed. Found C, 77.17; H, 4.97%. $C_{34}H_{26}O_2P_2$ requires C, 77.27; H, 4.96%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 31.2$ ppm. ^1H NMR ($CDCl_3$) $\delta = 7.1 - 8.2$ ppm (**26H**, m, Ar). IR ν_{PO} (KBr disk) = 1376 cm^{-1}.

Experiment 5.2.19 Synthesis of dcpn dioxide (dcno).

A sample of dcpn (0.05 g, 0.10 mmol) was weighed into a flask and dissolved in the minimum amount of toluene. Once dissolved, the phosphine solution was exposed to air and allowed to stand at room temperature for several days until the yellow colouration had disappeared to give a clear, colourless solution. The solvent was removed under vacuum to give an off-white solid which was washed with ether before analysis. Yield 0.04g, 78%. Found C, 73.79; H, 9.32%. $C_{34}H_{50}O_2P_2$ requires C, 73.88; H, 9.12%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 44.7$ ppm (s). ^1H NMR ($CDCl_3$) $\delta = 1.4 - 2.2$ ppm (**44H**, m, Cy), 7.2 - 8.1 ppm (**6H**, m, naphthalene), $\nu_{PO} = 1277$ cm^{-1}.

Table 5.5 Selected bond lengths for ($Ph_2P(O)$-C_6H_{10}-$P(O)Ph_2$)

Bond	Length/Å(error)	Bond	Length/Å(error)
P(1)-O(1)	1.488(5)	P(1)-C(21)	1.803(7)
P(1)-C(11)	1.824(6)	P(1)-C(1)	1.830(7)
P(2)-O(2)	1.494(4)	P(2)-C(41)	1.798(6)
P(2)-C(8)	1.822(6)	P(2)-C(31)	1.825(6)
C(1)-C(2)	1.377(9)	C(1)-C(8A)	1.445(8)
C(2)-C(3)	1.403(9)	C(3)-C(4)	1.371(8)
C(4)-C(4A)	1.410(9)	C(4A)-C(5)	1.428(8)
C(4A)-C(8A)	1.444(9)	C(5)-C(6)	1.352(9)
C(6)-C(7)	1.419(9)	C(7)-C(8)	1.377(8)
C(8)-C(8A)	1.451(8)	P(1')-O(1')	1.491(4)
P(1')-C(1')	1.812(6)	P(1')-C(11')	1.823(7)
P(1')-C(21')	1.830(7)	P(2')-O(2')	1.490(4)
P(2')-C(41')	1.814(7)	P(2')-C(8')	1.816(8)
P(2')-C(31')	1.824(6)	C(1')-C(2')	1.399(9)
C(1')-C(8A')	1.446(8)	C(2')-C(3')	1.415(10)
C(3')-C(4')	1.340(9)	C(4')-C(4A')	1.429(9)
C(4A')-C(5')	1.396(8)	C(4A')-C(8A')	1.434(10)
C(5')-C(6')	1.348(9)	C(6')-C(7')	1.419(10)
C(7')-C(8')	1.379(8)	C(8')-C(8A')	1.442(9)

Figure 5.6 Crystal Structure of [$Ph_2P(O)$-$C_{10}H_6$-$P(O)Ph_2$]

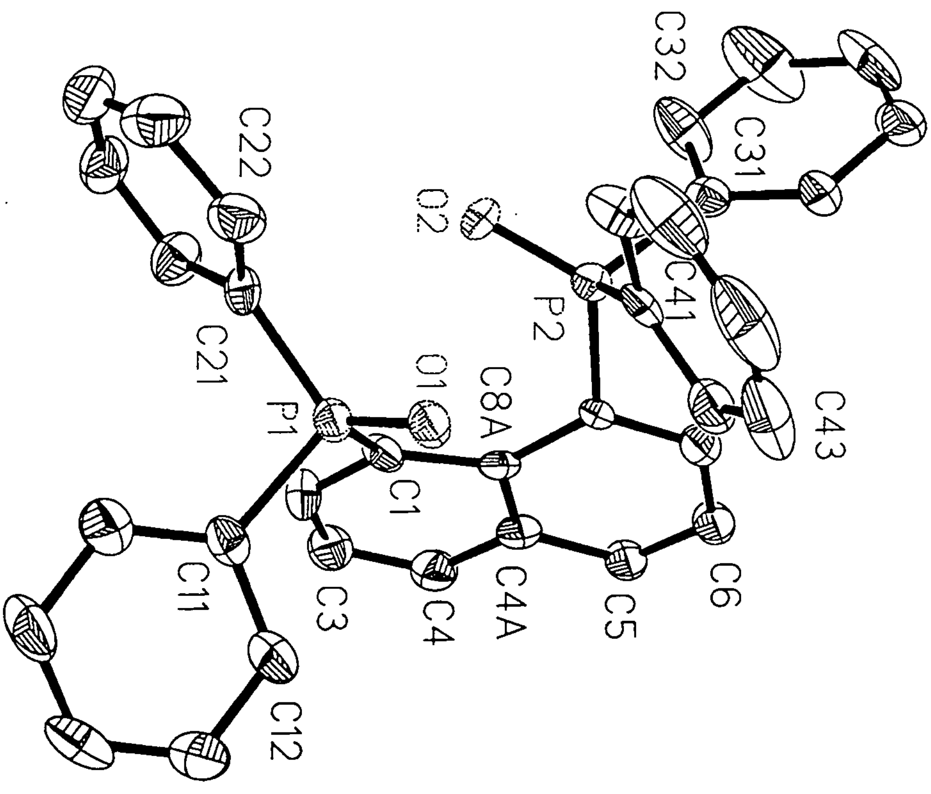


Table 5.6 Selected bond angles for [$PPh_2P(O)$-C_6H_{10}-$P(O)PPh_2$]

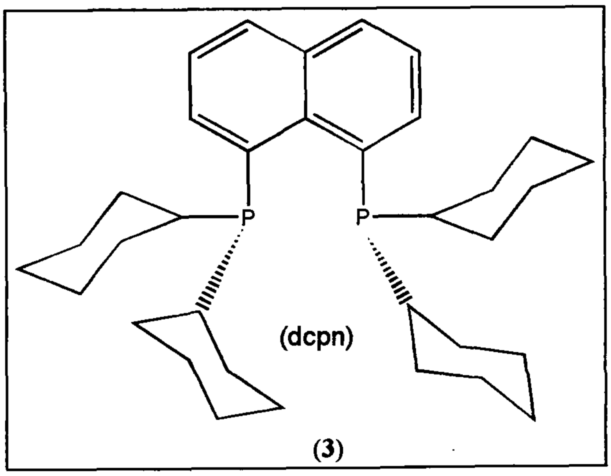
Atoms	Angle/° (error)	Atoms	Angle/° (error)
O(1)-P(1)-C(21)	115.8(3)	O(1)-P(1)-C(11)	107.9(3)
C(21)-P(1)-C(11)	104.3(3)	O(1)-P(1)-C(1)	113.2(3)
C(21)-P(1)-C(1)	111.6(3)	C(11)-P(1)-C(1)	102.6(3)
O(2)-P(2)-C(41)	117.2(3)	O(2)-P(2)-C(8)	113.0(3)
C(41)-P(2)-C(8)	110.1(3)	O(2)-P(2)-C(31)	109.2(3)
C(8)-P(2)-C(31)	109.2(3)	C(2)-C(1)-C(8A)	119.8(6)
C(2)-C(1)-P(1)	115.2(4)	C(8A)-C(1)-P(1)	122.5(5)
C(1)-C(2)-C(3)	123.0(6)	C(4)-C(3)-C(2)	118.7(6)
C(3)-C(4)-C(4A)	120.4(7)	C(4)-C(4A)-C(5)	118.9(6)
C(4)-C(4A)-C(8A)	121.6(6)	C(5)-C(4A)-C(8A)	119.5(6)
C(6)-C(5)-C(4A)	121.6(7)	C(5)-C(6)-C(7)	118.7(6)
C(8)-C(7)-C(6)	123.1(6)	C(7)-C(8)-C(8A)	118.8(6)
C(7)-C(8)-P(2)	116.1(5)	C(8A)-C(8)-P(2)	123.4(4)
C(4A)-C(8A)-C(1)	115.8(6)	C(4A)-C(8A)-C(8)	117.3(5)
C(1)-C(8A)-C(8)	126.9(6)	O(1')-P(1')-C(1')	113.2(3)
O(1')-P(1')-C(11')	108.3(3)	C(1')-P(1')-C(11')	108.3(3)
O(1')-P(1')-C(21')	116.1(3)	C(1')-P(1')-C(21')	111.1(3)
C(11')-P(1')-C(21')	104.1(3)	O(2')-P(2')-C(41')	117.2(3)
O(2')-P(2')-C(8')	112.5(3)	C(41')-P(2')-C(8')	110.8(3)
O(2')-P(2')-C(31')	108.5(3)	C(41')-P(2')-C(31')	102.3(3)
C(8')-P(2')-C(31')	104.2(3)	C(2')-C(1')-C(8A')	118.4(6)
C(2')-C(1')-P(1')	114.9(5)	C(8A')-C(1')-P(1')	125.1(5)
C(1')-C(2')-C(3')	122.9(6)	C(4')-C(3')-C(2')	118.9(7)
C(3')-C(4')-C(4A')	121.4(6)	C(5')-C(4A')-C(8A')	121.1(6)
C(4')-C(4A')-C(8A')	120.4(6)	C(6')-C(5')-C(4A')	122.3(7)
C(5')-C(6')-C(7')	117.6(6)	C(8')-C(7')-C(6')	123.1(7)
C(7')-C(8')-C(8A')	119.2(7)	C(7')-C(8')-P(2')	115.7(5)

C(8A')-C(8')-P(2')	124.0(5)	C(4A')-C(8A')-C(8')	116.2(6)
C(4A')-C(8A')-C(1')	117.0(6)	C(8')-C(8A')-C(1')	126.7(6)

5.3 Discussion

An improved synthesis for the ligand dppn (**1**) (see Figure 5.1) has been developed in this work, and isolated several new compoundshave been isolated with this ligand coordinated to a metal centre. Additionally, the first crystal structure of the ligand (**1**) coordinated to any metal other than palladium has been obtained. Furthermore, the phosphine oxide of (**1**) has been synthesised. In addition to the work on the original ligand, we have synthesised 1,8-bis-(dicyclohexylphosphino)naphthalene (dcpn-(**3**)) the cyclohexyl analogue of dppn (see Figure 5.7) and have looked more briefly at the coordination chemistry of this ligand. For certain compounds, we have observed unusual behaviour for the chelating ligand (**1**) in that it is entirely displaced by another chelating ligand, and may be partially displaced by monodentate ligands.

The unusual nature of the phosphine (**1**) (i.e. very bulky and strained, with a very restricted potential bite angle) was always likely to produce interesting results. It was partly these properties that made us consider the ligand's potential usefulness in catalysis.



(3)

Figure 5.7

5.3.1 Synthesis of 1,8-bis-(diphenylphosphino)naphthalene.

Initially, the synthesis carried out was based on the literature method.[2a,2b] These methods proved unsatisfactory from the view of purity and yield, however. We therefore combined the literature procedures and altered the work up in order to remove the lithium chloride that we found was still present at the end of the reaction when using the original preparation. The general reaction scheme followed is shown in Figure 5.8 below.

In the original preparation,[2a] there seemed to be no mention of any effort to remove the LiCl formed in the last stage. The second method (which was also repeated here)[2b] involved an aqueous work up which did remove the lithium chloride, but gave a lower yield, and made the product somewhat oily. The method of work-up employed in this work was to carry out a Soxhlet extraction with toluene. This method gave ligand (**1**) analytically pure and in good yield.

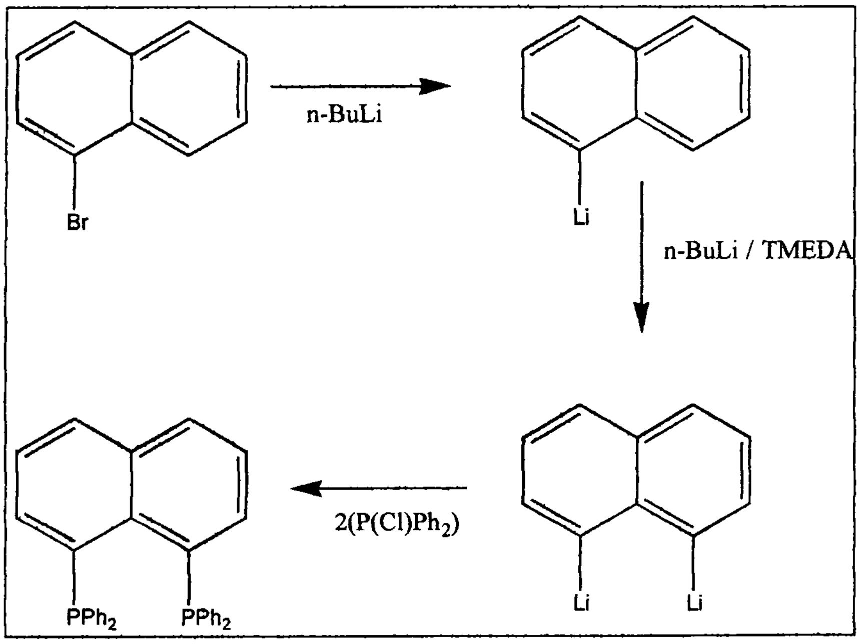


Figure 5.8

The double lithiation was then carried out in ether/hexane/THF before addition of the chlorophosphine ClPPh$_2$, solvent removal and extraction into first dichloromethane and then into toluene, leaving behind a fine white powder (LiCl). After filtration, the toluene was removed under reduced pressure to give a fine yellow solid. It was found that using dry degassed solvents and reagents at all stages was vital.

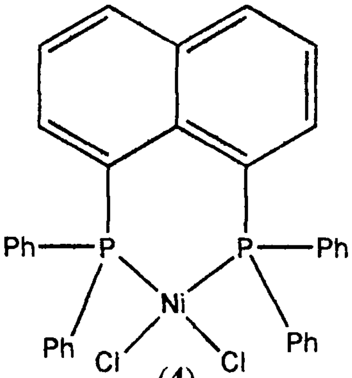
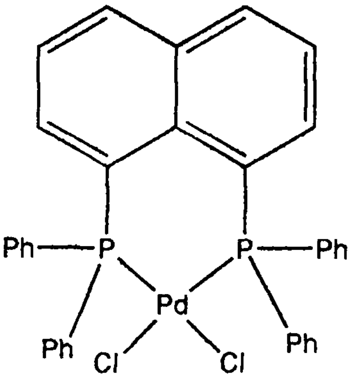
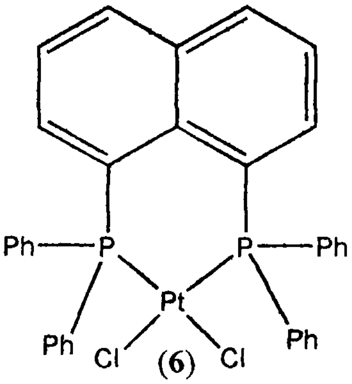
5.3.2 Synthesis of transition metal dichloride complexes of dppn.

We set out to synthesise a variety of late transition metal dichloride complexes of (1) in order to understand the nature of the ligand and to see, as claimed by the original authors,[2a] if the ligand did behave as a normal chelating diphosphine. The reactions of dppn with anhydrous [$NiCl_2$]; [$CoCl_2 \cdot (H_2O)_6$]; [$PdCl_2(PhCN)_2$] and [$PtCl_2(PhCN)_2$] were carried out. We obtained samples of [$NiCl_2$(dppn)] (**4**), [$PdCl_2$(dppn)] (**5**), [$PtCl_2$(dppn)] (**6**) and an oxidised cobalt complex which is discussed later. Of these, the nickel and cobalt complexes are new, the Pd and Pt complexes having been made in the original work.[2a] Summarised NMR data (except for the paramagnetic $CoCl_2$ complex) are given in the table below (Table 5.7). In the $^{31}P\{^1H\}$ NMR spectrum, the free ligand comes at -15 ppm. The coordination shift for the palladium species is 36 ppm.

Due to the paramagnetic nature of tetrahedral Co(II), no NMR data were obtained. Fortunately, crystals were obtained of the cobalt complex made in the reaction. A mixture of purple and blue products was formed, attributed to a polymeric octahedral system and a tetrahedral system respectively.

Suspension of the insoluble purple solid in dichloromethane produced a blue tetrahedral complex, which was characterised unambiguously by crystallography and elemental analysis, but not as the anticipated product [$CoCl_2$(dppn)]. Instead it was found to be the Co complex of the phosphine monoxide [$CoCl_2$(dppno)]. This complex is discussed further in section 5.3.7. The nickel complex, discussed in section 5.3.8, represents the first known complex of the ligand with a first row transition metal.

Table 5.7 A comparison of NMR data for dppn complexes

	$^{31}P\{^1H\}$ NMR (ppm)	^1H NMR (ppm)
 (4)	31.4 (s)	7.2 - 8.2 (m)
 (5)	21.0 (s)	7.2 - 8.2 (m)
 (6)	1.6 (s & d, $J_{P\text{-}Pt}$= 3312 Hz)	7.3 - 8.2 (m)

5.3.3 The synthesis of novel palladium derivatives of dppn.

Of more direct interest to this project was the potential use of the ligand for catalysis. To this end, several well known palladium compounds were combined with the ligand (**1**). Of particular interest was the palladium acetate dppn complex. This complex was synthesised in a straightforward manner by the addition of $Pd(OAc)_2$ to (**1**) in toluene and stirring at room temperature before a simple work-up. The complex $[Pd(OAc)_2(dppn)]$ (**7**) was obtained analytically pure.

One of the reasons that (**7**) is particularly interesting, is that the precursor used in Drent's polyketone synthesis is palladium acetate with dppp, a three carbon backbone phosphine. The newer phosphine (**1**) also has a three carbon backbone but has a substantially different structure (see Figure 5.1). It was our intention to use this complex (**7**) in catalytic experiments which are described in the next chapter.

One other complex synthesised was $[Pd(dppn)(MeCN)_2](BF_4)_2$ (**8**). This complex was made from the tetrakisacetonitrile complex $[Pd(MeCN)_4](BF_4)_2$ (**9**). Complex (**8**) was a deep red crystalline solid and proved to be a stepping stone to one of the more interesting aspects of the ligand's properties as discussed in the next section.

5.3.4 Ligand exchange and related reactions.

The addition of one equivalent of a chelating ligand (dppe) to complex (**8**) produced a surprising result. Rather than obtaining the mixed phosphine complex (**10**) (see Figure 5.9) as intended, the dppn ligand was displaced by the incoming ligand. In addition, the dppe ligand also displaced both of the acetonitrile ligands.

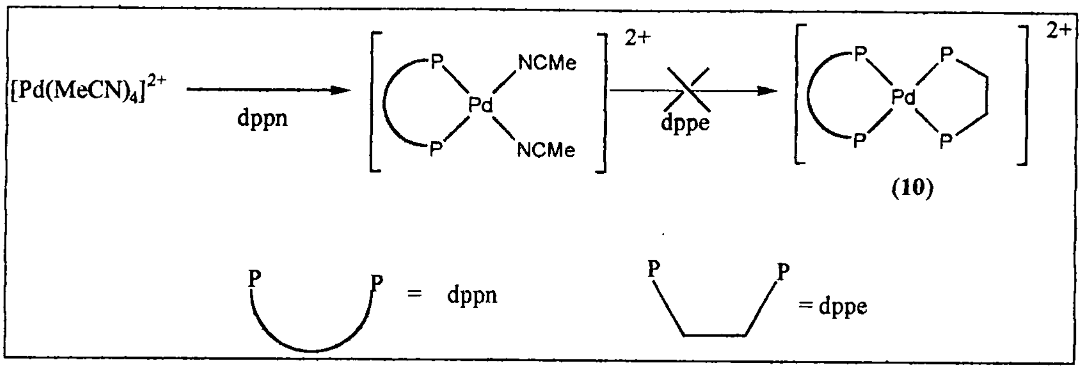


Figure 5.9

The product was the bis di-phosphine complex $[Pd(dppe)_2](BF_4)_2$ (**11**) as shown in Figure 5.10. The analogous reaction was observed with dppm, giving $[Pd(dppm)_2](BF_4)_2$ (**12**). The reactions were carried out at room temperature. It is interesting that the dppm ligand added in a chelating manner as it is a ligand which is quite likely to bridge. The chelating nature was determined by the size and the nature of the coordination chemical shift in the $^{31}P\{^1H\}$ NMR.

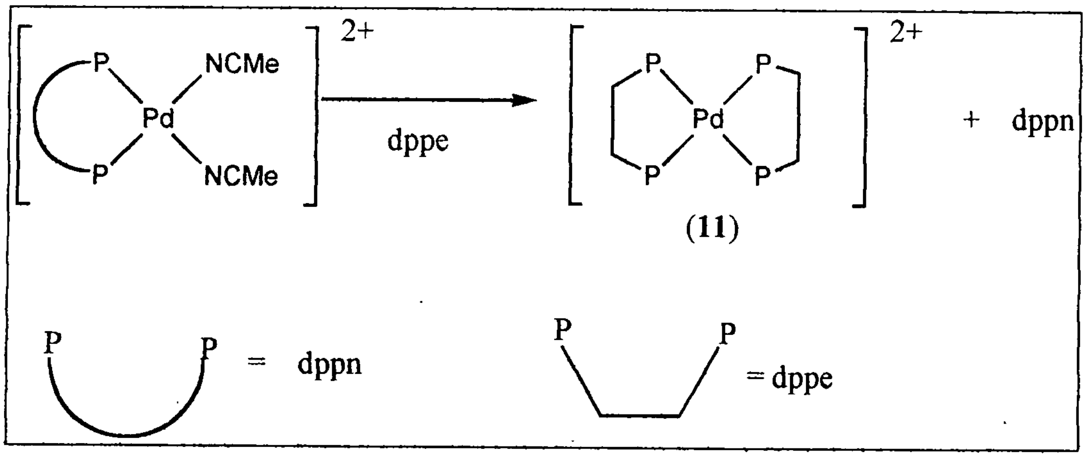


Figure 5.10

This chelating phosphine ligand exchange is, as far as we are aware, unprecedented. We decided to explore this chemistry further, using a system with non-labile ligands. We decided to look at the reaction of $[NiCl_2(dppn)]$ (**4**) with dppe.

$^{31}P\{^1H\}$ NMR monitoring of the reaction between [$NiCl_2$(dppn)] and dppe showed the formation of a 1:1 mixture of [$NiCl_2$(dppe)] ($\delta = 58$ ppm [5a]) and [$NiCl_2$(dppn)] ($\delta = 32$ ppm) under fairly mild conditions. The equilibrium could be pushed no further towards the [$NiCl_2$(dppe)] complex, despite heating for several hours. The further addition of excess dppe produced the species [$Ni(dppe)_2$]$(Cl)_2$ ($\delta = 49$ ppm [5b]) as well as reducing the amount of the [$NiCl_2$(dppn)] in solution. The addition of a large excess results in complete formation of the di-cationic species [$Ni(dppe)_2$]$^{2+}$, leaving only the free dppn ligand in solution, along with the excess dppe. The corresponding reaction was carried out with [$PdCl_2$(dppn)] and [$Pd(OAc)_2$(dppn)], but no analogous behaviour was observed.

5.3.5 Synthesis and coordination chemistry of 1,8-bis-(dicyclohexylphosphino)naphthalene (dcpn)

A new ligand analogous to dppn has been prepared. The new ligand has cyclohexyl substituents instead of the phenyl groups on (**1**). It was thought that the change might produce interesting effects in the reaction chemistry of the ligand. This new ligand (dcpn (**3**) - see Figure 5.7) was coordinated to palladium centres and its relative stability with regard to other chelating ligands was examined. The ligand itself is air sensitive, but like many phosphines, is stable once coordinated to a metal. Interestingly, in the $^{31}P\{^1H\}$ NMR spectrum, the free ligand (**3**) is almost isochronous with the phenyl derivative (**1**), despite having alkyl substituents which usually cause changes in the position of the signal for a given phosphine. Once the ligand was synthesised it was complexed with a selection of palladium systems. For instance, the ligand was added to the complex [$Pd(Cl)_2(PhCN)_2$]. The resulting yellow solid [$Pd(Cl)_2$(dcpn)] (**12**) was air stable and easily handled. The complex [$Pd(MeCN)_2$(dcpn)] $(BF_4)_2$ (**13**) was made by the addition of the ligand (**3**) to complex (**9**) (see Figure 5.10). This complex (**13**) was yellow and less crystalline than the dppn complex (**8**).

5.3.6 Reactivity of dcpn coordinated complexes.

Examination of the reactivity of the bis acetonitrile complex (**13**) with other chelating ligands gave results similar to those found for the phenyl analogue (**8**). For instance, upon addition of dppe, there was displacement of the MeCN ligands and the dcpn ligand resulting in formation of the bis dppe complex (**11**). The corresponding result was observed upon addition of dppm to (**13**) to give complex (**14**). These reactions are summarised in Figure 5.11. $^{31}P\{^1H\}$ NMR monitoring of the reaction did not show free dcpn, instead the phosphine oxide of dcpn (dcno) was observed at 45 ppm. The oxide dcno is discussed later.

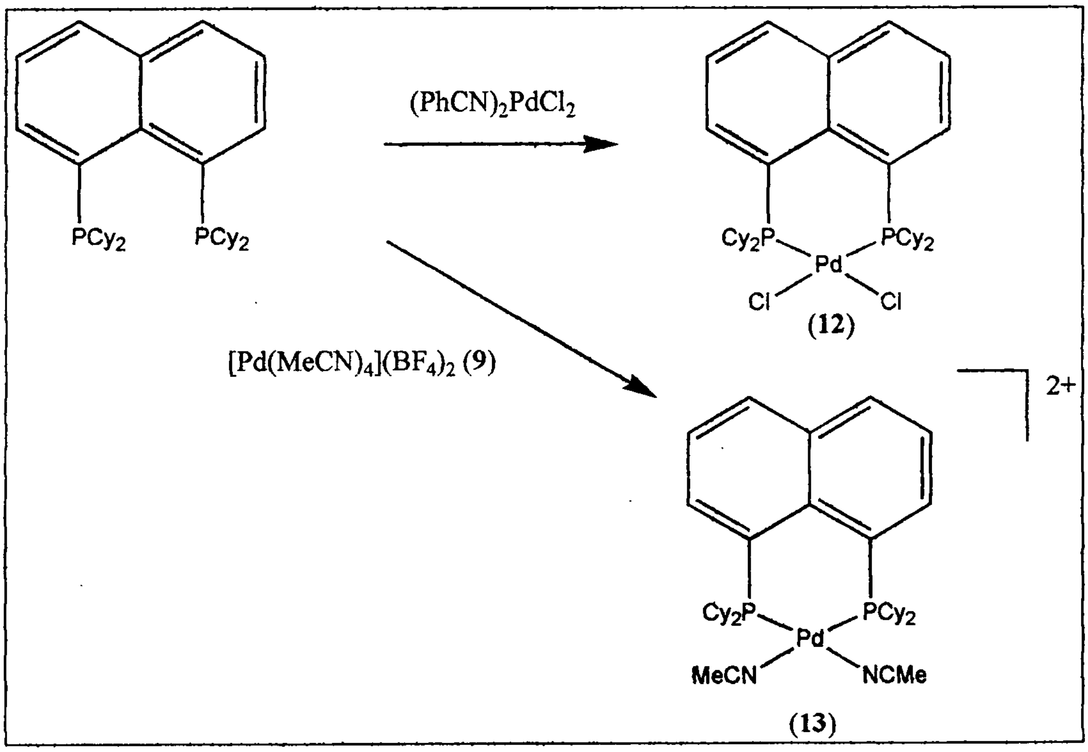


Figure 5.10

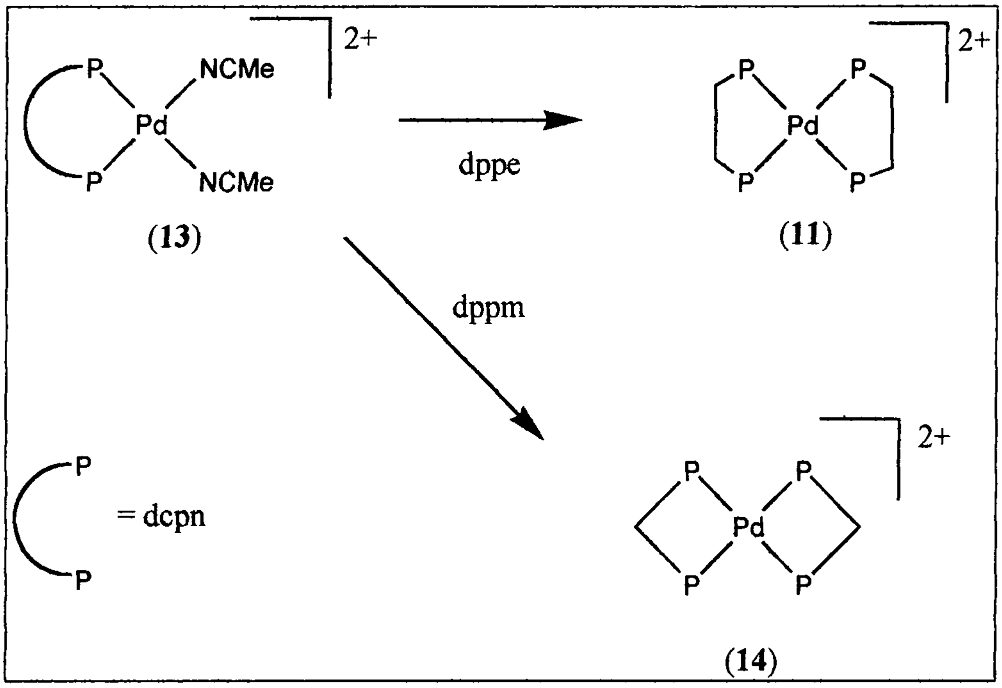


Figure 5.11

As observed for the dppn ligand, attempts to carry out similar exchange reactions on palladium chloride complex of dcpn were unsuccessful, giving only starting materials.

5.3.7 The [CoCl$_2$(dppno)] complex

The addition of dppn to [Co(H$_2$O)$_6$](Cl)$_2$ in ethanol gave a mixture of purple solid and blue solution. The purple solid was the major product. The solid was filtered and washed with ethanol several times before attempted dissolution in dichloromethane. The suspension was found to turn slowly blue, implying a change in coordination. Blue crystals were formed and successfully analysed by X-ray crystallography. It was found that the blue crystals were the phosphine monoxide complex [Co(Cl)$_2$(Ph$_2$P(O)-C$_{10}$H$_6$-PPh$_2$)] **(15)**. The crystal structure, shown in Figure 5.4, is worthy of discussion. Table 5.8 below shows some of the angle and bond data. The bite angle on the Co was very small for tetrahedral coordination. Instead of the ideal 109° geometry around a tetrahedron, the bite angle was only 95°. In addition, another view of the structure (Figure 5.12) showed that the naphthalene ring had buckled to help coordination.

One possible explanation for these phenomena could be the following. The $CoCl_2$ initially takes up a polymeric octahedral geometry using chloro-bridges (the cobalt complexes known to do this are normally purple and insoluble[6]). This fits in with our notion of the bite angle for a tetrahedral species being too large for the very sterically hindered ligand (**1**). Slow oxidation of the ligand complex could then occur, probably by a slow leak of air (the colour change occurred over about three days), thus producing the mono-phosphine oxide dppno complex (*not* dpno which is the dioxide) and allowing the $CoCl_2$ to assume the tetrahedral coordination. The idea that the steric repulsion and rigidity of the ligand is too great for any structure with a bite angle larger than that seen for square planar or octahedral coordination is backed up by the observation that all of the known crystals of coordinated dppn have square planar configuration, with a bite angle of about 90°.

The ring buckling of (**15**) could be a large contributor to the extended bite angle of the phosphine oxide structure. This ring buckling is not new; it was observed in the crystal structure of the original ligand,[2a] and has been observed in the dpno structure obtained in this work (see Figure 5.6).

The crystal structure of the complex (**15**) contains both coordinated phosphorus and coordinated oxygen atoms. It is thought to be the first example of a crystal structure of a Co complex of such a species. There are, however, several examples of $CoCl_2(P)_2$ crystal structures and these are now compared with the phosphine oxide structure (**15**) in Table 5.8. Also compared with (**15**) in the subsequent table (Table 5.9) are the data for some phosphine dioxide complexes of $CoCl_2$.

Table 5.8 Comparison of phosphine coordinated Co structures with (15)

	(15)	(16)	(17)	(18)
Co-P(1)	2.4067(11) Å	2.397(2) Å	2.405(2) Å	2.384(1) Å
Co-P(2)	N/A	2.402(2) Å	2.348(2) Å	see above
Co-Cl(1)	2.2285(10) Å	2.216(2) Å	2.205(2) Å	2.212(1) Å
Co-Cl(2)	2.2396(11) Å	2.196(2) Å	2.220(2) Å	see above
Co-O	1.985(2) Å	N/A	N/A	N/A
Cl-Co-Cl	112.44(4) °	117.9(1)°	114.32(9)°	117.28(3)°
Bite angle*	95.28(8) °	N/A	105.41(7)°	N/A

* defined as the angle P-Co-X where X is either P or O, for a chelating ligand

Key to Table 5.8: (**15**) [$CoCl_2$(dppno)] (**16**) [$CoCl_2$ ($Ph_2PCH_2C(O)PPh_2$)][7]
(**17**) { $CoCl_2$[1,1-bis(diphenylphosphino)-3,3'-bis(trimethylsilyl)ferrocene] }[8]
(**18**) [$CoCl_2(PPh_3)_2$][9]

It can be clearly seen from Table 5.8 that the bite angle for (**15**) is considerably smaller (by about 10°) than the ferrocenyl derivative (**17**), the angle of which (105°) is still smaller than the tetrahedral angle. The lengths of the bonds of (**15**) are unremarkable, and are of the same approximate value as for the other complexes shown.

The Co-O bond present in the structure of (**15**) has no equivalent in the dichloride structures discussed above. For this reason we now compare (**15**) with some examples of complexes of the form $(P=O)_2$-Co. This comparison is shown in Table 5.9 below. From this table, the difference in the size of the bite angle of (**15**) compared to other tetrahedral Co complexes can be appreciated.

Figure 5.12 Alternative view of crystal structure of [Co(Cl)$_2$(dppno)] (15)

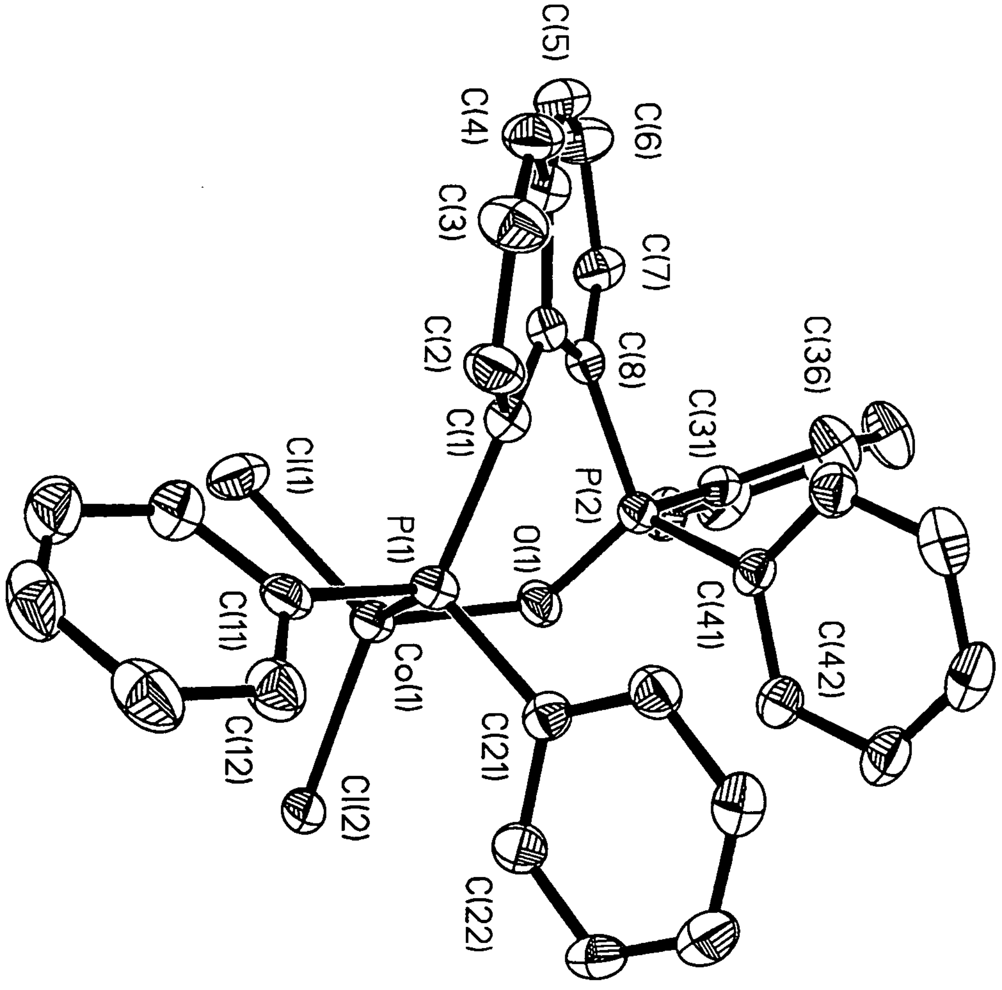
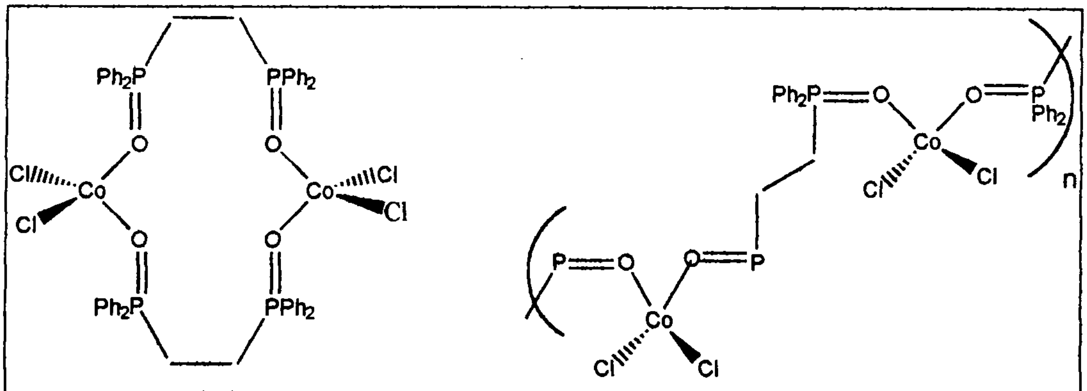


Table 5.9 Comparison of structures of Co complexes with (15)

	(15)	(19)	(20)	(21)
Co-O(1)	1.958(2) Å	1.958(5) Å	1.975(3) Å	1.972(6) Å
Co-O(2)	N/A	1.962(5) Å	1.984(3) Å	1.975(6) Å
Co-Cl(1)	2.2285(10) Å	2.256(2) Å	2.244(2) Å	2.246(3) Å
Co-Cl(2)	2.2396(11) Å	2.256(2) Å	2.211(2) Å	2.252(3) Å
P=O(1)	1.516(2) Å	1.508(5) Å	1.499(3) Å	1.479(6) Å
P=O(2)	N/A	1.508(5) Å	N/A	1.478(6) Å
Cl-Co-Cl	112.44(4) °	114.3(1) °	115.9(6) °	114.7(1) °
O-Co-X*	95.28(3) °	104.5(2) °	101.9(1) °	102.7(2) °

* X = P or O

Key for Table 5.9: (**15**)[$CoCl_2$(dpno)]; (**19**) [$CoCl_2(Me_3PO)_2$]; [10] see Figure 5.13 for (**20**)[11] and (**21**)[11]



(20)

(21)

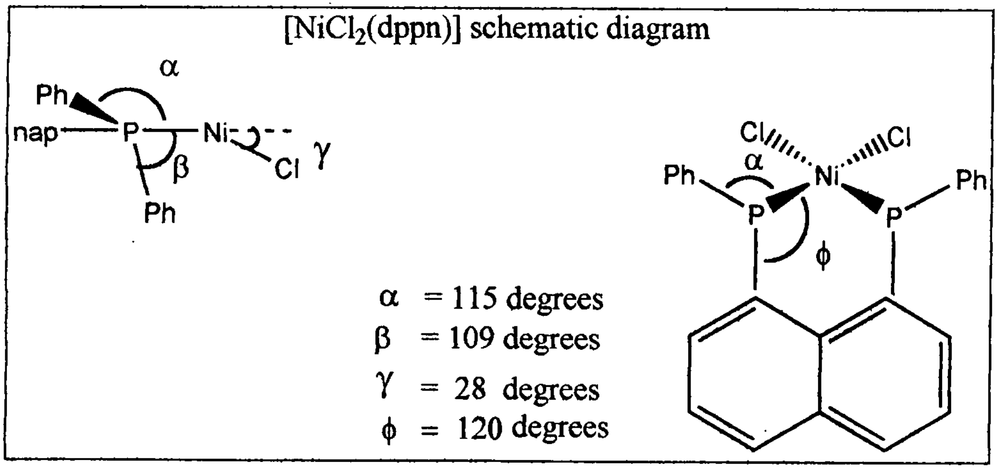
Figure 5.13

Compound (**21**) has a polymeric *catena* structure, and compound (**20**) contains a 14 membered ring. These compounds are isomers.

From Table 5.9 it is clear that the differences in P=O bond lengths are not very large between (**15**) and other Co-O complexes. The O-Co-P angle of (**15**) though, is significantly smaller (by about 6 degrees) than any of the O-Co-O angles for the other species. This is thought to be due to the stringent steric requirements of the dppno ligand.

5.3.8 The [$NiCl_2$(dppn)] complex

The nickel dichloride complex of dppn (**4**) (see Table 5.7) is the first example of the dppn ligand (**1**) coordinated to a first row metal. The crystal structure is shown in Figure 5.5. A comparison with other known $NiCl_2$ complexes is given in Table 5.10. The position of the nickel is interesting, in that the angle between the dppn ligand and the nickel di-chloro plane is 28°. This is illustrated schematically in Figure 5.14. It appears that one face of the nickel is more exposed than the other, this means that the open face of the nickel may be more prone to attack than in some of its other known complexes, and this seems borne out by the unusual behaviour observed for this complex in the presence of dppe. The bite angle (i.e. the P-Ni-P angle) for the structure of (**4**) is 89.47°.


[$NiCl_2$(dppn)] schematic diagram

α = 115 degrees
β = 109 degrees
γ = 28 degrees
ϕ = 120 degrees

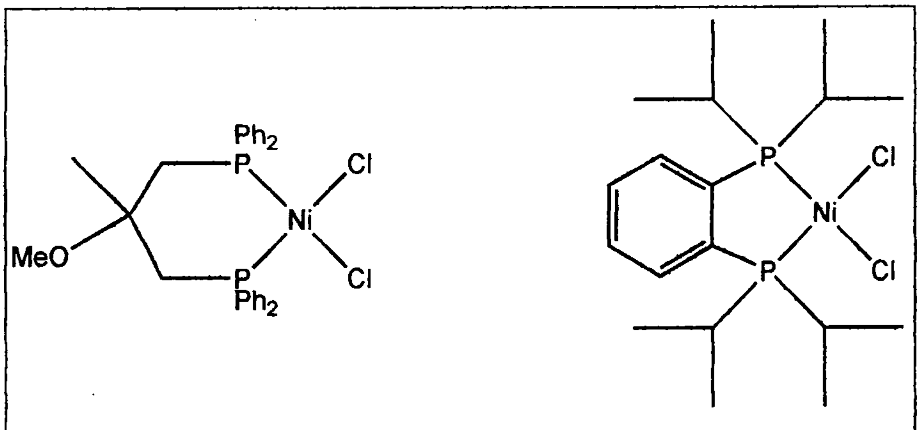
Figure 5.14

It is interesting that the bite angle observed in our complex (**4**) is on the large side when compared with other similar complexes such as those shown in Table 5.10 below. This may be partly due to the lack of flexibility in the backbone of the ligand. In consequence, the Cl-Ni-Cl angle of (**4**) is slightly smaller than the average, by one or two degrees. The Ni-P and Ni-Cl bond lengths seem to be fairly unremarkable.

Table 5.10 Comparison of (4) with other known $NiCl_2$ diphos structures

	(4)	(22)	(23)	(24)
Ni-Cl(1)	2.1986(11) Å	2.196(4) Å	2.207(2) Å	2.204(1) Å
Ni-Cl(2)	2.2033(11) Å	2.203(4) Å	2.207(2) Å	2.204(3) Å
Ni-P(1)	2.1627(11) Å	2.154(4) Å	2.164(2) Å	2.157(1) Å
Ni-P(2)	2.1641(11) Å	2.153(4) Å	2.164(2) Å	2.157(3) Å
Cl-Ni-Cl	90.06 °	94.6(2) °	92.24 °	93.16(5) °
Bite Angle	89.47 °	87.3(2) °	85.49(7) °	89.41(5) °

Key to Table 5.10: (**4**) [$NiCl_2$(dppn)]; (**22**) [$NiCl_2$(dppe)][12];
(**23**) [$NiCl_2(Ph_2PCH_2C(CH_3)(OCH_3)CH_2PPh_2)$][13];
(**24**) {$NiCl_2$ [$(iPr)_2P$-C_6H_4-$P(iPr)_2$]}.[14] See Figure 5.15 for (**23**) and (**24**).



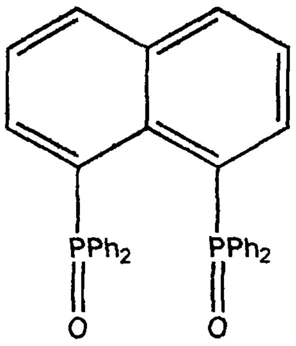
(23) **(24)**

Figure 5.15

A detailed analysis of the geometry (carried out by Dr. C.W. Lehmann) shows that the dppn ligand is essentially planar with only small deviations from the plane. The angle between the ligand and the $NiCl_2$ plane is 28° (see Figure 5.14) which is some 5° less than the corresponding angle found for the palladium allyl species ([Pd(η^3-allyl)(dppn)](BF_4)^3} of this ligand. The nickel is square planar coordinated. Considering a plane formed by the four coordination sphere atoms, the nickel sits about 0.11 Å above the plane. Noticeably, the Ni-P-C angles between the naphthalene ring and the nickel centre (ϕ in Figure 5.14) are approximately 120°, deviating considerably from the ideal tetrahedral geometry of about 109°. This may allow more access to the Ni centre.

5.3.9 Synthesis of dppn dioxide (dpno).

The phosphine oxide of dppn (dpno (**25**) - shown in Figure 5.16) can be synthesised in two ways. In one method, the addition of H_2O_2 to a dmso/THF solution of dppn gave a relatively fast reaction, but the presence of dmso made isolation difficult. The second method employed was to simply allow slow reaction with air in toluene. The second method, although slower, allowed easy separation, and gave cleaner products, as the phosphine oxide precipitated easily out of the toluene as colourless crystals. These crystals were found to be suitable for X-ray analysis. The crystal structure is shown in Figure 5.6. The rest of the product may be obtained from the solution by solvent removal followed by washing with ether and toluene. A comparison of selected bond lengths and angles is shown in Table 5.11.



(25)

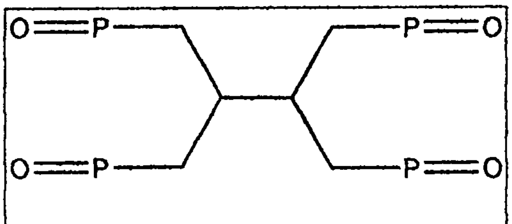
Figure 5.16

The phosphine oxide (**25**) is air stable. The structure of (**25**) is now compared with another phosphine oxide as well as the coordinated ligand in the Co dppno complex (**15**). The P=O lengths are unremarkable and are in the range expected for such bonds.[15]

Table 5.11 A Comparison of P=O bond lengths

Complex	P=O(1)	P=O(2)	P=O(3)	P=O(4)
(**15**)	1.516(2) Å	N/A	N/A	N/A
(**25**)	1.494(4) Å	1.488(5) Å	N/A	N/A
(**26**)	1.468(1) Å	1.511(1) Å	1.515(1) Å	1.547(2) Å

Key to Table 5.11: (**15**) [$CoCl_2$(dppno)]; (**25**) dpno; (**26**)[15] see Figure 5.17.

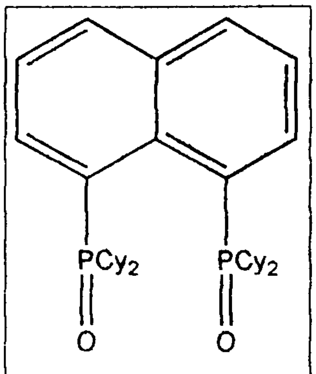


(**26**)

Figure 5.17

5.3.10 Synthesis of dcpn dioxide (dcno).

The oxide dcno (**27**) (see Figure 5.18) was synthesised in the same manner as the dppn oxide. The ligand was dissolved in toluene and allowed to react with atmospheric oxygen over the period of a few days. Once again, as for the synthesis of (**25**), the solution went from yellow to colourless. Characterisation was carried out by NMR, IR and elemental analysis, as discussed in the experimental section. The isolation was the same as for (**25**), except that no crystalline material was isolated.



(27)

Figure 5.18

5.4 Conclusions

In this chapter we have explored the chemistry of a relatively unknown phosphine (1), of interest to catalysis because of its aromatic backbone. A new, related phosphine (3) has been synthesised and the phosphine oxides of both of these compounds (25) and (27) have been isolated. We have made metal complexes of the ligand (1) which will be used in catalysis described in the subsequent chapter. Ni, Pd and Co complexes (4), (8), (13) and (15), which exhibit unusual coordination chemistry and reactivity, have been made.

Three of the complexes made have been isolated as crystalline material suitable for X-ray diffraction. Most compounds reported in this chapter, except for the ligand 1,8-bis(diphenylphosphino)naphthalene (1), its palladium dichloride (5) and platinum dichloride (6) adducts, and the bis-diphosphines (11) and (14), are new species. * We report the first crystal structure of a cobalt chloride complex to be coordinated to both P and O, and in the same crystal unusual buckling of a

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* Note added in proof: dcpn, dpno and dcpo have been made independently: A. Karacar, H. Thonneson, P.G. Jones, R. Bartsch and R. Schmutzler, *Abstracts*, Agichem, Marburg, 1997, 81

naphthalene ring is observed as for the original dppn ligand. In addition, we report the direct displacement, in certain systems, of one bidentate phosphine for another. The ring buckling and the ease of substitution of the ligand suggests that the ligand has a small bite angle, which cannot be easily increased. The main causes of this are thought to be largely to do with the steric bulk of the ligand. Also, the fact that the backbone is aromatic means that it is quite rigid.

The $NiCl_2$ complex is the first example of a first row transition metal complex of the ligand. In addition, another member of our research group has synthesised and obtained a crystal structure of the $[NiCl_2(dcpn)]$ species. [16] Clearly, this is a system which lends itself to ready crystallisation, making it possible to study and understand.

5.5 References

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Chapter 6

High Pressure Chemistry and Catalysis

The best laid schemes o' mice an' men
Gang aft a-glay

Robert Burns (1759 - 96)

6.1 Introduction

One of the goals of the work outlined in previous chapters was to provide precursors for catalytic experiments. This section discusses some of the practical aspects of the catalysis carried out.

The autoclave (or high pressure vessel) used throughout the work described in this chapter was made of a corrosion resistant alloy called Hastalloy. The autoclave was designed to withstand pressures up to about 1000 psi (or about 70 bar); in practice pressures were kept at, or below, about 700 psi (or 50 bar). A schematic of the autoclave system used is shown in Figure 6.1.

A glass sleeve is placed in the autoclave in order to make retrieval of the final product more simple and to minimise contact between the metal vessel and the reagents. This helps to prevent corrosion which may lead to stress fractures in the vessel. The bursting disk, a safety feature, is a piece of metal engineered to burst when the pressure inside the autoclave is at a pre-set limit that is lower than the upper limit of the rating of the vessel. Thus, if an excess of pressure has formed inside a vessel rated to tolerate pressures up to 130 bar, rather than having the entire vessel rupture, the bursting disk will give way. This releases the pressure in a more controlled manner into a catch pot, which allows examination of the products. The autoclave is attached to a pressure gauge, by which the internal pressure can be observed.

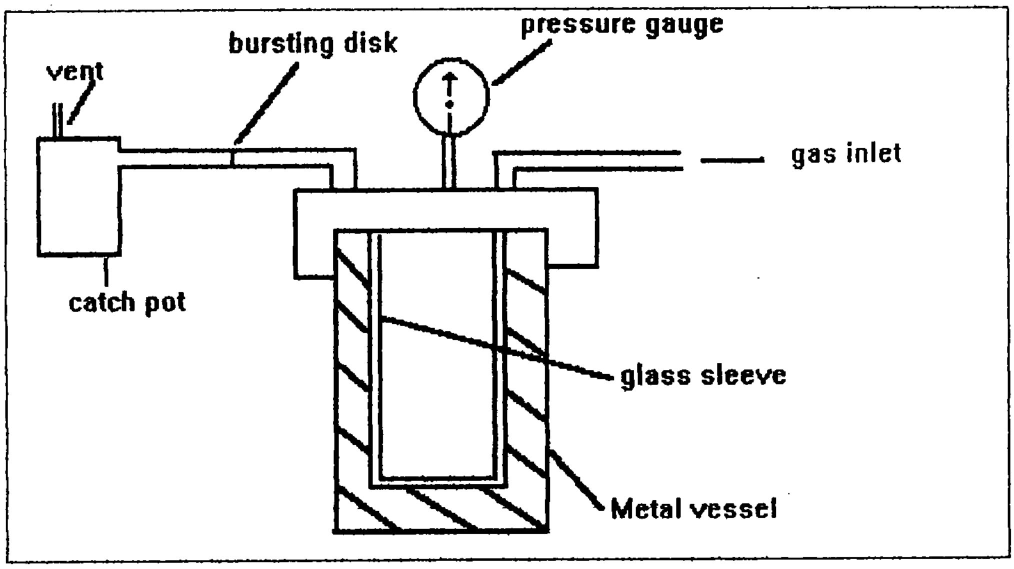

Figure 6.1

The work reported in this chapter consists of two parts. The first part deals with attempts to perform hydroesterification of ethene using methyl formate in the absence of added CO. The second part centres on attempts to use some of the materials synthesised in Chapter 5 to generate polyketone in a manner analogous to the process developed by Drent.[1] In both sets of experiments, the pressures used ranged from 10 to about 50 bar (or approximately 140 - 700 psi).

6.2 Experimental procedure for hydroesterification reactions

All procedures were carried out under very similar conditions. Since the reactions are so similar, only one experiment has been discussed in detail. Table 6.1 below summarises the variations used for each run.

Table 6.1 Variations in reaction conditions for esterification experiments

Reaction Number	Hydride	Co-catalyst (1)	Phosphine	Co-catalyst (2)
6.2.1	$NaBH_4$	none	PBu_3	none
6.2.2	none	$SnCl_2$	PBu_3	none
6.2.3*	$NaBH_4$	$SnCl_2$	PBu_3	none
6.2.4	$NaBH_4$	$AgBF_4$	PBu_3	none
6.2.5	$NaBH_4$	$SnCl_2$	PBu_3	$AgBF_4$
6.2.6	$NaBH_4$	$SnCl_2$	dppe	none
6.2.7	$NaBH_4$	$AgBF_4$	dppe	none
6.2.8	$NaBH_4$	$SnCl_2$	dppe	$AgBF_4$
6.2.9	$NaBH_4$	$AlCl_3$	PBu_3	none
6.2.10	$NaBH_4$	$AlCl_3$	dppe	none

*repeated under a variety of conditions: see text in discussion section.

Experiment 6.2.5

Hydroesterification using $AgBF_4$, $SnCl_2$ and PBu_3 with $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ and $NaBH_4$.

The autoclave was loaded with precatalyst $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ (0.05 g, 0.07 mmol) and sodium borohydride (0.003g, 0.09 mmol). To this solid mixture were also added the co-catalysts $SnCl_2$ (0.015 g, 0.08 mmol) and $AgBF_4$ (0.01g, 0.08 mmol). In a separate flask, 10 ml MeOH, 2 ml HCO_2Me and seven equivalents of PBu_3 (0.1g, 0.48 mmol) were mixed. The solution of methyl formate and phosphine was added immediately before the autoclave was sealed. Nitrogen was flushed through the system twice before a final flushing with ethene. The autoclave was then pressurised to 10 bar of ethene, before heating the closed system to 110°C. This took the pressure up to around 50 bar. The reaction was allowed to run for approximately eight hours before allowing the vessel to cool overnight. During the run, pressure readings were taken, but showed little overall change. Once the autoclave had cooled, the gas from the autoclave was vented before the darkly coloured solution in the vessel was distilled to give a clear, colourless liquid, and then analysed by passing through a gas chromatograph.

6.3 Experimental procedure for polyketone reactions.

The following table (Table 6.2) shows the variation in reaction conditions used for the attempted polyketone reactions. As above, only one detailed discussion of the experimental procedure is given, as all the reaction conditions were very similar.

Table 6.2 Variations in reaction conditions for polyketone experiments

Reaction	Precatalyst	Phosphine	Acid used
6.3.1	$Pd(OAc)_2(dppn)$	dppn	HCl
6.3.2	$Pd(OAc)_2$	dppn	none
6.3.3	$Pd(OAc)_2(dppn)$	dppn	HOTf
6.3.4	$Pd(OAc)_2$	dppn	HOTf

Experiment 6.3.3

Attempted polyketone synthesis using dppn, $[Pd(OAc)_2(dppn)]$ and HOTf

The autoclave was loaded with precatalyst $[Pd(OAc)_2(dppn)]$ (0.05 g, 0.07 mmol). To this solid were also added three equivalents dppn (0.1g, 0.2 mmol). In a separate flask, MeOH (20 ml) and HOTf (0.1 mmol) were mixed. The solution of acid was added to the autoclave immediately before it was sealed. Nitrogen was flushed through the system twice before a final flushing with ethene. The autoclave was then pressurised with 10 bar of ethene and 10 bar of carbon monoxide, before heating the closed system to 110°C. This took the pressure to around 50 bar. The reaction was allowed to run for ten hours before allowing the vessel to cool overnight. Once the autoclave had cooled, the gas was vented before the darkly coloured solution in the vessel was filtered, leaving trace amounts of white solid. An infra red spectrum was taken of the white solid. The results are discussed in section 6.5.

6.4 Discussion of hydroesterification reactions

The reactions shown above in sections 6.2 and 6.3 were all carried out in the same high pressure vessel. It was found for all of the hydroesterification reactions using methyl formate that there was no significant ester formation. This was disappointing in the light of the successful repetition of a similar literature method,[2] which used $[Pd(Cl)_2(PBu_3)_2]$ with $NaBH_4$ in methanol and methyl formate in the presence of ethene, that was found to produce methyl propanoate. There were a number of possible reasons for this lack of success. The most likely was the insolubility of the methoxycarbonyl precursor. Clearly, if the complex could not get into solution, it could not perform homogeneous catalysis. Another factor which was thought to be relevant was the instability of the methoxycarbonyl species, especially in the presence of other ligands. Previous work in this thesis has described the problems of solubility and instability associated with methoxycarbonyl complexes. We therefore attempted to modify the complex with a variety of initiators, in an attempt to enhance stability and/ or solubility. It was found, however, that none of these mixtures produced a system which catalysed the formation of methyl propanoate. The reactions all produced similar patterns. The observations made for these reactions are tabulated below. Gas chromatography was used to determine whether or not methyl propanoate had formed.

In each of the cases shown in Table 6.3, the GC analysis showed the presence of MeOH and HCO_2Me. The only run which provided any ester was experiment 6.2.3, which was the experiment consisting of the $SnCl_2$ as co-catalyst with the palladium methyl-chloroformate complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ and sodium borohydride as initiator. The amount of ester was very small (less than 1% conversion) and despite variations carried out in temperature, concentration of catalyst, pressure (between 30 and 65 bar) and run time, no visible improvement was made. The ester was detected by GC analysis. The other components of the distillate for the reactions were methanol and methyl formate which were recovered almost quantitatively.

Table 6.3 Results of esterification reactions

Reaction Number	P (bar)	Time	Temp.	Observations.	GC results
6.2.1	48	8 hrs	110°C	Dark red solution, white solid	No ester
6.2.2	48	8 hrs.	110°C	Black precipitate, palladium mirror	No ester
6.2.3	51	8 hrs.	110°C	Brown solution, black precipitate	Trace ester formation
6.2.4	43	8 hrs.	110°C	Orange solution, silver / palladium mirror.	No ester
6.2.5	53	8 hrs.	110°C	Orange solution	No ester
6.2.6	44	8 hrs.	110°C	Orange solution	No ester
6.2.7	45	8 hrs.	110°C	Orange solution, black precipitate, white precipitate.	No ester
6.2.8	60	8 hrs.	110°C	Orange solution, Black precipitate	No ester
6.2.9	52	8 hrs.	110°C	Black precipitate	No ester
6.2.10	46	8 hrs.	110°C	Dark brown solution	No ester.

The GC results for a typical run showed methanol and methyl formate having the same retention times, with the ester appearing slightly later, in the case where it had formed. The methyl formate and the methyl propanoate were identified by comparison with standard solutions of these compounds in methanol.

6.5 Discussion of polyketone reactions

From the work carried out on the polyketone chemistry, it seemed clear that much work would be needed to modify the conditions in order to obtain anything like reasonable yields. Traces of the polyketone were found in reactions 6.3.3 and 6.3.4. The amounts were so small (less than 0.01g) as to be almost negligible, however. The polyketone was identified by solid state IR which gave a strong carbonyl stretch for polyketone at 1690 cm^{-1}. It is likely that any improvement in the process will have to involve a radical change from the system used here which attempted to mirror the dppp based process developed by Drent.[1]

6.6 Conclusions

The main conclusion from the work covered in this chapter was that the catalytic systems tested did not produce the desired products, and that much more work would probably need to be carried out before any useful catalytic system emerged. A literature review relevant to the catalytic work has been presented in Chapter 1. In this section, the intention is to cover some of the more pertinent points that have arisen which relate to the literature already available.

The esterification process used here was based loosely on the successful scheme developed by Grevin and Kalck.[2] In that paper the authors reported the first use of methyl formate to generate methyl propanoate without the use of additional CO. This was repeated and comparable quantities of ester were produced. The conditions used in the work presented here were very similar, initially only substituting the

$[Pd(Cl)_2(PBu_3)_2]$ complex with the methoxycarbonyl complex $[Pd(Cl)(CO_2Me)(PPh_3)_2]$. The reaction that involved a straight swap showed no activity at all, and so the procedure was modified to try to activate the methoxycarbonyl complex. The addition (in a solvent S) of $AgBF_4$, to try to generate $[Pd(CO_2Me)(S)(PPh_3)_2](BF_4)$ *in situ*, also failed to produce any activity. A small measure of activity was, however, observed for the methoxycarbonyl system in the presence of $SnCl_2$ (experiment 6.2.3). Despite several attempts to improve the yield of the system (by adding more phosphine or more catalyst, varying the temperature, the pressure and the length of the run) no improvement was observed. The addition of the dppe ligand also had no positive effect on the system. Trying to combine $SnCl_2$ and $AgBF_4$ had no effect with any of the phosphines employed. $AlCl_3$ was used as an alternative Lewis acid, but no catalysis was observed for these systems either. From this it was concluded that the process in its present form was not promising as a catalytic system, but the formation of trace ester in 6.2.3 suggests that with more work a viable system may be possible.

The lack of success of the system was thought to be due to the insoluble nature of the methoxycarbonyl precursor. Earlier studies[3] showed that addition of $SnCl_2$ produces a more soluble but less stable species. This point and the limited success of 6.2.3 may be related. On the other hand, the species $[Pd(CO_2Me)(MeCN)(PPh_3)_2]^+$ was more soluble, but the attempts in catalysis and in synthesis to generate a methanol analogue $[Pd(CO_2Me)(MeOH)(PPh_3)_2]^+$, by repeating the synthesis in MeOH instead of MeCN, were not successful, yielding only palladium black.

The polyketone chemistry carried out was based on the Drent process.[1] The main difference between the experiments discussed here and Drent's original conditions was the phosphine employed. It was hoped that the ligand dppn, having a three carbon backbone between the P atoms, would have similar effects to the dppp ligand used in the literature process. It has been observed that the chelate ring size can be very important to a variety of chemical reactions. For example, oxidative addition of PhCl to Pd(0) is much faster for the three carbon backbone ligand dippp[$^iPr_2P(CH_2)_3P^iPr_2$] than for the two carbon backbone analogue dippe [$^iPr_2P(CH_2)_2P^iPr_2$].[4]

When the dppn phosphine was employed in similar conditions to the Drent process, however, very little polyketone was formed. The reason for this may lie in the restricted position of the dppn ligand which, as has been shown in Chapter 5, has a backbone so rigid that little variation in the bite angle can be expected. Also because of this, it is unlikely that dppn could coordinate in a monodentate manner to a metal centre. Shown in Chapter 5 was the propensity of the dppn ligand to detach from the ligand in the presence of better ligands, especially for complexes with weakly ligated coordination sites. These factors may be responsible for the lack of success with this reaction, although having performed a limited number of experiments, it may be too early to draw conclusions concerning the usefulness of the ligand in this context.

6.7 References

[1] E. Drent and P.H.M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663

[2] J. Grevin and P. Kalck, *J. Organomet. Chem.*, 1994, **476**, C23

[3] See Chapter 3.

[4] M. Portnoy and D. Milstein, *Organometallics*, 1993, **12**, 1655

Chapter 7

Summary

> *In contemplation, if a man begins with certainties,*
> *he shall end in doubts;*
> *but if he be content to begin with doubts,*
> *he shall end in certainties.*
>
> Francis Bacon (1561 - 1626)

In this thesis, a number of new compounds have been reported and some unusual chemical effects have been studied. The principal conclusions of each chapter have been summarised in that section. The overall conclusions for the work are now drawn.

At the start of the work one of the aims was to understand some of the factors which contribute towards a catalytically active system for the conversion of methyl formate and ethene to methyl propanoate. We attempted this by examining $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ **(1)**, an analogue of one of the proposed intermediates. Methoxycarbonyl complexes have also been proposed as intermediates in polyketone chemistry. Some of the studies (particularly olefin insertion reactions) were carried out with this in mind.

7.1 Summary for methoxycarbonyl work

Generation of a catalytic system directly from **(1)** does not seem feasible. One possible reason is the extremely insoluble nature of the material, which precludes fast interaction with any dissolved substrate. Another reason is that the complex, once in solution (a process which needs heating to about 50°C) is unstable with respect to the palladium dichloride complex. Attempts to change the halide to iodide or bromide did not produce isolable material.

Because of the reactivity of the dissolved material (**1**) discussed above, it was proposed that halo-methoxycarbonyl palladium species are unstable, especially in chlorinated solvents. This was observed in the formation of CO, methanol and $[Pd(Cl)_2(PPh_3)_2]$ from the methoxycarbonyl complex (**1**) when dissolved in chloroform. One of the new methoxycarbonyl compounds made in this work was the cationic palladium species $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)$ (**2**). The attributes of solubility and stability in solution suggest that the complex may make a better precursor for catalysis. The very air sensitive nature of the complex, as well as the presence of MeCN, makes this slightly less appealing, however. Attempts to modify the halide group on the chloromethoxycarbonyl adduct were all frustrated by decomposition to palladium metal or by formation of the di-halide complex. The only exception was the cationic species (**2**) mentioned above. Several structures of palladium di-halides have been obtained along with the structure of (**2**), which is the first isolated example of such a compound. Also made and studied was the complex $[Pd(Cl)(CO_2Me)(dppe)]$ (**3**). This complex was found to be even less soluble than (**1**).

We examined the reactivity of each of these methoxycarbonyl species (**1**), (**2**) and (**3**) in the presence of a variety of reagents. The activity of the methoxycarbonyl complexes in the presence of strained alkenes was examined to some extent as was their activity when strong nucleophiles such as MeLi were used. In several of these cases it was not possible to fully isolate the species formed, but a combination of literature precedent, NMR and IR spectroscopy was sufficient to give a good indication of what was happening. The reactions of (**1**) and (**2**) with strong nucleophiles seemed only to hasten the decomposition of the methoxycarbonyl complexes, usually with the formation of palladium metal as a precipitate. The reactions with olefins produced unstable species whose natures were inferred from a combination of analytical data and reference to known literature as being products of insertion into the Pd-C bond. These complexes represent analogues for the polyketone process, the high temperature initiation step of which is thought to involve insertion of the olefin into the methoxycarbonyl-palladium bond. The observations made in this work seem to support this proposition since no reaction occurred at room temperature. Questions remain about the stability of the insertion products, however. We looked at palladium methoxycarbonyl complexes of both monodentate and bidentate phosphines in order to compare their reactivities. The bidentate species seemed to be less stable, with the exception of [Pd(Cl)(CO_2Me)(dppe)] whose apparent stability was due to its extremely insoluble nature. A table of the methoxycarbonyl complexes made in this work, and the chapter in which it is described, follows (Table 7.1). The cationic species all have BF_4^- counter ions, except for [Pd($C_7H_9CO_2Me$)(dppe)]$^+$ whose counter-ion is Cl^-.

Table 7.1 Summary of palladium methoxycarbonyl complexes made

Complex	Ch.	Complex	Ch.
[Pd(Cl)(CO_2Me)(dppe)]	3	[Pd(MeCN)(CO_2Me)(PPh_3)$_2$]$^+$	3
[Pd(Cl)(CO_2Me)(dcpe)]	3	[Pd(Cl)($C_7H_9CO_2Me$)(PPh_3)]	3
[Pd(SCN)(CO_2Me)(PPh_3)$_2$]*	3	[Pd($SnCl_3$)(CO_2Me)(dppe)]*	4
[Pd($SnCl_3$)(CO_2Me)(PPh_3)$_2$]*	3	[Pd(I)(CO_2Me)(PPh_3)$_2$]	4
[Pd(I)(CO_2Me)(dppe)]	4	[Pd(Br)(CO_2Me)(PPh_3)$_2$]	4
[Pd(Br)(CO_2Me)(dppe)]	4	[Pd(CO_2Me)(triphos)]$^+$	4
[Pd($C_7H_9CO_2Me$)(dppe)]$^+$	4		

* identified only by IR

One feature of the methoxycarbonyl chemistry, which has been mentioned briefly above, is the tendency for the methoxycarbonyl compounds to decompose into the corresponding palladium di-halide complex. This was underlined by the fact that three novel crystal structures of palladium di-halide phosphine complexes were obtained, including the first known structure of $[Pd(I)_2(dppe)]$.

In catalytic terms, the use of $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ as a precursor appears to be something of a dead end and substantial modification would probably be needed to make it more appealing for such purposes.

7.2 Summary for naphthaphos chemistry.

Although not synthesised originally in this work, the chemistry of 1,8-bis-(diphenylphosphino)naphthalene (or dppn (**4**), see Figure 7.1) has been considerably developed. This has been done by producing a better synthesis and by using the ligand in other reactions to produce novel species. Although Jackson and co-workers[1] reported that the cyclohexyl analogue of the complex may be possible to make, no details of such a process were published. We have made this ligand (**5**). In addition we have made the bis-phosphine oxide of the original dppn ligand (**6**) as well as the phosphine oxide for the cyclohexyl analogue (**7**). The term 'naphthaphos' has been given to this family of compounds, where more than one of (**4**), (**5**), (**6**) or (**7**) are being discussed. Otherwise they are referred to as dppn, dcpn, dpno and dcno respectively.

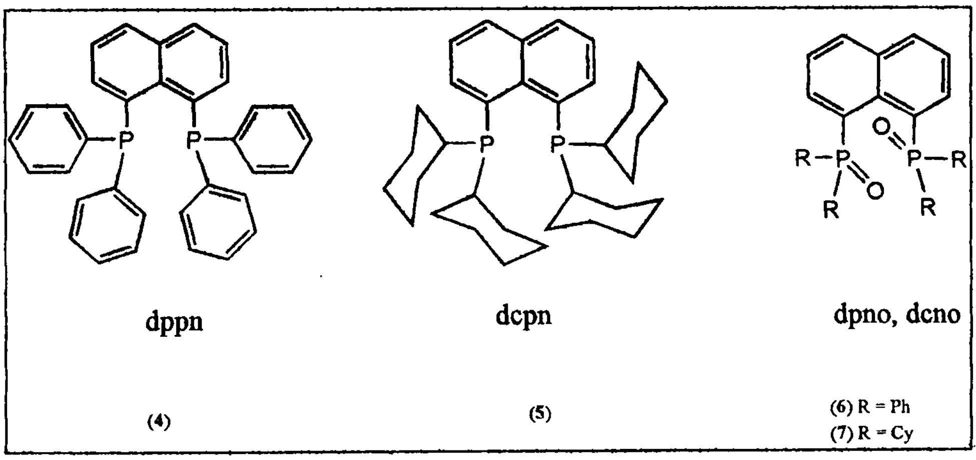

Figure 7.1

Several complexes containing the ligand dppn have been made (see Table 7.2). Unusual chelating ligand exchange chemistry involving dppn and dcpn has been observed for certain nickel and palladium complexes (e.g. see Figure 7.2). This is thought to be the first direct observation of chelating phosphine ligand exchange.

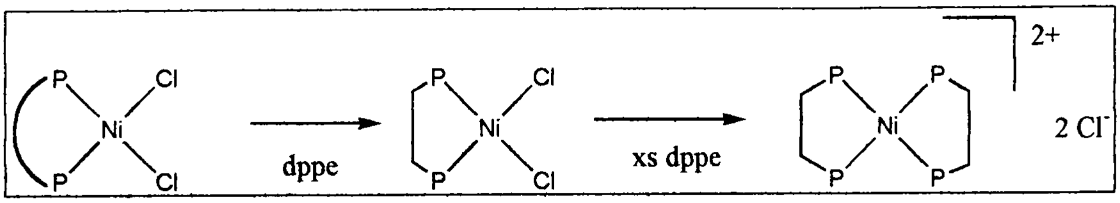

Figure 7.2

Several novel crystal structures have been obtained. One of these crystals was a Co complex of the dppn monoxide. This compound was formed from the reaction of $CoCl_2 \cdot (H_2O)_6$ with dppn (**4**). Slow oxidation caused one of the phosphorus atoms to oxidise to the phosphine oxide, giving a mixed phosphine/phosphine oxide ligand complex. This is the first crystal structure of a cobalt chloride complex (of either Co(II) or Co(III)) with bonds to both phosphorus and oxygen. In order, it is believed, for the ligand to chelate properly, loss of planarity in its aromatic backbone occurred. This can be seen more clearly from the diagrams in chapter 5 (particularly Figure 5.13). Crystals of the complex $[Ni(Cl)_2(dppn)]$ were also good enough for diffraction studies. The nickel structure is the first structure of the dppn ligand coordinated to any metal other than Pd. The structure (shown in Chapter 5, Figure 5.5) shows quite a lot of free space around the nickel centre; this may help to account for the displacement properties of the complexed ligand in the presence of dppe.

The phosphine oxides (**6**) and (**7**) were made by exposing the phosphines (**4**) and (**5**) to air in solution. The phenyl derivative ((**6**) - dpno) was obtained as crystals which were found to be suitable for X-ray studies. The crystal structure of (**6**), like the cobalt complex, also exhibited loss of planarity of the aromatic system. In the case of

(6), it was probably due to steric interaction of the two P=O bonds, and the large steric constraints imposed by the presence of aromatic groups.

Attempts to carry out catalytic reactions with the ligand (4) were started, but no significant polyketone formation was observed. Much work needs to be done, however, before the usefulness (or otherwise) of dppn in this field can be ascertained. A summary of the new naphthaphos compounds is shown in Table 7.2.

Table 7.2 New naphthaphos compounds synthesised.

Compound	Compound
$[Pd(OAc)_2(dppn)]$	$[Pd(MeCN)_2(dppn)]^{2+}$
$[NiCl_2(dppn)]$	$[Pd(MeCN)_2(dcpn)]^{2+}$
$[PdCl_2(dcpn)]$	$[CoCl_2(dppno)]$
(dcpn)	(dpno)
(dcno)	

7.3 Overview

In summary; it has been observed that most methoxycarbonyl complexes are generally too unstable to remain in solution for any period of time. Those complexes which do not rapidly decompose seem to have one of three attributes. The first of these attributes is insolubility. The complexes $[Pd(Cl)(CO_2Me)(dppe)]$ and $[Pd(Cl)(CO_2Me)(PPh_3)_2]$ are stable because they are not easily soluble in any common solvent except dmf. When forced into solution the compounds start to decompose. The second attribute of a stable methoxycarbonyl complex is being halide ligand free. The complex $[Pd(CO_2Me)(MeCN)(PPh_3)_2]^+$ is stable when no free halide is present in solution. Addition of halide ion rapidly produces the corresponding di-halide phosphine complex. Another factor that affects the stability is the presence of weakly ligated coordination sites. $[Pd(CO_2Me)(triphos)](BF_4)$, which has no such sites, is air stable at room temperature. This is in stark contrast to the complex [Pd(CO_2Me)(MeCN)(PPh_3)$_2$](BF_4) which has a (weakly) solvated coordination site and is air and temperature sensitive. The presence of a tridentate chelating ligand contributes to the greater stability.

The instability caused by halides and the loss of stability when adding $SnCl_2$ to [Pd(Cl)(CO_2Me)(PPh_3)$_2$] to give the Pd-$SnCl_3$ complex suggests that the *trans* effect of the X group opposite the methoxycarbonyl moiety could also be a contributory factor in the observed instability of *trans* CO_2Me systems with monodentate phosphine ligands. This does not explain the instability of *cis* methoxycarbonyl complexes of bidentate ligands, however. The factors causing the destabilisation of *cis* complexes are not known. Some possibilities are now discussed. The presence of halide on the metal (for both *cis* and *trans* complexes) may de-stabilise the Pd-CO_2Me moiety by taking electron density from the palladium, thus reducing the electron density available for back-bonding to the CO_2Me group. The methoxycarbonyl complexes seem to be less stable than the corresponding acyls. This probably has something to do with the presence of a methoxy group rather than a methyl group on the carbonyl. Two potential reasons for this present themselves. One possibility is that the MeO group pushes electron density towards the carbonyl, and hence back to the metal, as illustrated schematically in Figure 7.3. This would cause an overall weakening of the Pd-CO_2Me bond and hence lead more easily to decomposition. Alternatively, if we consider the proposed methoxycarbonyl decomposition route through a Pd(CO)(OMe) moiety, then the methoxide ligand is much more likely to decompose by a process such as β-elimination.[2] The methyl ligand, having no β-hydrogens does not have this option, and re-insertion to form the acyl once again is more likely. See Figure 7.4.

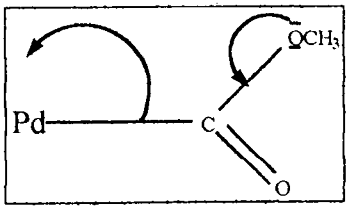

Figure 7.3

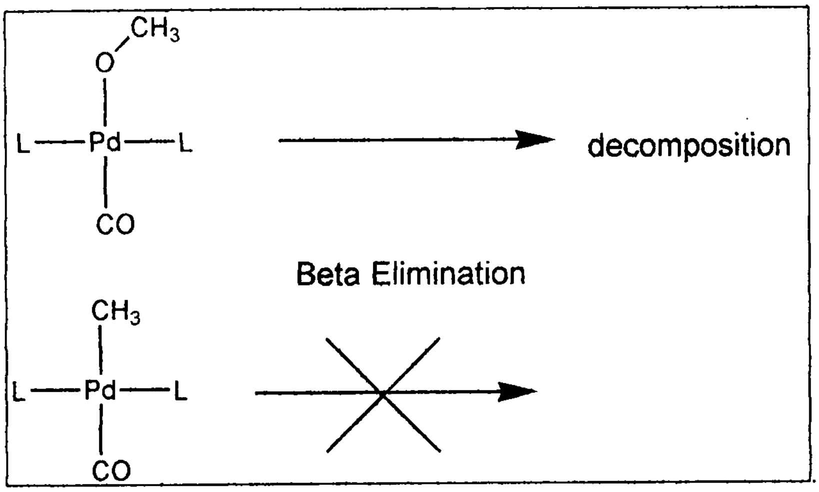

Figure 7.4

The work relating to the naphthaphos family of compounds has shown some surprising effects as discussed above and in chapter 5. While dppn is not a ligand of choice for polyketone work, it is clear that the rigidity of the backbone combined with the potential for varying the substituents on P does produce interesting chemistry in the presence of metal compounds. This combination of rigidity and 'tuneable' functionality, makes for an intriguing system for further study, possibly involving other catalytic systems and the development of a new range of ligands. The ligand dppn has a preferred bite angle of around 90°, although the ligand has been observed to deform to give slightly greater angles up to around 95°. This bite angle is small for such a bulky ligand. This steric bulk/small bite angle relationship may have to be modified for the ligand to be more catalytically interesting. Furthermore, exploration of the properties of the rest of the naphthaphos family needs to be undertaken.

7.4 References

[1] R.D. Jackson, S. James, A.G. Orpen and P.G. Pringle, *J. Organomet. Chem.*, 1993, **458**, C3

[2] Y.J. Kim, K.Osakada, K. Sugita, T. Yamamoto and A. Yamamoto, *Organometallics*, 1988, 7, 2182

Appendix 1

Supplementary Crystal Structure Data for Chapter 2

Compound numbering refers to the numbers given to the complexes in Chapter 2.

Supplementary data for $[Pd(Cl)_2(dppe)](CDCl_3)_3$ complex (3)

Empirical Formula	$C_{29}H_{21}Cl_9D_3P_2Pd$, $(CDCl_3)_3$
Formula Weight	936.8
Temperature	150 (2) K
Wavelength	0.71073 Å
Crystal System	Orthorhombic
Space Group	P2(1)2(1)2(1)
Unit Cell Dimensions	a = 16.292(1) Å α =90°
	b = 18.404(1) Å β =90°
	c = 25.317(2) Å γ = 90°
Volume	7591(1) Å^3
Z	8
Density (Calculated)	1.64 g/cm^3
Absorption Coefficient	1.369 mm^{-1}
F(000)	3712
Crystal Size	0.34 x 0.25 x 0.08 mm
θ range for data collection	1.37 to 26.83°
Limiting Indices	$-19 \le h \le 19$, $-22 \le k \le 22$, $-30 \le l \le 27$
Reflections collected	42512
Independent Reflections	13617 [R(int) = 0.0840]
Absorption Correction	Semi-empirical from psi-scans
Max and Min Transmissions	0.92 and 0.70
Refinement method	Full matrix least squares on F^2
Data / restraints / parameters	13426 / 15 / 787
Goodness of Fit	1.301
Final R indices [I > 2sigma(I)]	R1 = 0.0683, wR2 = 0.1176
R indices (all data)	R1 = 0.1138, wR2 = 0.1681
Absolute structure parameter	-0.01(5)
Largest diff. peak and hole	1.357 and -1.051 e.Å^3

Appendix 2

Supplementary Crystal Structure Data for Chapter 3

Compound numbering refers to the numbers given to the complexes in Chapter 3.

Supplementary data for $[Pd(CO_2Me)(MeCN)(PPh_3)_2](BF_4)\cdot(MeCN)$ complex (11)

Empirical Formula	$C_{42}H_{39}BF_4N_2O_2P_2Pd$
Formula Weight	858.90
Temperature	150 (2) K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 11.6864(12) Å α =110.659(5)°
	b = 12.5122(12) Å β =100.064(6)°
	c = 14.783 (2) Å γ = 90.577(5)°
Volume	1985.5(4) $Å^3$
Z	2
Density (Calculated)	1.437 Mg/m^3
Absorption Coefficient	0.605 mm^{-1}
F(000)	876
Crystal Size	0.40 x 0.30 x 0.10 mm
θ range for data collection	1.50 to 30.55°
Limiting Indices	$-16 \leq h \leq 16$, $-14 \leq k \leq 17$, $-20 \leq l \leq 20$
Reflections collected	16518
Independent Reflections	10591 [R(int) = 0.0274]
Absorption Correction	None
Refinement method	Full matrix least squares on F^2
Data / restraints / parameters	10587 / 0 / 487
Goodness of Fit	1.002
Final R indices [I > 2sigma(I)]	R1 = 0.0399, wR2 = 0.0853
R indices (all data)	R1 = 0.0656, wR2 = 0.0969
Largest diff. peak and hole	1.149 and -0.765 e.$Å^3$

Appendix 3

Supplementary Crystal Structure Data for Chapter 4

Compound numbering refers to the numbers given to the complexes in Chapter 4.

Crystal Data for [Pd(I)$_2$(dppe)] complex (6).

Empirical Formula	$C_{26}H_{24}I_2P_2Pd$
Formula Weight	758.59
Temperature	150 (2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 9.465(1) Å α =90° b = 19.821(1) Å β =105.51(1)° c = 14.208 (1) Å γ = 90°
Volume	2568.4(4) Å^3 ,
Z	2
Density (Calculated)	1.962 g/cm^3
Absorption Coefficient	3.263 mm^{-1}
F(000)	1448
Crystal Size	0.30 x 0.12 x 0.06 mm
θ range for data collection	1.81 to 27.50 °
Limiting Indices	$-12 \leq h \leq 12$, $-27 \leq k \leq 27$, $-20 \leq l \leq 20$
Reflections collected	18477
Independent Reflections	5903 [R(int) = 0.0563]
Absorption Correction	Integration
Max and Min transmission	0.8320 and 0.3552
Refinement method	Full matrix least squares on F^2
Data / restraints / parameters	5806 / 0 / 280
Goodness of Fit	1.135
Final R indices [I > 2sigma(I)]	R1 = 0.0404, wR2 = 0.0716
R indices (all data)	R1 = 0.0617, wR2 = 0.0832
Largest diff. peak and hole	0.651 and -0.972 e.Å^3

Crystal structure data for $[Pd(I)_2(PPh_3)_2]^{\cdot}(THF)_2$ complex (9)

Empirical Formula	$C_{44}H_{46}I_2O_2P_2Pd$
Formula Weight	1028.95
T/K	150(2)
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P2(1)/c
Unit Cell Dimensions	a = 12.011(1)Å, b = 20.234(1) Å, c = 8.265 (1)Å, α = 90 °, β = 90.35(1)°, γ = 90°
Volume	2096.1(3) $Å^3$
Z	2
Density (calc.)	1.630 g/cm^3
Absorbtion coefficient	2.207 mm^{-1}
F(000)	1016
Crystal size	0.20 x 0.15 x 0.12 mm
θ range for data collection	1.01 to 27.50°
Limiting Indices	$-11 \leq h \leq 16$, $-25 \leq k \leq 28$, $-12 \leq l \leq 12$
Reflections collected	15358
Independent reflections	4806 [R(int) = 0.0557]
Absorption correction	integration
Max and Min transmision	0.7945 and 0.7085
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4756 / 2 / 233
Goodness of fit on F^2	1.118
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0668
R indices (all data)	R1 = 0.0517, wR2 = 0.0754
Exttinction coefficient	0.0007(1)
Largest diff. peak hole	0.643 and -0.519 $eÅ^3$

Appendix 4

Supplementary Crystal Structure Data for Chapter 5

Compound numbering refers to the numbers given to the complexes in Chapter 5.

Crystal structure data for Ni complex (4)

Empirical Formula	$C_{35}H_{27}Cl_5NiP_2$
Formula Weight	745.47
T/K	200(2)
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 13.2276(2)Å, b = 18.1023(3) Å, c = 14.061 Å α = 90 °, β = 99.5990(10)°
Volume	3319.81 Å^3
Z	4
Density (calc.)	1.492Mg/m^3
Absorbtion coefficient	1.108 mm^{-1}
F(000)	1520
Crystal size	0.14 x 0.14 x 0.26 mm
θ range for data collection	1.85 to 27.46°
Limiting Indices	$-17 \leq h \leq 15$, $-22 \leq k \leq 23$, $-11 \leq l \leq 18$
Reflections collected	23880
Independent reflections	7558 [R(int) = 0.0796]
Absorption correction	none
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7553 / 15 / 415
Goodness of fit on F^2	1.157
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.0960
R indices (all data)	R1 = 0.1031, wR2 = 0.1231
Largest diff. peak hole	0.636 and -0.449 eÅ^3

Crystal Data for Co complex (15).

Empirical Formula	$C_{36}H_{30}Cl_6CoOP_2$
Formula Weight	812.17
Temperature	150 (2) K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 11.2057(2) Å α = 80.5340(10)°
	b = 12.9376(3) Å β = 67.4990(10)°
	c = 13.6528(3) Å γ = 82.7210(10)°
Volume, Z	1799.31(7) $Å^3$, 2
Density (Calculated)	1.499 Mg/m^3
Absorption Coefficient	1.041 mm^{-1}
F(000)	826
Crystal Size	0.4 x 0.1 x 0.1 mm
θ range for data collection	1.60 to 27.53 °
Limiting Indices	$-13 \leq h \leq 14$, $-16 \leq k \leq 16$, $-15 \leq l \leq 17$
Reflections collected	13195
Independent Reflections	8206 [R(int) = 0.0282]
Absorption Correction	SADABS
Refinement method	Full matrix least squares on F^2
Data / restraints / parameters	8914 / 6 / 431
Goodness of Fit	1.029
Final R indices [I > 2sigma(I)]	R1 = 0.0537, wR2 = 0.1212
R indices (all data)	R1 = 0.0905, wR2 = 0.1442
Largest diff. peak and hole	1.001 and -0.875 $e.Å^3$

Supplementary Data for dpno crystal structure (25)

Empirical Formula	$C_{34}H_{26}O_2P_2$
Formula Weight	528.49
T/K	150(2) K
Wavelength	0.710173 Å
Crystal System	Monoclinic
Space Group	C2
Unit Cell Dimensions	a = 34.7352(5) Å; b = 8.7303(2) Å; c = 19.2286(3) Å ; α = 90°; β = 112.3840(10) °; γ = 90°
Volume	5391.7(2) $Å^3$
Z	8
Density (calc.)	1.302 Mg/m^3
Absorbtion coefficient	0.192 mm^{-1}
F(000)	2208
Crystal size	0.04 x 0.1 x 0.2 mm
θ range for data collection	1.15 to 27.52 °
Limiting Indices	$-44 \leq h \leq 44$, $-9 \leq k \leq 11$, $-24 \leq l \leq 24$
Reflections collected	19537
Independent reflections	11368 [R(int) = 0.0727]
Absorption correction	none
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	11313 / 1 / 685
Goodness of fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0697 wR2 = 0.1039
R indices (all data)	R1 = 0.1522, wR2 = 0.1463
Largest diff. peak hole	0.344 and -0.376 $eÅ^{-3}$

Appendix 5

Experimental Parameters

Unless otherwise stated, all reactions were carried out under a dry, oxygen free nitrogen atmosphere, using standard vacuum line techniques, and the solvents were dried and freshly distilled prior to use. $Pd_2(dba)_3$·$(CHCl_3)$, the phosphines dtbpp and dcpe were kindly donated by ICI Acrylics, all other chemicals were bought commercially (from Aldrich, Lancaster or Acros) or synthesised as described.

The NMR spectra were recorded on a Bruker AC250 spectrometer at the following frequencies: phosphorus 101 MHz, carbon 70 MHz and proton 250 MHz. The proton and carbon NMR were referenced to the ^1H and ^{13}C chemical shifts of the solvent as the internal standard, and reported with respect to $SiMe_4$. The ^{31}P NMR spectra were referenced to an external frequency lock and reported with respect to 85% H_3PO_4 at 0 ppm. The IR spectra, unless stated otherwise, were recorded in a nujol / KBr matrix or in KBr disks at 4 cm^{-1} resolution on a Perkin-Elmer 1600 Series FT-IR Spectrometer.

The mass spectra were recorded on a VG analytical 707E spectrometer. Fast atom Bombardment using Xenon was used on the complexes in a nitrobenzylalcohol (NOBA) matrix. The electrospray mass spectrum was carried out in dichloromethane. The carbon, hydrogen, and nitrogen analyses were measured on a CE440 elemental analyser.

Appendix 6

Colloquia, Lectures and Conferences Attended.

8.1 Lectures and Colloquia at Durham.

1994

October 19	Prof. N. Bartlett, University of California, 'Some Aspects of Ag(II) and Ag(III) Chemistry'
November 2	Dr. P.G. Edwards, University of Wales, Cardiff 'The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands'
November 9	Dr. G. Hogarth, University College London 'New Vistas in Metal-Imido Chemistry'
November 16	Prof. M. Page, University of Huddersfield 'Four Membered Rings and β-Lactamase'
November 23	Dr. J.M.J. Williams, University of Loughborough 'New Approaches to Asymmetric Catalysis'

1995

January 25	Dr. D.A. Roberts, Zeneca Pharmaceuticals 'The Design and Synthesis of Inhibitors of the Renin-Angiotensin System'
February 1	Dr. T. Cosgrove, Bristol University 'Polymers do it at Interfaces'
February 8	Dr. D. O'Hare, Oxford University Synthesis and Solid State Properties of Poly-, Oligo-, and Multidecker Metallocenes'
March 1	Dr. M. Rossiensky, Oxford University 'Fullerene Intercalation Chemistry'

March 22	Dr. M. Taylor, University of Auckland 'Structural Methods in Main Group Chemistry'
May 4	Prof. A.J. Kresge, University of Toronto *The Ingold Lecture*, 'Reactive Intermediates: Carboxylic-acid Enols and other unstable species'
June 6	Dr. R. Snaith, Cambridge University 'Ionic Molecules Formed by S Block Metals, Synthesis, Structure and Uses'
June 9	Dr. N.G. Connelly, University of Bristol 'Studies on Redox Active Organometallic and Co-ordination Compounds'
June 20	Dr. K. Cavell, University of Tasmania 'Fundamental Studies on the Insertion Processes and Development of Catalysts for CO and Olefin Conversion'
November 1	Prof. W. Motherwell, University College London 'New Reactions in Organic Synthesis'
November 15	Dr. A. Sella, University College London 'Chemistry of Lanthanides with Polypyrazoylborate Ligands'
November 29	Prof. D. Tuck, University of Windsor, Ontario 'New Indium Co-ordination Chemistry'
December 8	Dr. Bill Henderson, Waikato University 'Electrospray Mass Spectrometry - a New Sporting Technique'

1996

February 28	Prof. E.W. Randall, Queen Mary & Westfield College 'New Perspectives in NMR Imaging'
March 6	Dr. R. Whitby, University of Southampton 'New Approaches to Chiral Catalysts'
March 12	Prof. V. Balzani, University of Bologna 'Supramolecular Photochemistry'

March 13	Prof. D. Garner, Manchester University ‘Mushrooming in Chemistry’
October 16	Prof. Ojima, State University of New York ‘Siliyformylation and Silylcarbocyclisation in Organic Synthesis’
October 22	Prof. L. Gade, University of Wurzburg ‘Organic Transformations with Early-Late Heterobimetallics: Synergism and Selectivity’
October 23	Prof. H. Ringsdorf, Johannes-Gutenburg University ‘Function Based on Organisation’
October 30	Dr. P. Mountford, Nottingham University ‘Recent Developments in Group IV Imido Chemistry’
November 13	Dr. G. Resnati, University of Milan ‘Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents’
November 18	Prof. G. Olah, ‘Crossing Conventional lines in my Chemistry of the Elements’
November 27	Dr. R. Templer, Imperial College ‘Molecular Tubes and Sponges’
December 11	Dr. C. Richards, Cardiff University ‘Stereochemical Games with Metallocenes’

1997

January 16	Dr. S. Brooker, University of Otago ‘Exciting yet Contolled Thiolate Coordination Chemistry’
January 22	Dr. N. Cooley, BP Chemicals (Sunbury) ‘Synthesis and Properties of Alternating Polyketones’
February 5	Dr. A. Haynes University of Sheffield ‘Mechanisms in Homogeneous Catalytic Carbonylation’

8.2 Scientific Meetings

1995

December	Perkin Regional Meeting (Durham)

1996

September	1st Anglo-Dutch Symposium on Organometallic Chemistry (Sheffield)
December	Durham University Chemistry Poster Session (Durham) (Poster Contribution)

1997

February	Scottish Dalton Meeting (Edinburgh)
September	XIIth FECHEM Conference in Organometallic Chemistry (Prague) (Poster Contribution)