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ALKENE AMINATIONS CATALYSED BY TRANSITION METALS

by

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(Grey College)

A thesis submitted to the University of Durham for the
degree of Master of Science

November 1986

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1984 and September 1986. It has not been submitted, either wholly or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

P. Nuttall

To My Parents,

Jean and Peter Nuttall

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Alkene Aminations Catalysed by Transition Metals

By P. Nuttall, B.Sc. (Hons.), Grey College

ABSTRACT

Amines, especially long chain tertiary alkylamines, are industrially useful compounds with a relatively high commercial value. They are currently synthesised by a variety of multi-step processes, but a simple "one pot" catalytic synthesis is a highly desirable alternative with considerable potential advantages over existing methods. This thesis is concerned with possible routes to alkylated amines via amination of alkenes promoted by transition metals. The chemistry of transition metal alkene complexes relevant to amination of the alkene, is reviewed in detail. A search is made for complexes suitable for use as models with which to study the catalytic process.

In an attempt to minimise nucleophilic attack at the metal centre, but maximise attack at coordinated alkenes, attempts were made to synthesise complexes containing strongly σ-donating anionic groups. In this context, reactions of palladium compounds with the dianion of N,N'-diphenyloxamide ($\text{Ph}\overset{\ominus}{\text{N}}\text{COCO}\overset{\ominus}{\text{N}}\text{Ph}$) are reported, which relate to the synthesis of previously unknown palladium alkene complexes. Also reported are some attempted reactions of amines with known metal alkene complexes.

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CHAPTER ONE

INTRODUCTION

INTRODUCTION

Many amines particularly long chain tertiary aliphatic amines are bulk intermediate chemicals with a fairly high commercial value. The biological activity of amines and their derivatives makes them very useful for pharmaceuticals, disinfectants and fungicides. Their chemical and physical properties make them suitable for many applications including mineral flotation, bitumen adhesion and fertiliser anticaking to name but a few.

The target of this thesis is to look at the proposed catalytic amination process shown in Figure 1. An important aim was to obtain information which could lead to a better understanding of the chemistry involved, and to a viable process. The principal routes which are currently used in the industrial production of amines are based on either aminolysis of alcohols or hydrogenation of nitriles. Both of these routes shown below involve several chemical stages from petroleum. The route to long chain tertiary amines requires hydroformylation at high pressure as an intermediate step. A simple "one pot" catalytic process eliminating intermediate stages has considerable attraction to industry and could be more advantageous than the existing routes.

Aminolysis of alcohols

$$RCH_2{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO \longrightarrow RCH_2CH_2CH_2OH \xrightarrow{+NH_3} RCH_2CH_2CH_2NH_2 + H_2O$$

Hydrogenation of nitriles

$$RCH_2CN + H_2 \longrightarrow RCH_2CH_2NH_2$$

1.1 The Proposed Catalytic Amination Process

Referring to Figure 1, the proposed catalytic amination process has four basic steps.

1. Coordination of the alkene, normally a terminal alkene, to the metal starting complex [M].

2. Nucleophilic attack by the amine at the coordinated alkene to produce a zwitterionic σ-alkyl complex.

3. 1,3-Hydrogen shift followed by spontaneous cleavage of the higher amine: the proton of the nitrogen is transferred to the ß-carbon, and the ethylamine complex thus formed spontaneously decomposes to give the substituted ethylamine and a metal complex. This step could be promoted in many ways, either by reduction using reagents such as lithium aluminium hydride, or by oxidative addition of reagents such as H_2 or HI followed by reductive elimination, (as shown in Figure 1).

4. Regeneration of catalyst: depending on how step 3 is achieved this step may or may not be needed. If the σ-alkyl intermediate complex is reduced to give the metal for example, then this must be reoxidised to produce the starting complex. In palladium chemistry this is often achieved using either copper chloride and air or benzoquinone.

In chapter two the chemistry of the alkene complexes of transition metals, which is relevant to amination of the alkene, is reviewed in detail.
In the third chapter the reactions of some metal alkene complexes with amines are investigated, and some chemistry related to synthesis of previously unknown alkene complexes of palladium is reported.

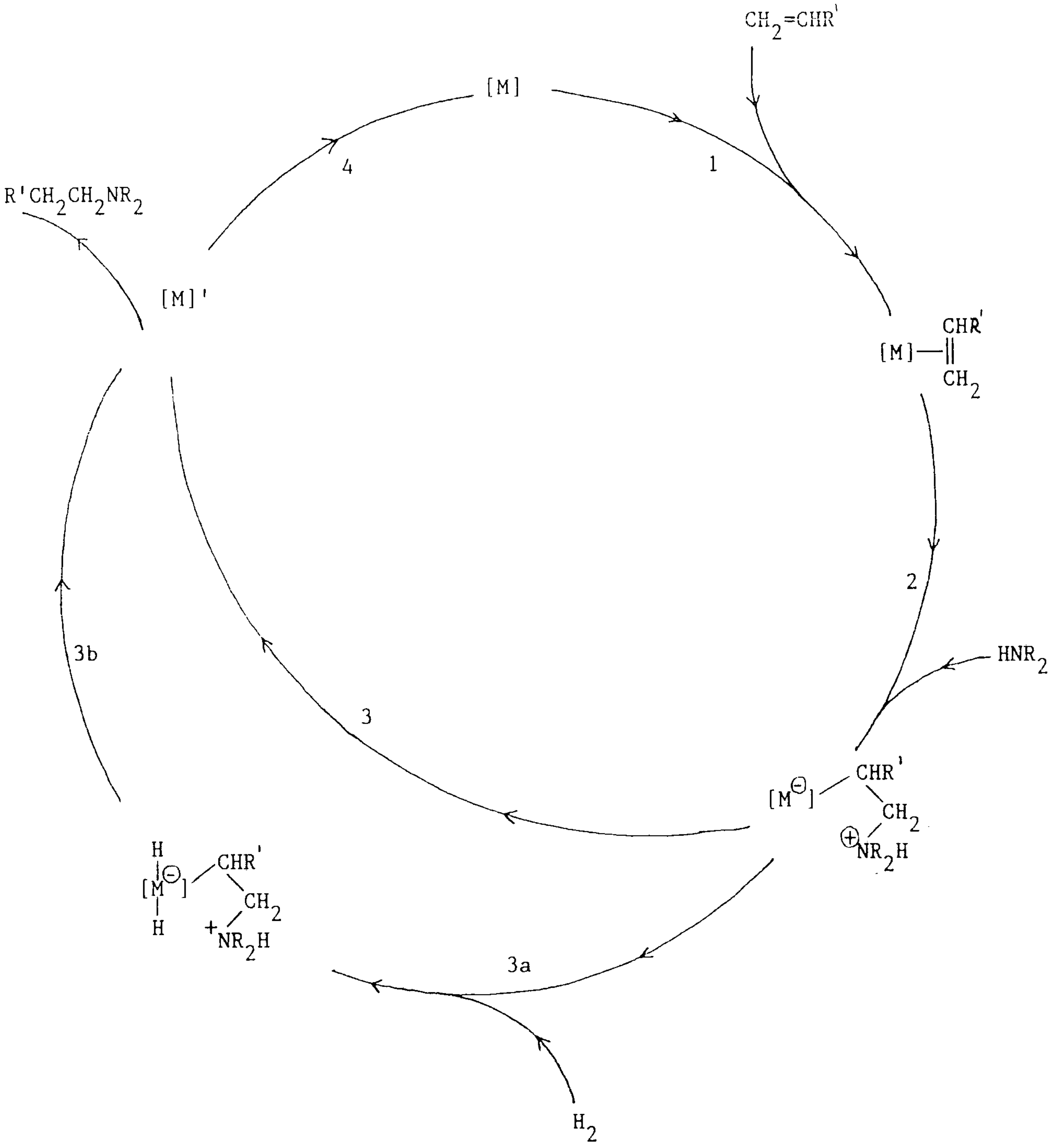


Figure 1. The proposed catalytic amination cycle.

CHAPTER TWO

A REVIEW OF TRANSITION METAL ALKENE COMPLEXES RELEVANT TO A CATALYTIC AMINATION PROCESS

INTRODUCTION

This review deals with the chemistry of known transition metal alkene complexes, which is relevant to developing the catalytic amination process, (Figure 1), discussed in the previous chapter. The primary aim was to find model complexes, with which to study the intermediate steps of the amination process. This would hopefully lead to the discovery of a catalytic system. Several reports of limited catalytic activity have already appeared. These are discussed together in one of the later sections. Alkene reactions which do not involve transition metals are not reviewed. A much less specific review by Gasc et al[1] covers the general amination of alkenes to the end of 1981.

As a preliminary to the review it is relevant to consider the properties required of an alkene complex in order for it to be suitable for the amination reaction.

2.1.1 Assessing the Suitability of Alkene Complexes for Amination

There are three main criteria an alkene complex must satisfy, in order to be suitable for testing for the catalytic process, (Figure 1).

(i) First and foremost the coordinated alkene must be susceptible to nucleophilic attack.

(ii) The complex must be sufficiently stable that displacement of the alkene by amine is not a strongly competing reaction.

(iii) Once nucleophilic attack has occurred, the σ-alkyl complex formed must be able to undergo a cleavage reaction, producing an easily obtainable amine, plus a metal complex readily convertable to the starting complex.

These factors will be considered now in more detail.

2.1.2 Susceptibility to Nucleophilic Attack

For the alkene to be susceptible to nucleophilic attack, its coordination to the metal must result in an overall depletion of electron density from the double bond. The bonding between a transition metal and an alkene, as postulated by the Chatt-Dewar-Duncanson model,[2,3] has two different components which reinforce one another in a synergic process. A forward bonding component illustrated in Figure 2, results from transfer of electron density in the π-bonding MO of the alkene to a suitable orbital on the metal. The back bonding component results from transfer of electron density of a metal d orbital, into the π* antibonding MO of the alkene. This is illustrated in Figure 3. For the alkene to be relatively electron deficient, hence susceptible to nucleophilic attack, the back bonding component must be smaller than the forward bonding component. There are many ways of estimating the extent to which back bonding is involved, hence it is usually possible to predict if the alkene will be susceptible to nucleophilic attack.

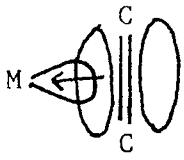


Figure 2. The forward bonding component.

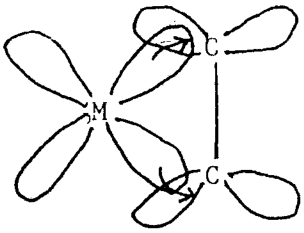


Figure 3. The back bonding component.

As back bonding increases the carbon-carbon bond length increases, (due to filling of the alkene π* MO), and the olefinic protons are pushed back out of the plane of the alkene. This is illustrated in Figure 4, and is evident in the crystal structures of the relevant

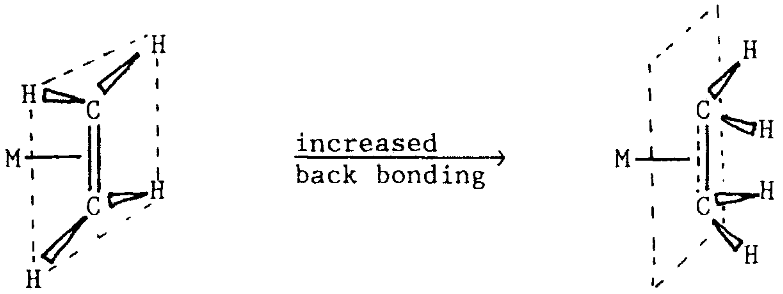


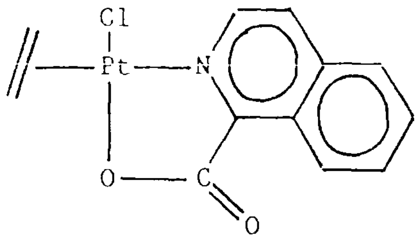
Figure 4

complexes. For example the alkene bond length in $(C_5Me_5)Ta(PMe_3)$-$(CHCMe_3)(C_2H_4)$ is 1.477 Å compared with 1.337 Å for ethene. The angle α, (defined as the angle between the two normals to the CH_2 planes), was reported to be 68.5°.[4]

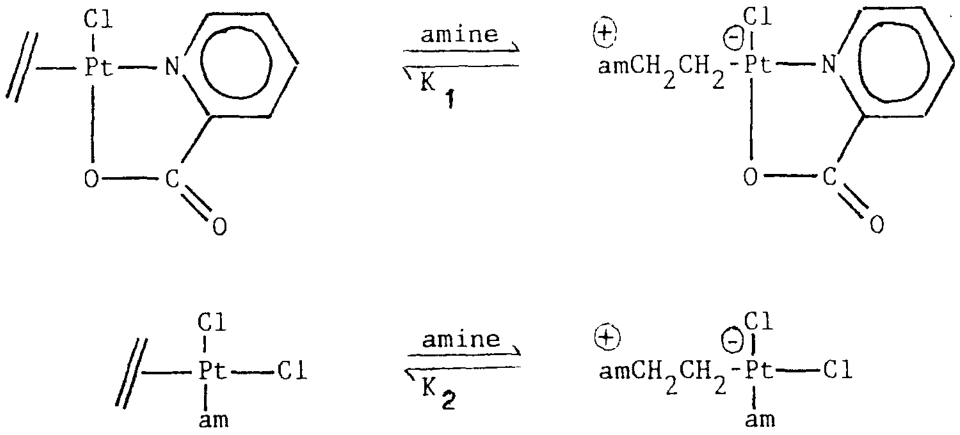
The backbonding component of the metal alkene bond is not symmetrical with respect to rotation about the metal alkene axis, (see Figure 3). If only one orbital on the metal is available for back-bonding, or if the available orbitals differ greatly in energy, then rotation of the alkene in this way is hindered. The greater the extent of back bonding the larger the activation energy for this rotation will be. This can be estimated by using nmr techniques, to observe the temperature at which the olefinic protons become equivalent in a non-symmetrical complex: hence the extent of back bonding to the alkene can be estimated. A whole series of substituted cyclopentadienylbis-ethenerhodium complexes have been studied in this way[27] and provide a good example of this phenomena. It should be noted that this phenomena does not occur for all alkene complexes, and hindrance to rotation can result from other factors, e.g. steric considerations.

The greater the electron density on the metal, the larger the extent of back bonding. The lower valent complexes such as with Pt $\underline{\bar{0}}$ for example, have carbon-carbon bond lengths up to 0.2 Å greater than that of the free alkene. Complexes with good electron releasing ligands will also enhance extensive backbonding, e.g. $(C_5Me_5)Rh(PPh_3)(C_2H_4)$, the C=C bond length is 1.408 Å (cf. 1.337 Å for ethene), and the hydrogens are bent back significantly out of the olefinic plane.[60]

As well as electronic considerations, there are also kinetic and thermodynamic factors to be taken into account. Any ligand that increases the stability of the σ-alkyl intermediate with respect to the ethene starting complex, will promote nucleophilic attack at the alkene. A good example of this is the chloroisoquinoline-1-carboxylato-η-etheneplatinum(II) complex[5] shown below.



The equilibrium constants for attack of amines at this complex were found to be up to 100 times larger than those for related dichloroamine complexes.



K_1 is 100 times greater than K_2.

The explanation given for this observation was as follows. Coordination of the carboxylate group forces the pyridine to lie in the PtClNO plane. This results in the pyridine and ethene which are both good π accepting ligands, competing with each other for the electron density of the same d orbital. Hence the complex is less stable than the corresponding dichloroamine complex. Reaction to give the σ-alkyl complex removes this instability, as the two ligands no longer compete for the same electron density: hence the equilibrium is displaced to the right. This process bears some analogy with the <u>trans</u>-effect and the enhanced rate of attack by nucleophiles at the trans position to π-acid ligands. A similar displacement would occur if the σ-alkyl complex could be made more stable in other ways. This might be achieved, by using ligands capable of delocalising the formal negative charge placed on the metal as a result of attack.

To summarise, a complex with a relatively electron deficient centre is required, cationic complexes are ideal. Any ligand which will stabilise the σ-alkyl complex in model systems to be used to study the amination process is also desirable.

2.1.3 Displacement of the Alkene

Irreversible alkene displacement by amines is one of the most frequently encountered problems with the reaction. For example, in much of the reported palladium work reactions have to be performed at low temperatures in order to minimise this strongly competing side reaction.

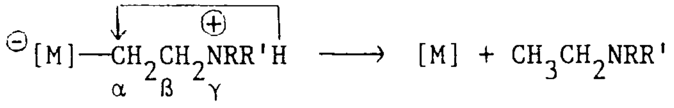
Strong metal alkene bonds usually result when a considerable amount of back bonding is present, enabling the synergic bonding process to have maximum effect.

One of the commonest ways of stabilising metal alkene complexes is through the use of good electron donating ligands, eg cyclopentadienyl, attached to the metal. Unfortunately, as previously mentioned, this is the opposite of what is required to promote nucleophilic attack. The need for seemingly conflicting electronic requirements, is one of the fundamental problems facing the proposed catalytic process.

Alkenes are normally classed as soft bases and as such will tend to bond more successfully with soft acids. As a broad generalisation therefore, one would expect the alkene complexes to increase in stability on going from left to right in the transition metal series, or on descending a specific group of the Periodic Table. This is usually found to hold true. There are very few alkene complexes of the earlier transition metals stable under normal temperature and pressure conditions, whereas there are a large number of palladium and platinum complexes. Also in descending the nickel group, platinum complexes are usually much more stable than the palladium analogues.

2.1.4 Cleavage of the σ-Alkylamino Group

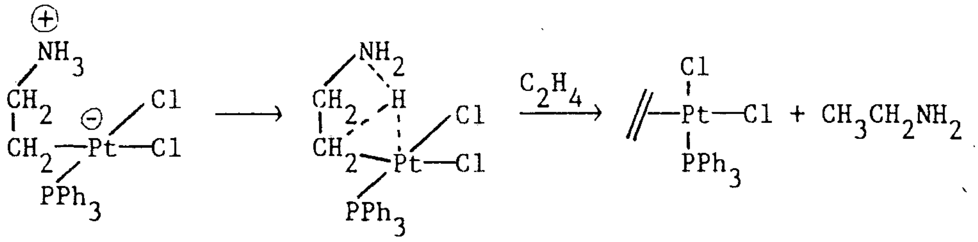
The final step of the catalytic process, illustrated below, involves transfer of the ammonium proton to the α carbon with cleavage of the higher amine. Unfortunately, this reaction has rarely been



$${}^{\ominus}[M]\text{—}\underset{\alpha}{CH_2}\underset{\beta}{CH_2}\underset{\gamma}{\overset{\oplus}{N}}RR'H \longrightarrow [M] + CH_3CH_2NRR'$$

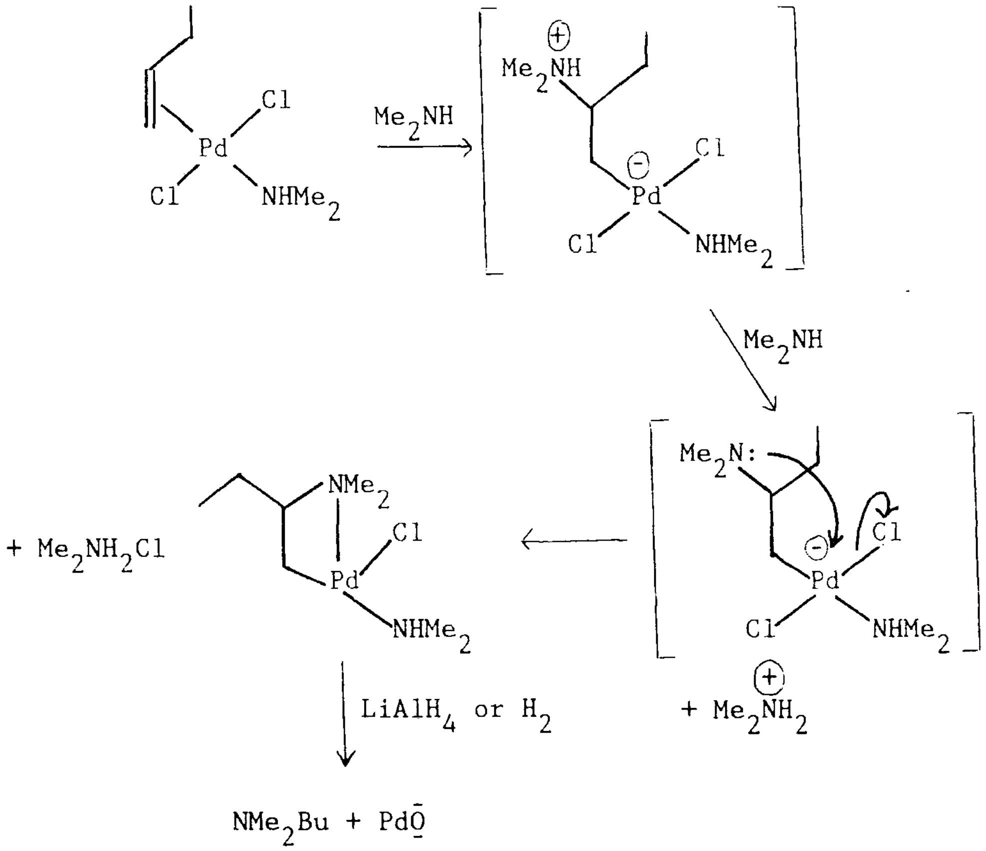
found to occur spontaneously. It may proceed in several ways.

(i) The ammonium proton may be transferred in one step, interacting directly with both the metal and the α-carbon. This has been postulated to occur during the successive alkylation of ammonia or ethylamine using the platinum complex shown below.[6]

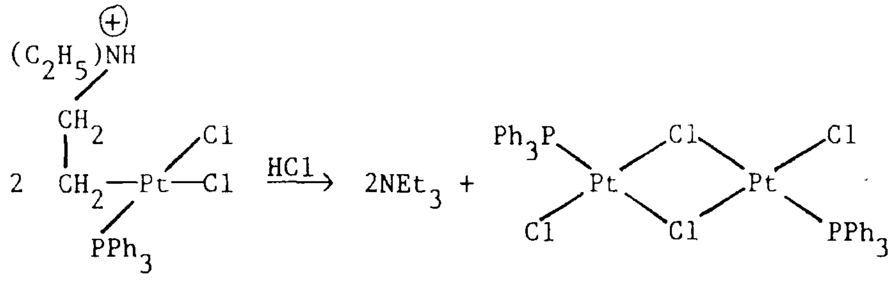


The above reaction occurred rapidly with ammonia, to a lesser extent with ethylamine and not at all with diethylamine. The protons of more substituted ammonium ions, e.g. diethylamine, were postulated to be insufficiently acidic to undertake the transfer.

(ii) The ammonium proton is first removed by a base, which in many cases may be excess of the amine. A different source of hydrogen is then used to cleave the α carbon. This can be metal bound hydrogen, resulting from oxidative addition of H_2 or HX, or it may occur as hydride when the complex is destructively reduced using reagents such as $LiAlH_4$. A good example of this type of cleavage is the palladium promoted reaction shown below.[7]



(iii) The higher amine may be liberated as its hydrohalide salt by direct acid hydrolysis, e.g. the platinum promoted reaction shown below.[6]



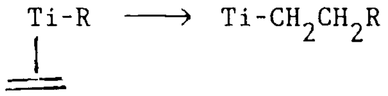
One important property the σ alkyl complex must possess to undergo any of the methods of cleavage, is the ability to expand its coordination number, e.g. by oxidative addition. If it is already coordinatively saturated it must be able to lose ligands easily in order to achieve this property.

2.2.1 Literature Survey

Having considered the properties required of an alkene complex for undergoing the amination reaction, we shall now survey the known complexes and the chemistry concerning them. There exists many very unstable short lived alkene complexes, and although they have never been isolated and fully characterised, they are often assumed to be intermediates in many reactions. It is likely that a short lived complex will act as the catalytic species in the amination process. This survey, however, does not include an exhaustive survey of such intermediates, but concentrates on those complexes suitable as model materials.

2.3.1 Group IV. Titanium, Zirconium, Hafnium

There are no reports of thermally stable π-bonded alkene complexes of these metals. There are, however, numerous examples of short lived intermediate complexes. These include the intermediates in the Ziegler Natta polymerisation of alkenes,[26] and the intermediates in the more recently reported zirconium promoted synthetic reactions.[61] The exact mechanism of the Ziegler Natta reaction is not known, but migration of an alkyl group onto titanium coordinated alkene, has been postulated as an intermediate step.



$$\text{Ti-R} \longrightarrow \text{Ti-}CH_2CH_2R$$

This could be thought of as internal nucleophilic attack of the alkyl upon the alkene. External nucleophilic attack on alkenes coordinated to these metals has not been achieved.

2.4.1 Group V. Vanadium, Tantalum, Niobium

Thermally stable simple alkene complexes of vanadium are not known. The alkene complexes of tantalum and niobium fall into three main categories.

(i) $(\eta_5C_5H_5)_2MX$ (alkene) $X = H, Cl, Me, Et, Pr$ etc.

(ii) $(\eta_5C_5H_5)MX_2$ (alkene) $X = Cl, Br, OMe$

(iii) MX_3L_2 (alkene) $X = Cl, L = PMe_3$

The first category is the most common. The complexes are all very electron rich and experimental reports indicate extensive backbonding. The crystal structure of $Cp_2NbEt(C_2H_4)$[8] showed the C=C bond length as 1.406 Å, (cf. 1.377 for ethene), and the angle between the two normals of the CH_2 planes (α) was 52°. NMR studies of this complex showed free rotation of ethene to be extraordinarily slow. The four protons were inequivalent even at room temperature.

Preliminary investigations[9] have shown, as expected, that backbonding to alkenes in the second category of complex is not quite as extensive as for the first category complexes.

Examples of the final category of complex are limited, they are formed during metathesis-like reactions of the corresponding alkylidene complexes e.g. $Ta(PMe_3)_2Cl_3(C_2H_4)$.[39]

In general the experimental reports indicate that the alkene complexes of metals in this group are better thought of as metallocyclopropane structures. This does not encourage nucleophilic attack at the alkene.

2.5.1 Gp VI. Chromium, Molybdenum, Tungsten

As expected the alkene complexes of this group increase in stability on descending the group. Simple monoalkene complexes of chromium are not known. Much of the molybdenum and tungsten chemistry is very similar and has been developed in parallel. Although the molybdenum complexes are more reactive, the tungsten complexes are often more difficult to prepare. This is due to the relative inertness of many tungsten precursors towards ligand substitution reactions.

There are only a few neutral alkene complexes of these metals known. Complexes of formulae $M(CO)_{6-n}(alkene)_n$ (n = 1 or 2), have been isolated for M = tungsten, and there is IR evidence for M = molybdenum complexes.[40] The only other simple neutral alkene complex reported is $Mo(diphos)_2(C_2H_4)_2$.[41] Nucleophilic attack at the alkenes of the neutral complexes has not been reported, the alkenes being very labile and readily displaced.

There are, however, several reports of nucleophilic attack at cationic complexes. The complexes involved are of the two main types.

(i) $[(\eta_5C_5H_5)M(CO)_3(alkene)]^+$ M = Mo or W

(ii) $[(\eta_5C_5H_5)_2MR(alkene)]^+$ M = Mo or W, R = H, alkyl

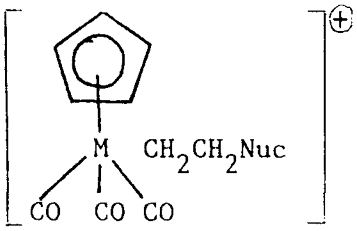
2.5.2 $[(\eta\text{-}C_5H_5)M(CO)_3(alkene)]^+$ Complexes

Nucleophilic attack by nitrogen and phosphine bases at the alkenes of these complexes was first reported by W.H. Knoth.[10] The results are summarised in Table 1.

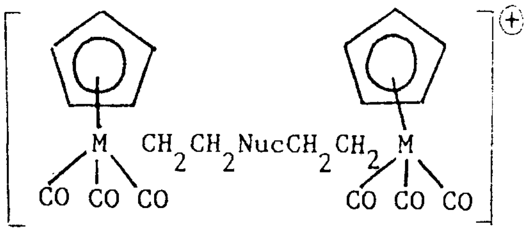
Table 1

Nucleophile	C_5H_5N	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	NH_3	$(C_6H_5)_3P$
Complex	Type of Product Formed					
$CpMo(CO)_3C_2H_4^+$	1	2	-	1	1,2	1
$CpW(CO)_3C_2H_4^+$	1	2	1,2	1	1,2	1

Product Types 1 =



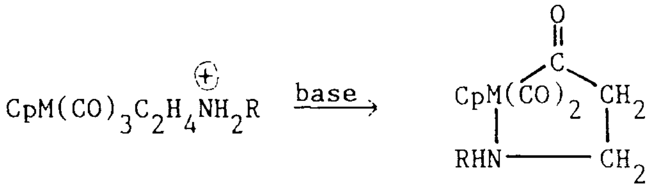
2 =



With ammonia the type of product was found to be dependent on experimental conditions. On passing gaseous ammonia over the solid starting complex, the dialkylated product $\underline{2}$ predominates though with tungsten a small amount of monoalkylated product $\underline{1}$ was also obtained.

$$[CpM(CO)_3C_2H_4]^+ \xrightarrow{NH_3} \underset{1}{CpM(CO)_3C_2H_4\overset{\oplus}{N}H_3} \xrightarrow{NH_3} \underset{2}{(CpM(CO)_3C_2H_4)_2\overset{\oplus}{N}H_2} + \overset{\oplus}{N}H_4$$

Action of base, e.g. hydroxide, on either product results in deprotonation followed by cyclisation, and insertion of one of the carbonyls as illustrated below.



R = H or $CpM(CO)_3C_2H_4$

Unfortunately, the amines, being bases, also cause this reaction to take place, and hence some cyclised product is always formed.

If the reaction with ammonia is carried out in a benzene solution, the molybdenum complex gives predominantly monoalkylated product 1 (Table 1). This spontaneously deprotonates and cyclises as previously shown.

With methylamine the dialkylated product 2 (Table 1) was produced. This also deprotonated to give an analogous cyclic product, though with tungsten a small amount of the simple deprotonated $CpW(CO)_3CH_2CH_2NHCH_3$ was also produced.

Cleavage of the σ alkyl group to yield alkylated amines proved extremely difficult. Bases cause cyclisation to occur. Hydrochloric acid caused the pyridine adducts to decompose whereas the ammonia adducts were largely unaffected. Treating the molybdenum complex with refluxing alcoholic HCl resulted in formation of the simple chloride salt.

$$(CpMo(CO)_3C_2H_4)_2NH_2^{\oplus}PF_6^{\ominus} \xrightarrow[\text{reflux}]{\text{HCl, ROH}} (CpMo(CO)_3C_2H_4)_2NH_2^{\oplus}Cl^{\ominus}$$

Action of aqueous acetonitrile on both the molybdenum and tungsten trimethylamine adducts resulted in decomposition with loss of ethene. Refluxing the tunsten ammonia adduct in the presence of triphenyl phosphine resulted in exchange of ammonia for phosphine.

$$(CpW(CO)_3C_2H_4)_2NH_2^{\oplus}PF_6^{\ominus} \xrightarrow[\substack{\text{THF}\\ \text{16 hr}\\ \text{reflux}}]{\text{PPh}_3\text{ in}} 2\ CpW(CO)_3CH_2CH_2PPh_3^{\oplus}PF_6^{\ominus}$$

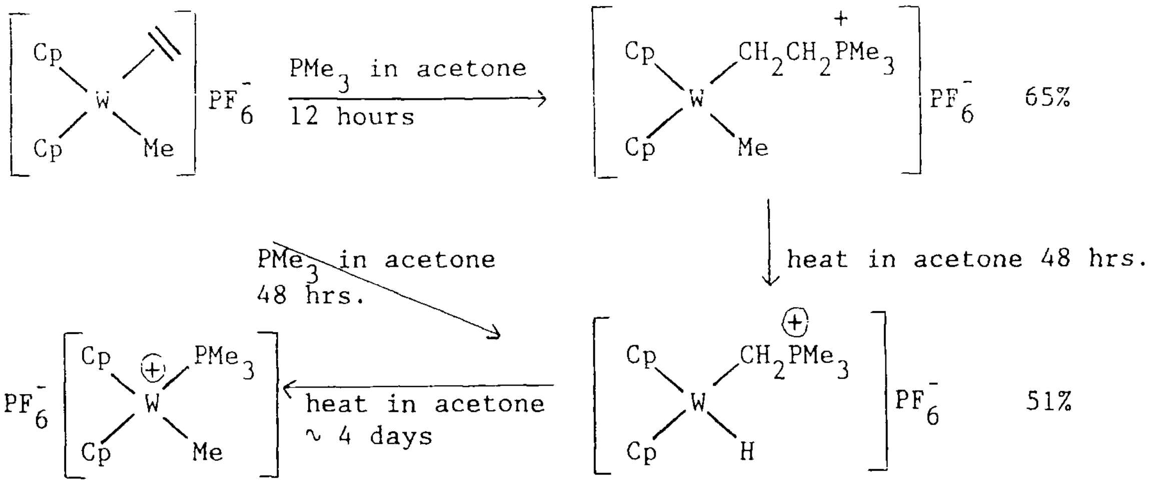
A limited success was achieved with the tungsten phosphine product. Refluxing for 16 hours in methanolic hydrochloric acid produced a black residue found to contain a small amount of $\overset{\oplus}{PPh_3}(CH_2CH_3)$.

Summarising the chemistry of these complexes; the alkene has been activated towards nucleophilic attack by amines, but only in a few specific cases is a reasonable yield of the simple σ-alkylamine complex formed. In most reactions a large amount of cyclised product results and the presence of carbon monoxide is detrimental to simple amine formation. Cleavage of the 2-aminoethyl group could not be achieved. Bases are unsuitable and acids were unsuccessful. The complexes have 18 electrons therefore they are not immediately susceptible to oxidative addition reactions.

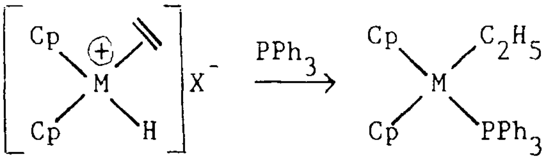
2.5.3 $[Cp_2MR(alkene)]^{\oplus}$ Complexes

Nucleophilic attack at the alkenes of these complexes is much less common and straightforward than for the previous category.

Nucleophilic attack was one of several reactions found to occur, on treating the complex $Cp_2WMe(C_2H_4)$ with phosphines.[11] Unfortunately the reactions were complex, with products arising from major side reactions and thermal decomposition. A typical example using trimethylphosphine is illustrated below.



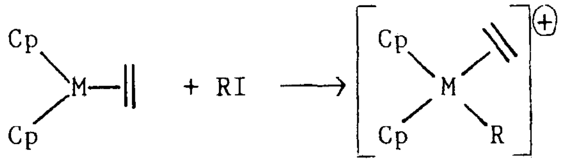
The remaining complexes in this category reacted to give insertion or substitution products. Treatment of the complexes $[Cp_2MH(alkene)]^+$ with triphenylphosphine[12] resulted in insertion of the ethene into the metal hydride bond.



M = Mo or W

$X^- = BF_4^-$ or PF_6^-

Reaction of the same complexes with hydroxide caused deprotonation to give the neutral ethene complexes. These actually behave as nucleophiles, reacting with alkyl halides to give the alkyl complexes as shown below.[13]



M = Mo or W

R = alkyl

2.6.1 Group VII. Manganese Technetium, Rhenium

The reported technetium chemistry is limited because of the radioactivity of the metal but closely relates to that of rhenium. Most of the known alkene complexes of metals of this group fall into one of two categories: (i) $CpM(CO)_2$alkene Cp = $\eta_5C_5H_5$; (ii) Derivatives of $M(CO)_6^{\oplus}$.

(i) The neutral $CpMn(CO)_2$(alkene) complexes are prepared by photo induced substitution of carbonyl groups in the $CpMn(CO)_3$ complex.[14] The alkenes of these complexes are very easily displaced by donor ligands to give direct substitution products.

$$CpMn(CO)_2(\text{alkene}) \xrightarrow{L} CpMn(CO)_2L + \text{alkene}$$

$$L = \text{phosphine, amine, } (C_6H_5)_2S$$

Kinetic studies showed a slight increase in the rate of substitution on going from sulphur to phosphine to nitrogen ligands.[15] Unpublished work at Durham,[16] has involved reaction of a variety of nitrogen nucleophiles with $CpMn(CO)_2$-alkene complexes of hex-1-ene and ethene. No evidence was obtained for nucleophilic attack at the alkene in any of the reactions.

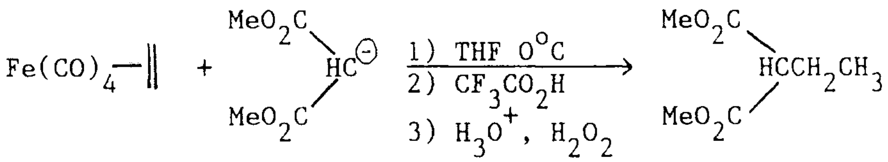
(ii) The alkene derivatives of $M(CO)_6^+$ complexes are also unstable with respect to displacement of alkene. The manganese complexes $[Mn(CO)_5\text{alkene}]^+BF_4^-$ decompose immediately in water with loss of alkene.[17] Reaction with triphenylphosphine resulted in displacement of the alkene and a carbonyl.

$$[Mn(CO)_5\text{alkene}]^{\oplus}BF_4^{\ominus} \xrightarrow{PPh_3} [Mn(CO)_4(PPh_3)_2]^{\oplus}BF_4^{\ominus}$$

The rhenium complexes $Re(CO)_5(C_2H_4)^{\oplus}$ and $Re(CO)_4(C_2H_4)_2^{\oplus}$ are prepared by heating $Re(CO)_5Cl$ in the presence of aluminium trichloride under a pressure of 60 or 250 atmospheres of ethene respectively.[18] Analogous complexes of higher alkenes are not reported. An autoclave reaction of $Re(CO)_5(C_2H_4)^+$ with the nucleophilic alkoxide ion resulted in a very complex reaction.[19] No products were isolated, other than a small amount of white solid postulated to be $Re_2(CO)_{10}O$.

2.7.1 Group VIII. Iron, Ruthenium, Osmium

The known iron alkene complexes are mostly of two major types. Neutral complexes which are generally substitution derivatives of $Fe(CO)_5$, and cationic complexes of the type $[CpFe(CO)_2alkene]^+$. There is only one isolated report of nucleophilic attack at alkenes bound to neutral iron complexes. Reaction of $Fe(CO)_4(C_2H_4)$ with sodium dimethylmalonate followed by acidification and oxidation gave dimethylethylmalonate,[62] the proposed σ bonded alkyl intermediate was not isolated. With the



exception of this reaction nucleophilic attack at the alkene of the neutral iron complexes has not been achieved. The typical reaction with nucleophiles is displacement of the alkene. With triphenylphosphine[20] one of the carbonyls is replaced in an analogous reaction to the related manganese complexes.

$$Fe(CO)_4(alkene) + 2PPh_3 \longrightarrow Fe(CO)_3(PPh_3)_2 + CO + C_2H_4$$

Attack at cationic complexes is already well documented. Unfortunately, the difficulties encountered in cleaving the organic moieties thus formed, have prevented the development of these reactions into useful synthetic routes. A summary of the reaction of $[CpFe(CO)_2C_2H_4]^{\oplus}$ with a variety of amines is shown below in Figure 6.

The propene complex, $[CpFe(CO)_2(CH_2CHCH_3)]^+$, is also known. It reacts with dimethylamine or benzylamine to give a 1:1 adduct resulting

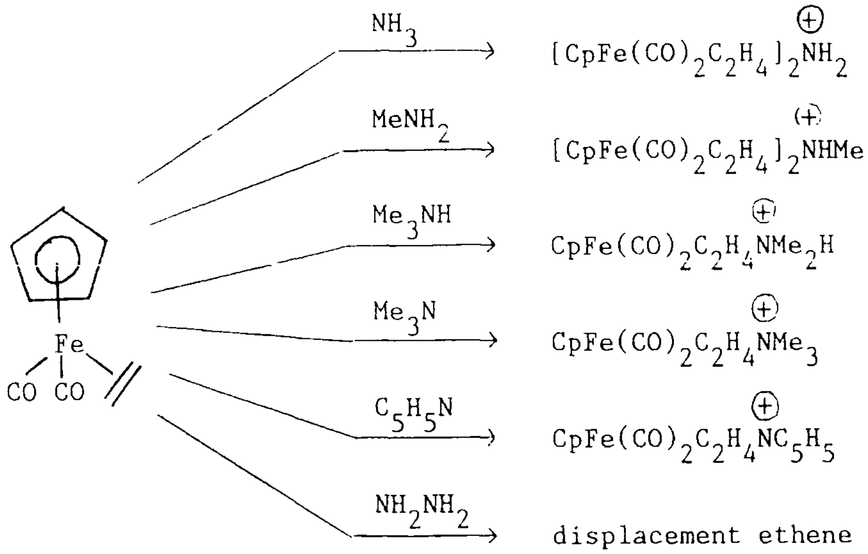
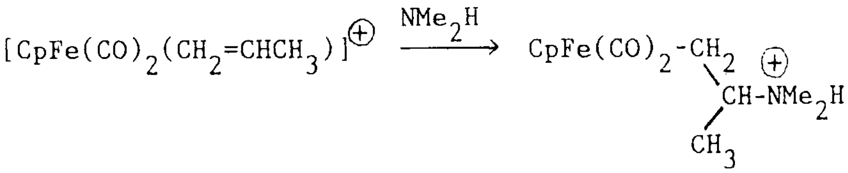


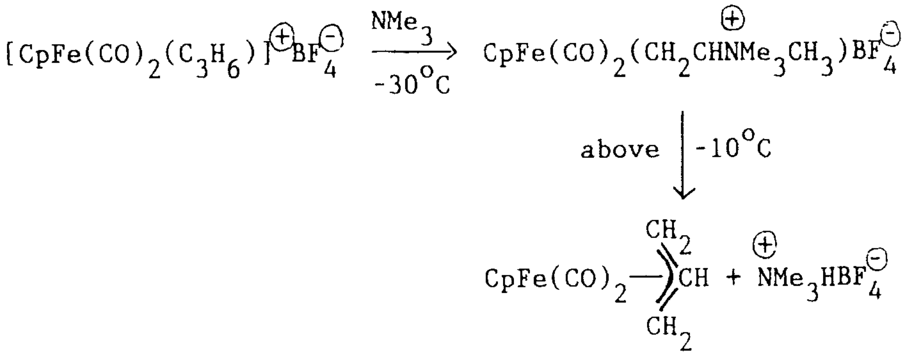
Figure 6

from attack at the internal carbon.[21]



$$[CpFe(CO)_2(CH_2{=}CHCH_3)]^{\oplus} \xrightarrow{NMe_2H} CpFe(CO)_2\text{-}CH_2\text{-}\overset{\oplus}{CH}(NMe_2H)\text{-}CH_3$$

Trimethylamine reacts at -30°C to form the 1:1 adduct but reverses on allowing to warm above -10°C. Deprotonation also occurred to form the allyl complex.[21]



$$[CpFe(CO)_2(C_3H_6)]^{\oplus}BF_4^{\ominus} \xrightarrow[-30^{o}C]{NMe_3} CpFe(CO)_2(CH_2CHNMe_3CH_3)^{\oplus}BF_4^{\ominus} \xrightarrow{\text{above } -10^{o}C} CpFe(CO)_2\text{—}\overset{CH_2}{\underset{CH_2}{CH}} + \overset{\oplus}{NMe_3H}BF_4^{\ominus}$$

As mentioned previously, the major problem with the iron complexes is cleavage of the alkylated amine. The numerous σ alkyl complexes all reacted or decomposed without yielding the higher alkylated amine. Action of hydrochloric acid for example, results in formation of the starting ethene complex. Treatment of the pyridine and trimethylamine adducts with aqueous acetonitrile has the same effect.

One distinct advantage the iron complexes have over the molybdenum and tungsten analogues is the fact that they do not undergo cyclisation. A disadvantage is that with higher alkenes amination does not occur at the terminal carbon. Ideally for commercial application we require terminally substituted alkylamines.

It may be possible to "fine tune" the complexes for our purposes, by altering one or more of the ligands. For example replacement of one of the carbonyls with a variety of phosphines (replacement with PPh_3 has already been reported). Great care would have to be taken when doing this, not to place any more electron density on the iron. This is well illustrated by the fact that no addition of ammonia was observed on reaction with $[CpFe(P(OPh)_3)_2C_2H_4]^+$.[10]

Surprisingly little has been reported on the attack by amines at ruthenium bound alkenes.

There are only a handful of neutral ruthenium alkene complexes known and none have demonstrated susceptibility to nucleophilic attack. Known complexes include the ethene complexes $Ru(CO)_2(PPh_3)_2(C_2H_4)$[42] and $RuCl_2(CO)(PMe_2Ph)_2(C_2H_4)$. Ethene is displaced from the latter complex by excess phosphine or CO, which can in turn be displaced by ammonia, pyridine and piperidine.[43,44]

Extensive IR, NMR and electronic spectra studies of the complex $[Ru(NH_3)_5(C_2H_4)]$ showed backbonding to the ethene to be quite strong.[45] The other known cationic ruthenium alkene complexes are mostly of the type $[CpRuL_2\ alkene]^+X^-$ L = CO or phosphine $X^- = BF_4^-$, PF_6^-. Attack of ammonia at $[CpRu(CO)_2C_2H_4]^+$ was reported to give a 1:1 reaction as shown below.[22] Surprisingly there appears to have been no further

$$[CpRu(CO)_2CH_2{=}CH_2]^{\oplus} + NH_3 \longrightarrow CpRu(CO)_2(CH_2CH_2\overset{\oplus}{N}H_3)$$

reports on the attack of nucleophiles at this complex. A group of complexes of the general formula $[CpRu(PMe_3)alkene]^+$ was reported by Bruce et al in 1981.[23] Despite his announced intention of studying their susceptibility to nucleophilic attack,[24] no reports on this subject have appeared. A similar group of complexes, $[CpRu(dppe)alkene]^+$, have also been reported,[25] but again there are no reports of their interaction with nucleophiles. Alkene complexes of osmium are relatively scarce. The ethene in $Os(C_2H_4)(CO)_4$ is very labile, it is readily displaced by CS_2.[46] the cationic nitrosyl alkene complex, $[Os(NO)(CO)(PPh_3)_2(C_2H_4)]^+PF_6^-$ [47] also loses ethene unless it is stored under an ethene atmosphere. No reactions of nucleophiles with this complex have been reported.

The complexes, $[C_6H_6OsH(PMe_3)(C_2H_3R)]^+$, $[C_6H_6OsMe(PMe_3)(C_2H_3R)]^+$, $[C_6H_6Os(PMe_3)(C_2H_3R)I]^+PF_6^-$ and $[C_6H_6Os(PMe_3)(C_2H_3R)]$, R = H or Me, have been investigated by Werner et al.[48] Reaction of the hydride complexes with NaH in THF gave the neutral complexes corresponding to loss of a proton. Reaction with NaI in acetone caused insertion of the alkene into the metal hydride bond, e.g.

$$[C_6H_6OsH(PMe_3)(C_2H_3R)]^{\oplus} \xrightarrow[\text{acetone}]{\text{NaI}} [C_6H_6OsI(PMe_3)(C_2H_4R)].$$

Reaction of the methyl complexes with sodium iodide resulted in displacement of the alkene. The hydridoethene complex reacted with PMe_3 to give products from both insertion of the alkene, and nucleophilic attack at the alkene.

$$[C_6H_6OsH(PMe_3)(C_2H_4)]^{\oplus} \xrightarrow{PMe_3} [C_6H_6OsH(PMe_3)(C_2H_4PMe_3)]^{\oplus} + [C_6H_6OsEt(PMe_3)_2]^{\oplus}$$

The methyl ethene complex reacted to give only $[C_6H_6OsMe(PMe_3)(C_2H_4PMe_3)]^+$, whereas the methyl propene complex reacted with displacement of the alkene.

2.8.1 Group VIII. Cobalt, Rhodium, Iridium

Simple alkene complexes of cobalt are relatively scarce. They are virtually all d^8 cobalt(I) complexes, though a few examples are known of cobalt $\bar{0}$ and -I complexes.

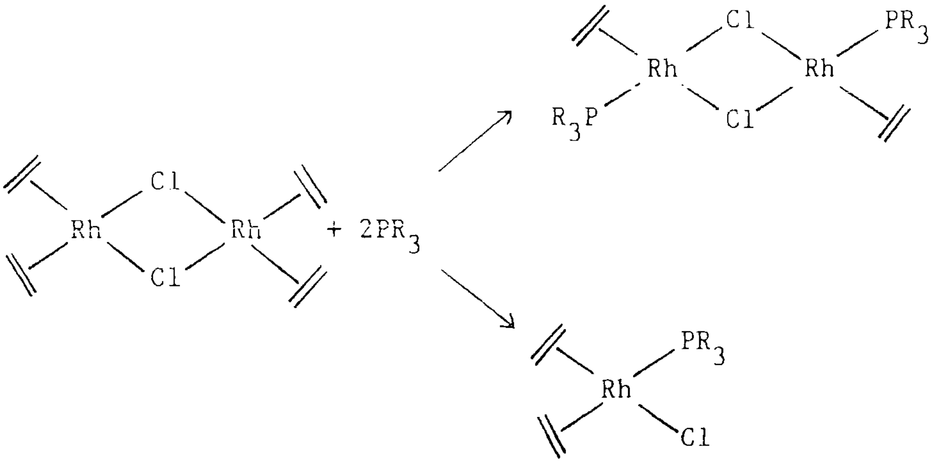
The complexes $Co(C_2H_4)(PPh_3)_3$, and $Co(C_2H_4)(acac)(PPh_3)_2$, are very air sensitive and although thermally stable up to 80°C, they rapidly decompose with loss of ethene in THF or aromatic solvents.[28] Ammonia and acetonitrile cause displacement of the alkene from the cationic complexes $[Co(alkene)(P(OMe)_3)_4]^+PF_6^-$, (alkene = ethene, propene or hex-1-ene). These complexes also catalyse isomerisation of alkenes.[29] The complex $(C_5Me_4Et)Co(C_2H_4)_2$ was reported to show similar properties to $CpRh(C_2H_4)_2$.

In general the alkene complexes of cobalt are all of the metal in low oxidation states, with auxillary ligands that are good electron releasing groups, e.g. PMe_3. This will not help to promote nucleophilic attack at the alkene.

Most of the rhodium alkene complexes fall into one of four general categories: (i) Binuclear complexes, $[(alkene)_2RhX]_2$ X = halogen; (ii) $L_2RhX(alkene)$ X = halogen, L = phosphine; (iii) Cyclopentadienyl, or chelating ligand complexes eg.$CpRh(C_2H_4)_2$, $(acac)Rh(C_2H_4)_2$; (iv) Anionic complexes $[(alkene)_2RhX_2]^-$ X = halogen.

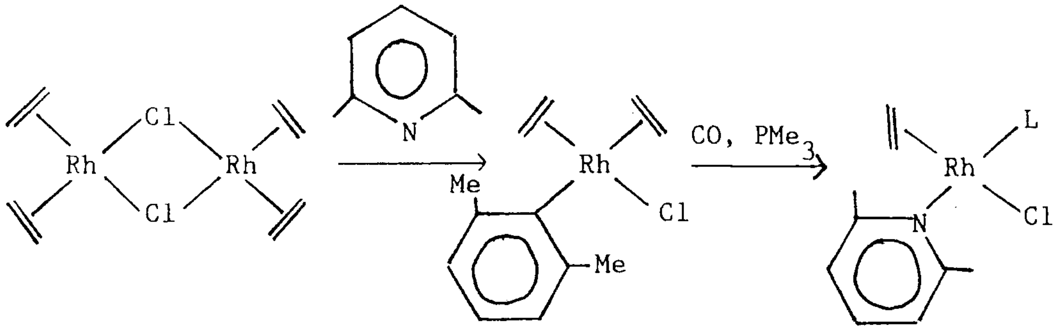
(i) Binuclear Complexes

The complex $[(C_2H_4)_2RhCl]_2$ is easily prepared by bubbling ethene through an alcoholic solution of $RhCl_3.3H_2O$.[31,32] It is a very useful starting complex for other alkene complexes. Unfortunately the typical reaction displayed by complexes in this category is displacement of the alkene. One equivalent of phosphine, either splits the halogen bridge or replaces one of the alkenes as shown below.[33,34]



Two equivalents of phosphine results in formation of type (ii) complexes $(PR_3)_2RhCl(alkene)$.

Reactions of $[(C_2H_4)_2RhCl]_2$ with pyridine, acetonitrile and hydrogen cyanide, all resulted in displacement of ethene.[31] Reaction with 2,6 lutidine resulted in splitting of the halogen bridge.[35] Treatment of the monomeric lutidine complex with PMe_3 or CO resulted in displacement of ethene.

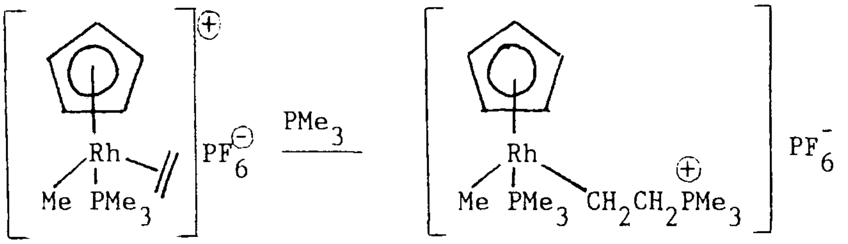


Attack of NEt_2H, $NH_2{}^nPr$, pyridine and 3,5-dimethylpyridine, on the complex $[(CO)(C_2H_4)RhCl]_2$ resulted in coordination of the amine followed by loss of ethene.[36,37,38]

(ii) $L_2RhCl(alkene)$ Complexes

Complexes of the type $[(PR_3)_2RhCl(alkene)]$ have been known for over twenty years. They have been extensively investigated for their role in the catalytic hydrogenation of alkenes. The classic example is the complex, $[(PPh_3)_2RhCl(C_2H_4)]$, obtained from Wilkinson's catalyst. Attack of nucleophiles such as amines or phosphines on these complexes generally causes displacement of the alkene. Excess phosphine for example displaces ethene from solutions of $[(PPh_3)_2RhCl(C_2H_4)]$[49] unless the latter is subjected to a pressure of ethene. If pyridine is added to Wilkinson's catalyst in the hydrogenation reaction, hydrogenation is stopped due to irreversible displacement of the alkene by pyridine.

(iii) There are numerous cyclopentadienyl rhodium alkene complexes and they have been extensively studied, particularly with respect to free rotation of the alkene. The alkenes in the neutral complexes are very inert to addition or displacement reactions with nucleophiles. For example, the substitution of ethene in $CpRh(C_2H_4)_2$ with pyridines, phosphines or nitriles, will not occur below 115°C. The rate determining step for the substitution reaction was found to be dissociation of the ethene.[50] Nucleophilic attack at cationic complexes of this type has been observed. The complex $[CpRh(Me)(PMe_3)(C_2H_4)]^+PF_6^-$ reacts with trimethylphosphine as shown below, though no reactions with amines are reported.[51] The related hydride complex $[CpRhH(C_2H_4)PMe_3]^+$ is also known.[52] In solution it exists in equilibrium with the ethyl complex.



$$[CpRhH(C_2H_4)PMe_3]^{\oplus}BF_4^{\ominus} \rightleftharpoons [CpRhEt(PMe_3)]^{\oplus}BF_4^{\ominus}$$

The doubly cationic complex $[CpRh(PMe_3)_2C_2H_4]^{2+}X_2^-$, ($X = BF_4^-$ or PF_6^-), is very susceptible to nucleophilic attack at the ethene.[53] A variety of nucleophiles including triethylamine reacted as shown below.

$$[CpRh(PMe_3)_2C_2H_4]^{2+} + Nuc \longrightarrow [CpRh(PMe_3)_2(C_2H_4Nuc)]^{2+}$$

$$Nuc = PPh_3,\ PMe_3,\ P^iPr_3,\ NEt_3$$

The $Rh\text{-}C_2H_4Nuc$ bonds formed were extremely stable, e.g. heating the PMe_3 complex in nitromethane for two hours gave no reaction.

It is interesting to note that the isoelectronic ruthenium complex $[C_6H_6Ru(PMe_3)_2C_2H_4]^{2+}$, was susceptible to nucleophilic attack by tertiary phosphines or phosphites, but not with tertiary amines.

In direct contrast to the 18 electron cyclopentadienyl complexes, the alkenes of the 16 electron acetyl acetonate-rhodium bis alkene complexes are very labile. Exchange of C_2H_4 for C_2D_4 in chloroform is very rapid[54] and the alkene is displaced by PPh_3, CO and cyanide.[55] No reactions with nitrogen nucleophiles are reported.

(iv) Not surprisingly, the alkenes of the final category complexes, $[(alkene)_2RhCl_2]^-$, are not susceptible to nucleophilic attack. Examples of the $[(alkene)_2RhCl_2]^{\ominus}$ complexes have not been isolated. They are formed in dilute HCl containing solutions by chloride ion splitting the bridge of the dimeric bis alkene complexes.[75] No reactions of the anionic complexes with

$$[(C_2H_4)_2RhCl]_2 + 2Cl^- \rightleftharpoons 2[(C_2H_4)_2RhCl_2]^{\ominus}$$

nucleophiles are reported.

Many of the rhodium alkene complexes have iridium analogues. In general the iridium alkene bonds tend to be slightly stronger than the rhodium analogues, but the chemistry is often similar. In reactions of amines and phosphines with $[(alkene)_2IrCl]_2$ and related complexes, the alkenes were not susceptible to nucleophilic attack.[56] Triphenyl phosphine reacted with the bis ethene complex, to progressively displace ethene and break the halogen bridge. The mixed tetrafluoroethene ethene

$$[(C_2H_4)_2IrCl]_2 \xrightarrow{PPh_3} [(C_2H_4)PPh_3IrCl]_2 \xrightarrow{PPh_3} [IrCl(C_2H_4)(PPh_3)_2]$$

$$\xrightarrow{PPh_3} [IrCl(PPh_3)_3]$$

or cyclooctene complexes react with a variety of nucleophiles as shown below.[56] It might have been hoped that the electron withdrawing properties of the C_2F_4 ligand, would help to activate the alkenes to nucleophilic attack. Although ethene rotation was observed to be faster for the tetrafluoroethene substituted complex, compared to the bis ethene complex, (showing a reduction in back bonding to the ethene), nucleophilic attack at the alkene did not occur.[56]

$$[(alkene)(C_2F_4)IrCl]_2 \xrightarrow{PPh_3} Ir(C_2F_4)Cl(PPh_3)_3$$

$$[(alkene)(C_2F_4)IrCl]_2 \xrightarrow{MeCN} [Ir(alkene)(C_2F_4)(CH_3CN)Cl]_n$$

$$[(alkene)(C_2F_4)IrCl]_2 \xrightarrow{NH_3} [Ir(NH_3)_3(alkene)(C_2F_4)]^{\oplus}Cl^{\ominus}$$

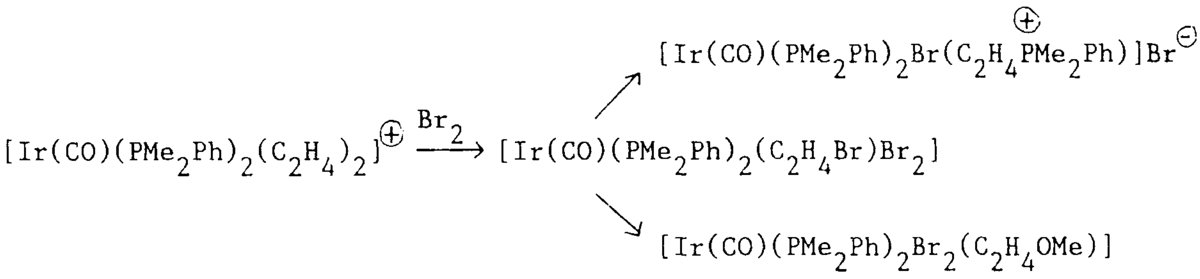
$$[(alkene)(C_2F_4)IrCl]_2 \xrightarrow{Py} \text{evolution of ethene for ethene complex}$$

$$[(alkene)(C_2F_4)IrCl]_2 \xrightarrow{Py} [Ir(C_8H_{14})(C_2F_4)(py)_2Cl]$$

alkene = ethene or cyclooctene; py = pyridine.

Similar reactions were observed for the acetylacetonato complexes $[(acac)Ir(alkene)_2]$. Nucleophiles react to displace the alkene, or add to the metal to give five coordinate complexes.[56]

As well as forming many analogues of the rhodium complexes, iridium also forms numerous five coordinate alkene complexes. Many of these are alkene adducts of Vaska-type complexes. They have the general formula $[(\text{phosphine})_2\text{Ir(CO)Cl(alkene)}]$. Unfortunately complexes of this type with simple mono alkenes, are unstable with respect to dissociation or displacement of alkene. There is, however, one complex that undergoes a very interesting reaction worthy of note. Treatment of the Vaska type complex $[(\text{PMe}_2\text{Ph})_2\text{Ir(CO)Cl}]$ with ethene in the presence of NaBPh_4 produced the cationic complex, $[\text{Ir(CO)(PMe}_2\text{Ph)}_2(\text{C}_2\text{H}_4)_2]^+\text{BPh}_4^-$.[57] This reacted with bromine followed by phosphine or methanol as shown below.[58]



$$[\text{Ir(CO)(PMe}_2\text{Ph)}_2(\text{C}_2\text{H}_4)_2]^{\oplus} \xrightarrow{\text{Br}_2} [\text{Ir(CO)(PMe}_2\text{Ph)}_2(\text{C}_2\text{H}_4\text{Br})\text{Br}_2]$$

$$\nearrow [\text{Ir(CO)(PMe}_2\text{Ph)}_2\text{Br}(\text{C}_2\text{H}_4\overset{\oplus}{\text{P}}\text{Me}_2\text{Ph})]\text{Br}^{\ominus}$$

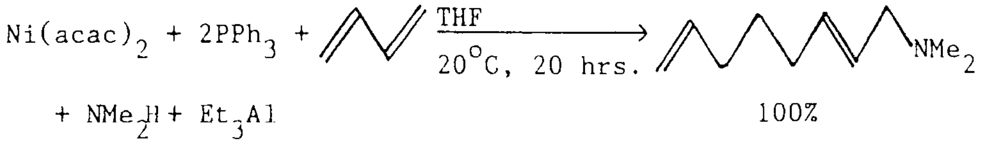
$$\searrow [\text{Ir(CO)(PMe}_2\text{Ph)}_2\text{Br}_2(\text{C}_2\text{H}_4\text{OMe})]$$

Although this is not direct nucleophilic attack by the phosphine or methoxide on coordinated alkene, the reaction effectively gives products that could be thought of as arising from this. The analogous reaction with amines was not tried, but there appears to be no reasons why amines would not react in a similar manner to give, $[\text{Ir(CO)(PMe}_2\text{Ph)}_2\text{Br}(\text{C}_2\text{H}_4\overset{\oplus}{\text{N}}\text{R}_3)]\text{Br}^{\ominus}$.

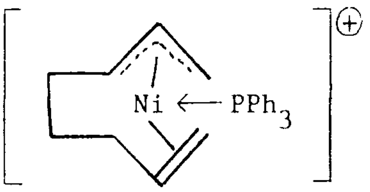
This would be particularly interesting as there are no previous reports of complexes containing the $\text{Ir-CH}_2\text{CH}_2\overset{\oplus}{\text{N}}\text{R}_3$ moiety.

2.9.1 Group VIII. Nickel, Palladium, Platinum

Amination of alkenes bound to palladium(II) and platinum(II) complexes has been reported extensively. By contrast direct attack of amines at alkene complexes of nickel is unknown, though amination of the allyl and crotyl intermediates formed during nickel promoted oligomerisation of butadiene has been observed.[67] The reaction of secondary amines with butadiene in the presence of bisacetylacetonato nickel(II), triphenylphosphine, and triethylaluminium, gave high yields of dialkyloctadienylamines[67] e.g.



It was postulated that amination occurred by external attack of the amine upon the cationic allyl intermediate shown below.

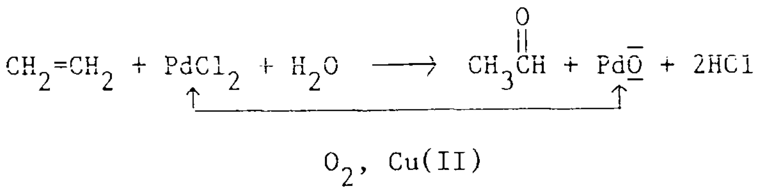


The majority of nickel alkene complexes are 16-electron trigonal complexes of the zerovalent metal e.g. Ni(C_2H_4)$_3$.[59] The metal alkene bonds in these complexes are best represented by the metallo-cyclopropane structure, with extensive back bonding occurring.

The crystal structure of Ni(PPh_3)$_2$(C_2H_4)[60] has a carbon-carbon bond length of 1.43(1)Å, (cf. 1.337 for ethene). The angle the CH_2 group makes with the C-C unit is 31.4°, and the angle between the methylene hydrogens is 100.4°. Not surprisingly the alkenes in these complexes are generally not susceptible to nucleophilic attack. The characteristic reaction with donor ligands, e.g. acetonitrile, is displacement of the alkene.[63] This is also true for alkene complexes of palladium$\underline{0}$ and platinum$\underline{0}$, which normally exhibit physical properties indicative of substantial back bonding.[64] The complexes [M(C_2H_4)$_3$], M = Pd or Pt, readily decompose with deposition of the metal unless they are stored under a pressure of ethene.[65] There are no reports of the interaction of these complexes with amines.

The literature on nucleophilic attack at alkenes coordinated to palladium(II) and platinum(II) is vast.

A classic example is the catalytic Wacker process shown below, acetaldehyde is effectively produced through nucleophilic attack of water at the ethene in $[(C_2H_4)Pd(H_2O)Cl_2]$.[76]



$$CH_2{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}H + Pd\overline{\underline{0}} + 2HCl$$

O_2, Cu(II)

We shall only discuss in detail those reactions concerned primarily with attack by amines. A review by L.S. Hegedus[66] deals in general with palladium assisted reactions of mono alkenes.

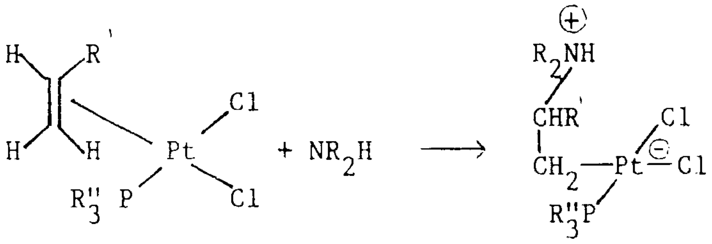
In 1961, Stern and Spector reported that reaction of propene and butylamine in the presence of palladium dichloride and disodium hydrogen phosphate, yielded isopropylenebutylamine,[68] as shown below.

$$CH_3\text{-}CH{=}CH_2 + C_4H_9NH_2 + PdCl_2 \xrightarrow{Na_2HPO_4} CH_2{=}C(CH_3)\text{-}NHC_4H_9 + 2HCl + Pd$$

Since this first report, numerous detailed investigations of platinum and palladium alkene complexes, have established the following basic points. Nucleophilic attack on the metal, is a strongly competing side reaction which often results in displacement of the alkene. This is particularly true of the palladium complexes, which also undergo isomerisation of the alkene as another major side reaction. The extent to which amination occurs at the alkene and not the metal, is dependent on many factors. These include the basicity and steric bulk of the amine, the electrophilicity and steric factors of the alkene, the choice of solvent, and the reaction temperature. Nucleophilic attack on the alkene was generally found to occur trans with respect to the metal, and involved external attack as opposed to internal.

The palladium alkene complexes are usually more reactive towards nucleophiles than their platinum analogues; thus a catalytic reaction is more likely to involve palladium complexes, while platinum complexes will be more useful as models. All of these points are illustrated in the following examples.

The alkenephosphineplatinum(II) complexes, (alkene = ethene, propene or but-1-ene), reacted with secondary amines to give isolable zwitterionic σ alkyl complexes as shown below.[6]



R'' = C_6H_5 and R' = H

R'' = n-C_4H_9 and R' = H, Me or Et

R = Me, Et, ^nBu

Hydrolysis of the σ-alkyl complexes with aqueous HCl gave the alkylated amines as the hydro salts in varying yields as summarised in Table 2.

Table 2. Yields of higher amine obtained from reaction of alkene-t-butylphosphineplatinum dichloride complexes

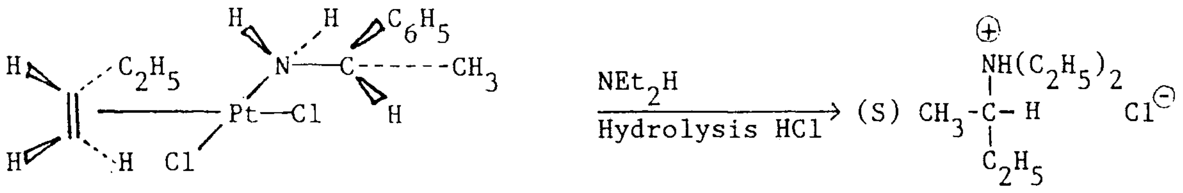
Alkene	Amine used R_2NH		
	R = CH_3	R = C_2H_5	R = $^nC_4H_9$
ethene	$C_2H_5N(CH_3)_2$ 68%	$(C_2H_5)_3N$ 62%	$C_2H_5N(C_4H_9)_2$ 55%
propene	$(CH_3)_2CHN(CH_3)_2$ 47%	$(CH_3)_2CHN(C_2H_5)_2$ 45%	$(CH_3)_2CHN(C_4H_9)_2$ 38%
but-1-ene		$CH_3(CH_2)_2CH_2N(C_2H_5)_2$ 20% $CH_3(C_2H_5)CHN(C_2H_5)_2$ 17%	$(nC_4H_9)_3N$ 16% $CH_3(C_2H_5)CHN(C_4H_9)$ 14%

As can be seen from Table 2, the yields generally decrease as the steric requirements of both the amine and the alkene increase. Similar results were obtained aminating diene complexes of palladium & platinum chloride.[70]

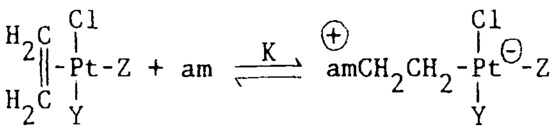
On reacting ammonia or ethylamine with the tributylphosphine or triphenylphosphineethene complexes, successive alkylation occurred to give after hydrolysis a mixture of mono, di and triethylamines. (See discussion of this reaction in the introduction, page 9). This is one of the very few examples in which ammonia or a primary amine successfully attacks the alkene.

By studying the attack of diethylamine on the resolved diastereoisomeric complex of prochiral but-1-ene shown below, it was shown that nucleophilic attack on the alkene occurs trans with respect to the metal and involves external amination.[69]

Attack of diethylamine on (+)-cis-dichloro[(S)-1-butene][(S)-α-methylbenzylamine]platinum(II) produced (in high optical purity) the dextrorotatory enantiomer of N,N-diethyl-sec-butylamine which has the S configuration.



The effect of the basicity and steric properties of the amine upon its ability to attack the alkene of platinum(II) complexes, is well illustrated in a series of experiments by Green et al.[71] The equilibrium constant for the reversible amination reaction shown below, was determined experimentally for a whole series of heterocyclic and aliphatic amines. A selection of the values of K obtained are summarised



$$\begin{array}{c}H_2C\\ \|\\ H_2C\end{array}\text{-}\overset{\displaystyle Cl}{\underset{\displaystyle Y}{Pt}}\text{-}Z + am \overset{K}{\rightleftharpoons} \overset{\oplus}{am}CH_2CH_2\text{-}\overset{\displaystyle Cl}{\underset{\displaystyle Y}{Pt^{\ominus}}}\text{-}Z$$

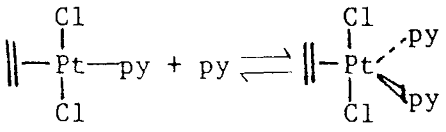
Y = Cl and Z = amine

in Table 3.

Table 3

Amine	pK_a of amine	K
$^{n}BuNH_2$	10.7	25
$^{n}Bu_2NH$	11.3	8
$^{i}Bu_2NH$	11.0	ca. 0.2
NEt_3	10.7	< 0.2
Piperidine	11.1	> 500
3-Me-Piperidine	11.1	> 500
2-Me-Piperidine	11.0	30
Pyridine	5.2	< 0.1
2-Me-Pyridine	5.9	< 0.1

The nucleophilicity of the amine with respect to attack at the alkene, decreases with increasing steric bulk. This is evident in the fall in values of K on going from primary to tertiary, or linear to branched aliphatic amines. The reason for the large values obtained with alicyclic amines, was ascribed to their steric compactness. This is backed up by the much smaller value of K observed for the substituted piperidine with the methyl in the 2 position. Basicity of the amine was not as important as the steric considerations, though very weak bases, (pK_a < 6 or 7), did not form stable σ-adducts to any useful extent. With some of the heterocyclic weak bases, e.g. pyridine, there was a tendency for attack at the metal to give five coordinate complexes as shown below.[72] This was observed only at low temperature; on allowing to warm to 25°C loss of ethene occurred with formation of $PtCl_2(py)_2$



and $[Pt(py)_4]Cl_2$.

The palladium promoted amination of alkenes has been developed mostly by B. Akermark, L.S. Hegedus and co-workers. In an optimised procedure[73] bis(benzonitrile)palladiumdichloride is stirred with an excess of the alkene in tetrahydrofuran at 0°C. The temperature is then lowered to -50°C and amine slowly added as a solution in THF. After stirring for one hour the system is flushed with hydrogen and allowed to warm to room temperature under a hydrogen atmosphere. This generally gave the higher alkylated amines in varying yields. The reactivity of the amine was found to depend on both high basicity and relative freedom from steric hindrance. This is illustrated by the yields shown in Table 4.

Table 4. Yields of alkylated amine obtained from reaction of amines with decene in the presence of $(PhCN)_2PdCl_2$

Amine	pK_a	% Yield
NH_3	9.2	4
$MeNH_2$	10.6	40
Me_2NH	10.8	90
Et_2NH	11.0	88
$(i\text{-}Pr)_2NH$	11.0	3

Yields were also dependent on the steric properties of the alkene. Terminal alkenes gave higher yields than internal alkenes and trans alkenes gave higher yields than cis. This is illustrated by the yields shown in Table 5.

The reaction temperature was also very important. At temperatures above -50°C displacement of the alkene by amine becomes the dominant reaction and yields fall rapidly. At temperatures above 0°C alkene

Table 5. Percentage yields of alkyldimethylamines from reaction of $HNMe_2$ with alkenes and $(PhCN)_2PdCl_2$

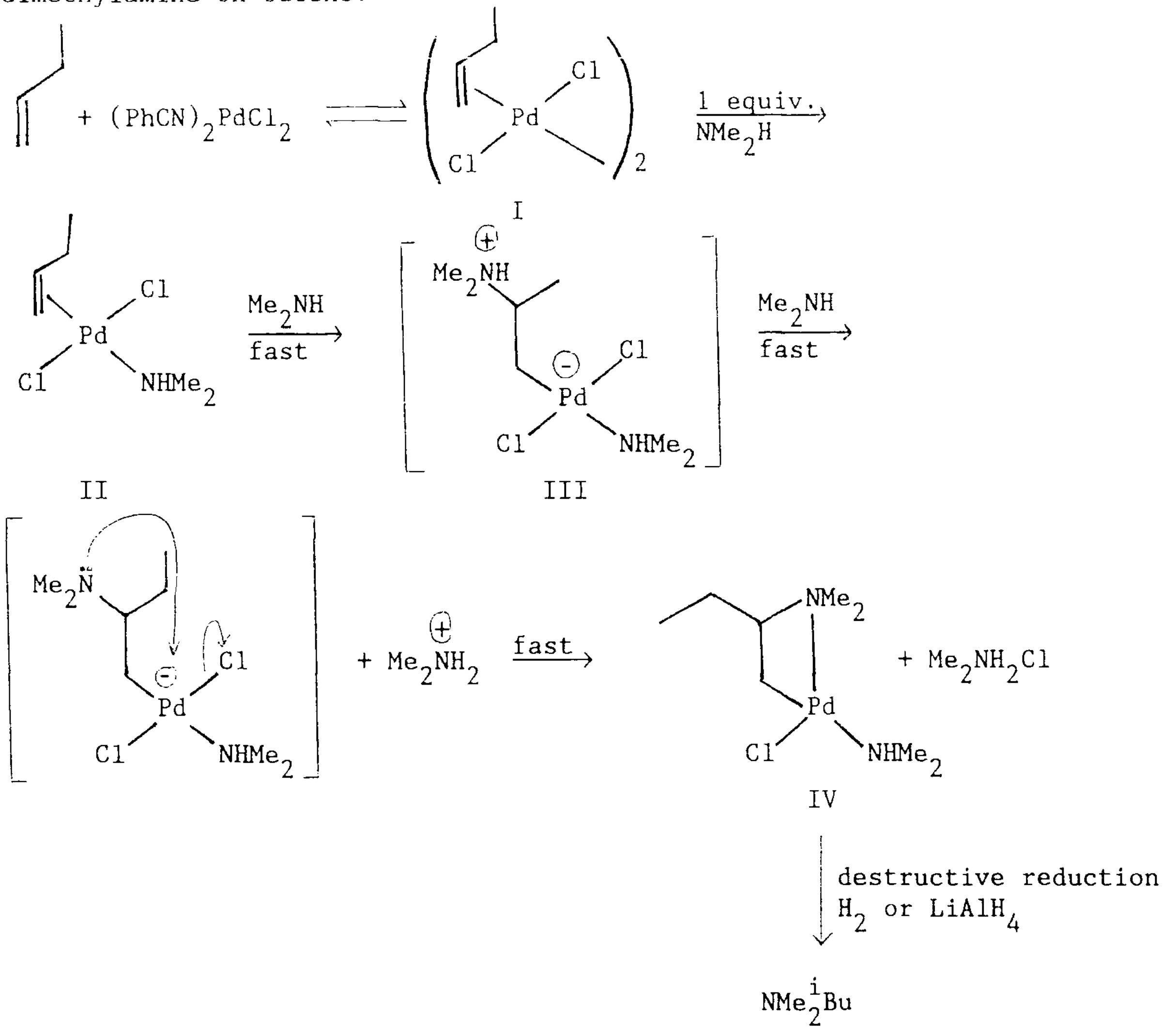
Alkene	% Yield of higher amine
ethene	100
1-butene	90
trans-2-butene	44
cis-2-butene	10
3,3-dimethyl-1-butene	0
cyclooctene	0

isomerisation was also a strongly competing reaction. Many other palladium(II) complexes were tested along with different solvents and additional ligands, but none of these systems were as efficient as that involving only $(PhCN)_2PdCl_2$, Table 6. The alkene amination was shown

Table 6. The effect of different complexes and added ligands on the amination of decene with dimethylamine

Complex	Added ligand	% Yield
$(PhCN)_2PdCl_2$	-	90
$(PhCN)_2PdBr_2$	-	63
$(PhCN)_2PdCl_2$	DMSO	0
$(PhCN)_2PdCl_2$	DMFA	70
$Pd(OAc)_2$	-	0
Na_2PdCl_4	-	74
Na_2PdCl_4	Ph_3P	8
Na_2PdCl_4	Bu_3P	38
$(Me_2NH)_2PdCl_2$	-	0

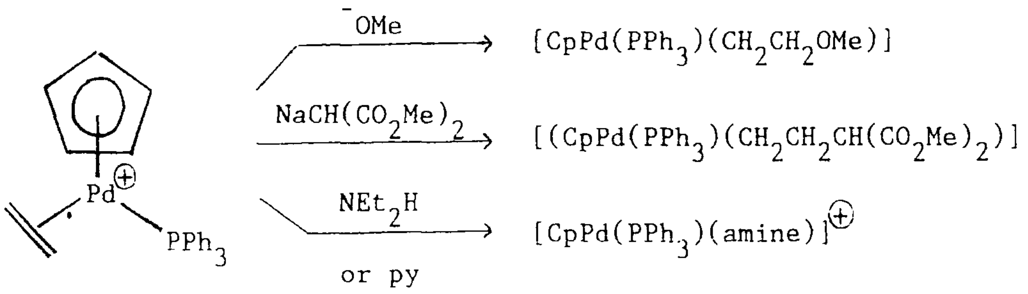
to occur trans with respect to the metal,[74] and required at least three equivalents of amine to achieve maximum yields. After much detailed investigation the following mechanism was proposed for the attack of dimethylamine on butene.[7]



The first equivalent of amine is consumed in splitting the chloride bridge of the dimeric alkene complex I. The second and third equivalents are consumed attacking the alkene to give the σ-alkyl zwitterionic complex III, which is rapidly deprotonated by the amine to give complex IV.

The mechanism for the reaction with diethylamine and ethene[7] was found to be similar but the zwitterionic analogue of complex III did not deprotonate as quickly. Hence, after addition of two equivalents of diethylamine, the zwitterionic complex was present as a discrete noncyclised intermediate, requiring the third equivalent to convert it to cyclised product.

The cationic palladium complex $[CpPd(PPh_3)(C_2H_4)]^{\oplus}ClO_4^-$ was found to be readily susceptible to nucleophilic attack at the alkene by oxygen and carbanion nucleophiles.[77] Unfortunately reaction of the same complex with diethylamine or pyridine even at -50°C caused displacement of the alkene.[78]



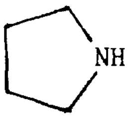
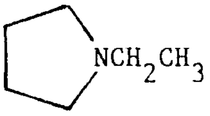
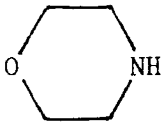
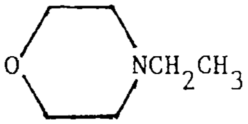
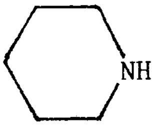
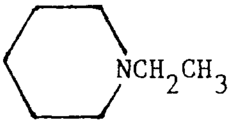
2.10.1 Catalytic Reactions

The transition metals that have been observed to catalyse the amination of alkenes include rhodium, iridium, iron, ruthenium and palladium.

Rhodium and iridium complexes were reported to catalyse the addition of secondary amines to ethene fifteen years ago.[79] A variety of rhodium and iridium compounds when reacted with 350 equivalents of amine and 100 equivalents of ethene, at 200°C for 3 hours, produced tertiary ethylamines in varying yield as summarised in Table 7.

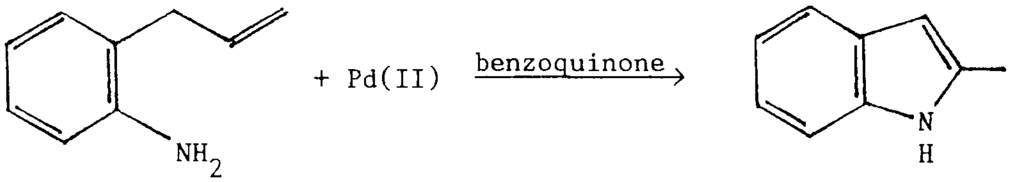
The initial oxidation state of the rhodium in the complex used was found to be immaterial; results using the tetraethene-μ-dichloro-dirhodium(I) complex were just as good as those with rhodium trichloride trihydrate. Higher alkenes were found to be completely unreactive, as were ammonia and primary amines. In the reaction of piperidine with rhodium trichloride as the catalyst, the rate was found to be independent of amine concentration, and first order with respect to the rhodium complex.

Table 7. Yields of tertiary N-ethylamines produced using rhodium trichloride as a catalyst[79]

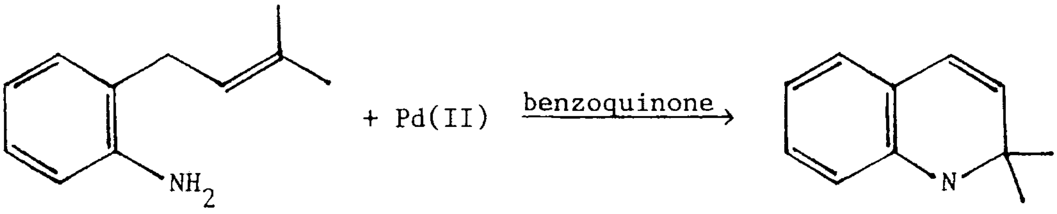
Amine	Product	Yield(%)	pk_a of amine
$(CH_3)_2NH$	$(CH_3)_2NCH_2CH_3$	54	10.7
$(C_2H_5)_2NH$	$(C_2H_5)_3N$	4	10.5
$CH_3(CH_2)_3NH(C_2H_5)$	$CH_3(CH_2)_3N(C_2H_5)_2$	3	10.5
		36	11.3
		2	8.3
		70	11.1

The ruthenium complexes that are patented as catalysts for the amination reaction are $RuCl_3.3H_2O$, Cp_2Ru and $[Ru(NH_3)_4(OH)Cl].2H_2O$.[80] Dimethylamine and ammonia were the amines used for attack and ethene was the alkene generally studied. Reactions were performed in an autoclave at temperatures of approximately 150°C with ethene pressures of between 200 and 300 psi and a typical reaction time of 5 hours. The percentage conversion to products varied between 1% and 35%, but in some reactions more than one amine was produced. For example, with $RuCl_3.3H_2O$ and dimethylamine both dimethylethylamine and diethylmethylamine were produced. The iron complexes that have proved successful are $Fe(CO)_5$ and $Fe(butadiene)(CO)_3$.[80] Reactions of ammonia, piperidine, diethylamine and aniline with ethene in the presence of the iron catalysts produced the corresponding substituted ethylamines with 28% conversion. Addition of triphenylphosphine to the reaction seemed to increase the percentage conversion; with iron pentacarbonyl and triphenylphosphine in a 1:1.5 ratio, diethylamine reacted to give mainly triethylamine with 47.4% conversion of the diethylamine.[80] This work has recently been extended to the amination of higher alkenes up to $C_{18}H_{36}$.[81]

Although it has so far proved too difficult to develop an intermolecular palladium catalysed alkene amination process, an intramolecular catalytic process has been developed. Bisacetonitrile palladium dichloride with benzoquinone was found to catalyse the cyclisation of 2-allylanilines as shown in the example below.[82]



The position of attack of the amine depended upon the conditions used and the alkene substituents. Terminally substituted alkenes gave quinoline ring systems,[82] e.g.



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CHAPTER THREE

EXPERIMENTAL WORK AND DISCUSSION

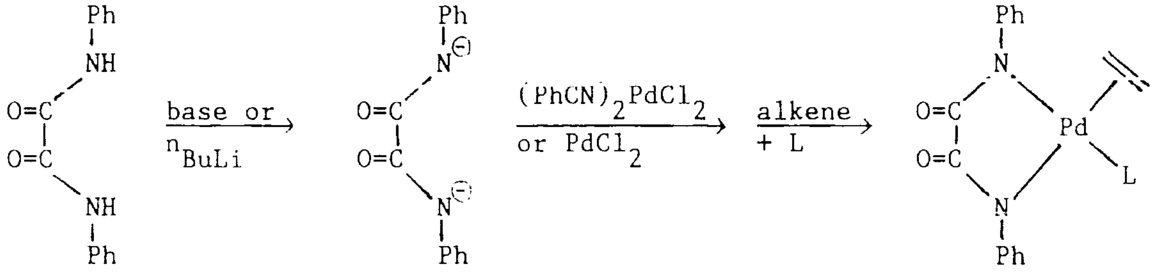
INTRODUCTION

The experimental work is divided into two main sections, reflecting two different strategies. Section 1 deals mainly with attempts to synthesise previously unknown alkene complexes, which were designed with a view to enhancing the susceptibility to attack by amine of the alkene. The research concentrated mainly on palladium complexes containing the dianionic oxanilide ligand, $[\mathrm{Ph}\overset{\ominus}{\mathrm{N}}\mathrm{COCO}\overset{\ominus}{\mathrm{N}}\mathrm{Ph}]$. Section 2 concentrates on the reactions of amines with known alkene complexes, mainly of rhodium and iridium. It was hoped to produce and characterise previously unknown σ-alkyl complexes arising from attack of the amine on the alkene. These target complexes were often analogous to those already known for platinum and palladium.

SECTION 1. REACTIONS OF PALLADIUM COMPOUNDS WITH N,N'-DIPHENYL OXAMIDE

3.1.1 Introduction

One of the major problems with palladium promoted amination of alkenes is that alkene displacement by the amine is a strongly competing reaction. This is due to the fact that aliphatic amines act as hard, strong donors and coordinate very strongly to palladium. In an attempt to try and discourage coordination of the amine, it was decided to synthesise a palladium alkene complex, already containing several hard nitrogen donors. The dianion of the N,N'-diphenyloxamide group commonly known as oxanilide appeared to be suitable for our purposes. It would provide hard nitrogen donors on 2 adjacent positions, which would largely satisfy the σ-donor requirements of Pd(II), while leaving 2 vacant sites for potential alkene coordination. A coordination site would also be available for an additional ligand with which to electronically and sterically fine tune the complex. This is illustrated below.



L = additional ligand e.g. PPh_3

These complexes would also be of interest because the dianionic oxanilide group does not appear to have been reported before as a ligand.

While attempting to synthesise and characterise the N,N'-diphenyloxamide complex $[(PhNCOCONPh)PdCl_2]^{2-}$, by reaction of oxanilide with ^nBuLi and $(PhCN)_2PdCl_2$, we came across a report of the improved synthesis of the dioxamide complex $[(NHCOCONH)_2Pd]K_2$, obtained by treating a suspension of oxamide and $PdCl_2$ in dimethylsulphoxide (DMSO) with concentrated potassium hydroxide.[1] Attempts were made to synthesise and characterise the analogous N,N'-diphenyloxamide complex by the same method, to find out more about the general properties of palladium oxanilide complexes.

3.1.2 Reaction of Oxanilide with 2 Equivalents of ^{n}Butyl Lithium

Experimental

Oxanilide (0.72 g, 3.0 mmoles) was placed in a schlenk tube with tetrahydrofuran (50 ml). The oxanilide remained largely undissolved but was stirred rapidly to produce a suspension to which ^{n}butyl lithium (3.6 ml, 1.65M; 6.0 mmoles) was slowly added at room temperature. On addition of the first equivalent of ^nBuLi the suspension started to dissolve, and a green colouration appeared in the solution. On addition of the second equivalent a white powder precipitated, which was separated by filtration, washed with THF and dried under vacuum.

Results

Elemental Analysis:

Found : C, 66.5; H, 5.80; Li, 3.17; N, 6.65%

$C_{14}H_{10}Li_2N_2O_2$ requires: C, 66.6; H, 3.96; Li, 5.55; N, 11.1%

$C_{18}H_{14}Li_2N_2O_3$ requires: C, 66.6; H, 5.55; Li, 4.32; N, 8.64%

$C_{22}H_{18}Li_2N_2O_4$ requires: C, 66.6; H, 6.56; Li, 3.53; N, 7.07%

Infra Red Spectrum:

The spectrum of the white powder, as a mull prepared under nitrogen, has two notable features; there is no peak in the NH stretching region, (3300 cm^{-1}), and the region between 1200 cm^{-1} and 1700 cm^{-1} is significantly different to the spectrum of oxanilide. On exposure of the mull to air for several seconds the spectra obtained develops features similar to that of oxanilide. On exposure for over 45 seconds the spectrum obtained is virtually identical to that of oxanilide. This is illustrated in Figure 5. The majority of the peaks in the spectrum of the filtrate from which the white product was separated corresponded to tetrahydrofuran. There were no peaks present in the NH stretching region (3300 cm^{-1}).

Discussion

The infra red spectra show that the hydrogens attached to the nitrogen are removed by the n-butyl lithium as desired. It is very likely that some tetrahydrofuran will be coordinated to the diionic species formed, analysis did not permit the exact amount to be established precisely. The elemental analyses gave the best fit for $(PhNCOCONPh)Li_2.2THF$

3.1.3 Preparation of Bisbenzonitrile palladium dichloride

Bisbenzonitrile palladium dichloride was synthesised using the standard method as described by Kharasch et al.[2] In a typical preparation palladium dichloride (2.0 g), and benzonitrile (∿ 75 ml) were placed in a 2 neck round bottom flask fitted with a water condenser. The reaction was heated to approximately 95°C and stirred for several

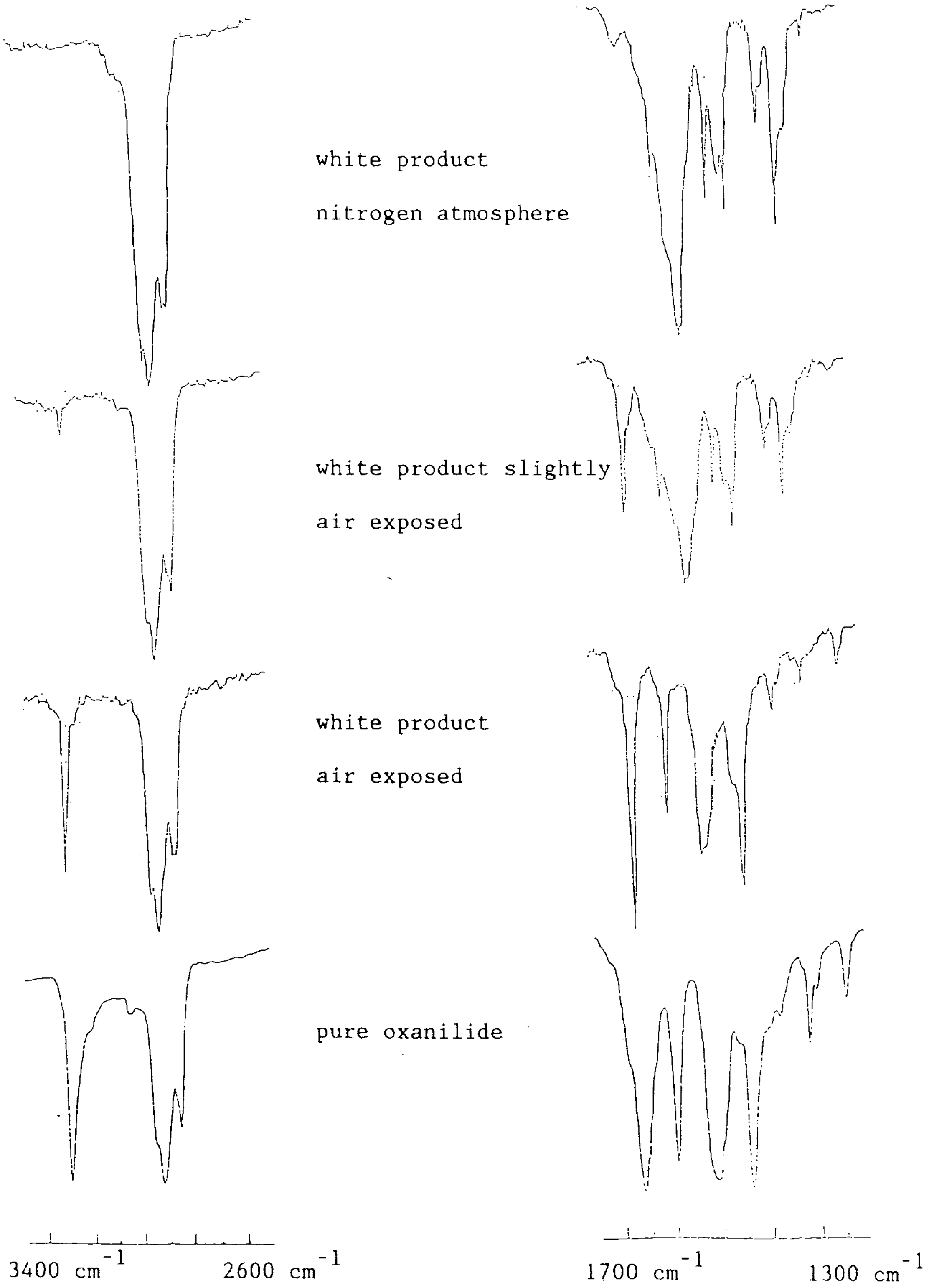


Figure 5. IR spectra of white powder from reaction 3.1.2 compared with spectrum of pure oxanilide.

hours until all the palladium dichloride had dissolved. Specific care was taken not to allow the reaction temperature to exceed 100°C as this results in decomposition of the product. The resulting red brown solution whilst still warm was filtered into 40/60 petroleum ether (100 ml). The yellow product precipitated immediately, and was separated by filtration, washed with hexane and dried in vacuo. The filtrate was concentrated by warming under vacuum, and more 40/60 petroleum ether added to precipitate more product. This process was repeated until no more product could be obtained. Yield was approximately 95% based on palladium dichloride.

Typical Elemental Analysis

Found :	C, 43.89;	H, 2.61;	N, 7.06%
$C_{14}H_{10}Cl_2N_2Pd$ requires:	C, 43.85;	H, 2.61;	N, 7.30%

Infra Red Spectrum:

A spectrum recorded as a nujol mull was found to be identical to that of an authentic sample.[3]

3.1.4 Reaction of Oxanilide with 2 Equivalents of ^nBuLi and Bisbenzonitrile Palladium Dichloride

Experimental

Bisbenzonitrile palladium dichloride (1.15 g, 3.0 mmoles), was added as a solid to a stirred suspension of the dilithiooxanilide (3.0 mmoles) prepared as described previously. A dark red brown solution resulted which contained no undissolved solid. This was concentrated to yield a yellow orange solid which was separated by filtration. Attempted recrystallisation from THF gave a semi crystalline powder much more yellow in colour than the previous solid. The product was dried in vacuo.

Results

Elemental Analyses:

Found :	C, 47.10;	H, 2.80;	Cl, 10.29;	Li, 1.91;	N, 4.00%
$C_{14}H_{10}Cl_2Li_2N_2O_2Pd$ requires:	C, 39.12;	H, 6.52;	Cl, 16.53;	Li, 3.26;	N, 6.52%
$C_{18}H_{14}Cl_2Li_2N_2O_3Pd$ requires:	C, 43.08;	H, 3.59;	Cl, 14.16;	Li, 2.79;	N, 5.58%
$C_{22}H_{18}Cl_2Li_2N_2O_4Pd$ requires:	C, 46.04;	H, 4.53;	Cl, 12.38;	Li, 2.44;	N, 4.88%
$C_{28}H_{20}Cl_2Li_4N_4O_4Pd$ requires:	C, 49.31;	H, 2.94;	Cl, 10.42;	Li, 4.10;	N, 8.21%

Infra Red Spectra:

The spectra of the orange powder and yellow semi crystalline solid prepared under nitrogen are very similar. There are no peaks present in the NH stretching region of oxanilide (3300 cm^{-1}), and the C=O stretching region is significantly different to that of oxanilide. There is a notable absence of any peaks in the C≡N stretching region. On exposing the mulls to air there is still an absence of any NH stretching peaks but a broad peak of medium intensity appears at approximately 3400 cm^{-1}: the C=O stretching region remains largely unaltered. The solution spectrum of the red brown filtrate has a sharp intense peak at 2238 cm^{-1} which corresponds to the C≡N stretching frequency of uncoordinated benzonitrile, (the C≡N stretching frequency in $(PhCN)_2PdCl_2$ occurs at 2287 cm^{-1}). All the other major peaks in this spectrum correspond to tetrahydrofuran. There is an absence of NH peaks.

Discussion

The elemental analyses give the best agreement with those required for $[(PhNCOCONPh)PdCl_2]Li_2.2THF$. Since both the dianionic lithium oxanilide salt and the oxanilide starting material are quite insoluble in tetrahydrofuran, it is a virtual certainty therefore that the oxanilide moiety will be contained in the yellow/orange solid. The presence of the C≡N stretching peaks in the spectrum of the red brown filtrate shows that the benzonitrile has probably been displaced by the oxanilide dianion as desired. On exposure of the material to air, the spectrum shows peaks corresponding to oxanilide starting material showing that the dianion of oxanilide has coordinated to the palladium as desired. This conclusion is further supported by the appearance of the peak at 3400 cm^{-1} which probably corresponds to lithium hydroxide formation. To summarise, all the data tends to suggest that $[(PhNCOCONPh)PdCl_2]Li_2 \cdot 2THF$ is formed but further investigations are required to fully confirm this.

3.1.5 Reactions of Palladium Dichloride with Oxanilide and Potassium Hydroxide

Experimental

Palladium dichloride (0.50 g, 2.82 mmoles), was ground in a mortar and pestle with oxanilide (1.35 g, 5.64 mmoles), and the resulting powder was suspended in DMSO (100 ml) at 70°C for 2 hours to give a red brown solution. Potassium hydroxide (0.47 g, 8.47 mmoles) in water (8 ml) was slowly added dropwise to this solution with continuous stirring. An off-white precipitate was slowly produced which turned yellow in colour over a period of several hours. The reaction was performed several times using slightly different methods of separation and washing in an attempt to obtain an uncontaminated product which could be characterised. In the first reaction the yellow solid was allowed to settle and the DMSO removed by syringe. Absolute ethanol (40 ml) was added and the solid stirred for 20 minutes before separating by filtration. The solid was then washed 3 times with dry acetone (20 ml). On trying to remove the residual ethanol by using vacuum, the yellow solid turned orange then brown. On washing with more ethanol the yellow colour was restored again. In the optimised procedure the DMSO was mostly removed by syringe after allowing the solid to settle; the residual DMSO was removed by filtration and the solid washed three times with dry degassed acetone (30 ml). Use of vacuum to speed up filtrations was kept to a minimum despite these processes being extremely slow.

Results

Elemental Analyses:

Typical ethanol washed product: C, 43.61; H, 3.85; N, 6.22%

Typical acetone washed product: C, 51.96; H, 2.96; N, 7.90%

$C_{28}H_{20}K_2N_4O_4Pd$ requires : C, 50.85; H, 3.05; N, 8.48%

Infra Red Spectra:

The spectrum of the ethanol washed solid prepared under nitrogen has a sharp peak of medium intensity at 3300 cm^{-1} which corresponds to the NH stretching frequency of oxanilide. The CO stretching region of the spectrum was also very similar to that of oxanilide, exposure of the mull to air had very little effect on its spectrum.

The spectrum of the acetone washed product has no peaks in the NH stretching region, the CO stretching region contains several intense peaks but is very different to that of oxanilide. On exposure of the mull to air the only significant change in the spectrum is the appearance of a broad peak of weak intensity at 3400 cm^{-1}.

Mass Spectrum:

The mass spectrum of the acetone washed yellow product has clusters of peaks corresponding to palladium species at m/e 699, 661, 623, 541, 462, 422 and 383. Single large peaks occurred at m/e 654, 585, 563, 497, 453, 409, 365, 317, 265, 222, 185, 169 and 149. None of the palladium containing fragments could be positively assigned, but it was noted that the difference between many of the pairs of peaks was m/e 237 to 240 which corresponds to oxanilide fragments.

Thermogravimetric Analyses:

Thermogravimetric analyses of several samples of the product both exposed and unexposed to air proved unhelpful in characterising the product.

The TGA traces from the air exposed samples were significantly different from those studied under a nitrogen atmosphere.

Solubility:

The yellow solid was found to be insoluble in acetone, methanol, THF, diethyl ether, ethyl acetate, carbon disulphide, toluene, dichloromethane, hydrocarbon solvents and acetonitrile. It was found to be sparingly soluble in pyridine.

Discussion

The elemental analyses for the acetone washed product suggest $K_2[Pd(PhNCOCONPh)_2]$ is formed, as desired. Obtaining the product in a pure form proved difficult especially as it was too insoluble in most solvents for recrystallisation. The lack of any peaks in the NH stretching region of the infra red spectrum of the acetone washed solid also suggests that the oxanilide is deprotonated as desired. The infra red spectrum for the ethanol washed solid seems to suggest that washing with ethanol causes reprotonation of the oxanilide, though this is more likely to be caused by water present in the ethanol, than ethanol itself.

The mass spectrum shows that palladium species are present in the yellow solid and that oxanilide is probably also present. The thermogravimetric analyses provided little information other than the fact the solid is air sensitive, as evidenced by the different results obtained with air exposed material. To summarise, the product we desired is probably formed but complete characterisation proved difficult, this is probably due to the following factors. The complex is susceptible to hydrolysis. The analogous N,N'- dioxamide complex.

has in the past also proved difficult to obtain in pure form, due to contamination with hydrolysed product.[1] Numerous successive experiments gave quite widely fluctuating elemental analyses. It is thought that several products other than that desired are formed in smaller but varying amounts, dependent upon factors such as reaction time, temperature, and product washing procedure etc.

3.1.6 Recrystallisation/Reaction of the Yellow Product from Reaction 3.1.5 Using Pyridine

Experimental

Approximately 0.5 g of the yellow product from reaction of palladium dichloride with oxanilide and potassium hydroxide was placed in a 250 ml round bottom 2 neck flask with 75 ml of pyridine. On warming to 90°C and stirring for one hour some of the solid dissolved to give a yellow solution. This was filtered from the undissolved solid, and on allowing the filtrate to slowly cool it gave a pale yellow microcrystalline solid. This was separated by filtration and washed with dry degassed toluene followed by dry degassed hexane. It was then dried in vacuo. No matter how slowly the solution was cooled larger crystals of the product could not be obtained.

Results

Elemental Analyses:

Found sample 1. :	C, 58.50;	H, 4.00;	N, 10.25;	Pd, 18.40%
Found sample 2. :	C, 61.78;	H, 4.48;	N, 12.08;	Pd, 16.67%
$C_{24}H_{20}N_4O_2Pd$ requires:	C, 57.40;	H, 3.97;	N, 11.10;	Pd, 21.10%

Infra Red Spectrum:

The infra red spectrum prepared under nitrogen was very similar to that of the original yellow solid from reaction 3.1.5, but with peaks corresponding to pyridine also present.

Infra red ν_{max} (nujol mull made in glove box)

3080 wsh, 3050 w, 3019 w,
$2920^{\dagger}$ s, $2850^{\dagger}$ s, 1640 s, 1620 s, 1602 s, 1586 s, 1480 m,
$1460^{\dagger}$ m shoulder, 1446 s, 1405 m, $1375^{\dagger}$ m, 1320 m, 1260 w,
1240 w, 1188 vw, 969 w, 952 w, 1071 m, 1020 w, 1000 vw,
951 w, 900 w, 862 w, 809 w, 752 s, 745 m, 695 s,
649 w, 620 w, 569 w, 510 w, 460 w.
(† ν_{max} nujol)

The following peaks were assigned 3080 cm^{-1}, 3019 cm^{-1} aromatic C-H stretch of pyridine. 1602 cm^{-1}, 1586 cm^{-1}, 1480 cm^{-1}, 1446 cm^{-1} $\mathrm{C}\underline{\cdots}\mathrm{C}$ and $\mathrm{C}\underline{\cdots}\mathrm{N}$ ring stretching of pyridine. 752 cm^{-1}, 695 cm^{-1} C-H out of plane bending.

Mass Spectrum:

The mass spectrum contains many clusters of peaks corresponding to both monomeric and dimeric palladium species. These were assigned as shown in Table 9. Typical peaks which correspond to monomeric species are shown in Figure 6 which illustrates parts of the actual spectrum obtained. The numerous peaks from dimeric palladium species are much less intense than those for the monomeric species or non-palladium containing fragments. No peaks corresponding to masses higher than 847 were observed. None of the single peaks were assigned; surprisingly none corresponded to fragments of oxanilide or pyridine. For example no peak was observed at m/e 238.

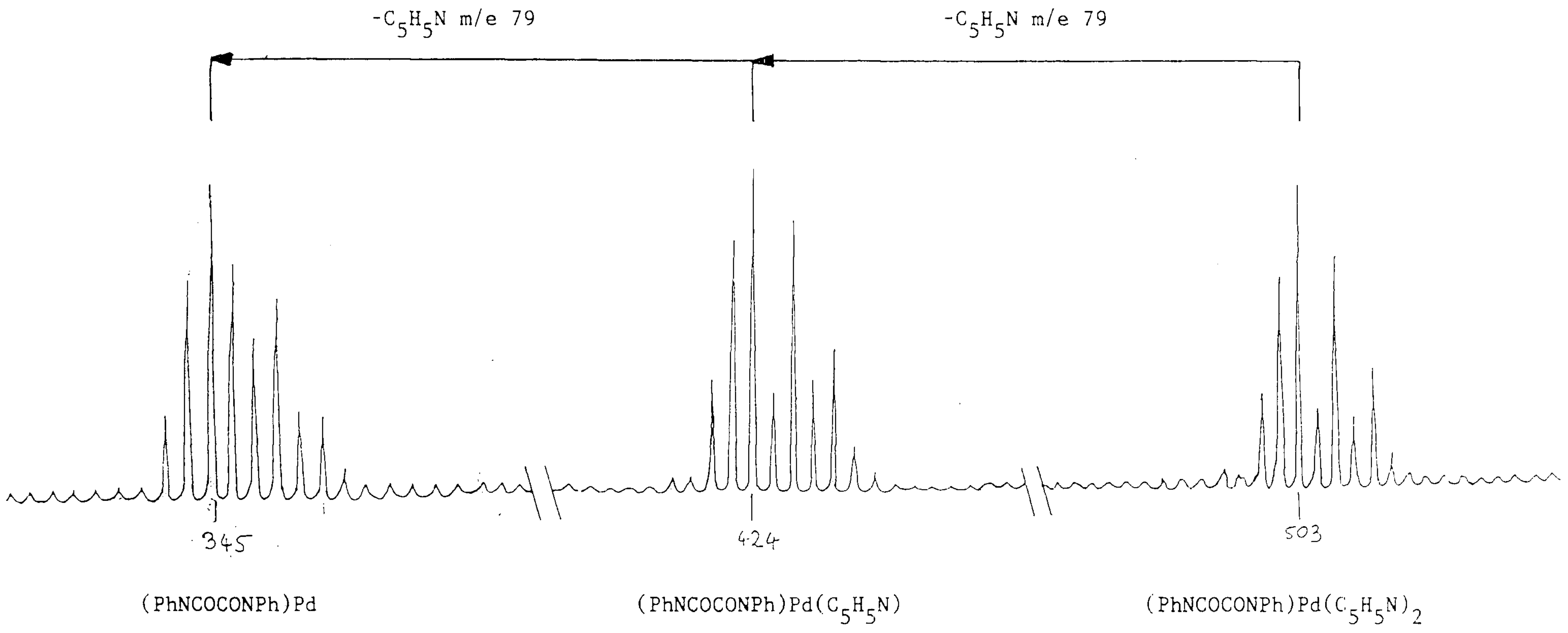


Figure 6. Mass spectrum peaks of monomeric palladium species obtained in reaction 3.1.6. (Palladium peaks shaded.)

Table 9. Mass Spectrum Peaks of Pyridine Recrystallised Yellow Solid

Peak (mass units)	Type of species (monomeric/dimeric)	Fragment assigned to peak
345	monomeric	Pd(PhNCOCONPh)
424	monomeric	Pd(PhNCOCONPh)(C_5H_5N)
503	monomeric	Pd(PhNCOCONPh)$(C_5H_5N)_2$
530	dimeric	Pd_2(PhNCOCONPh)(C_5H_5N)
609	dimeric	Pd_2(PhNCOCONPh)$(C_5H_5N)_2$
689	dimeric	$Pd_2(PhNCOCONPh)_2$
768	dimeric	$Pd_2(PhNCOCONPh)_2$(C_5H_5N)
847	dimeric	$Pd_2(PhNCOCONPh)_2(C_5H_5N)_2$

Thermogravimetric Analysis:

The trace obtained from the thermogravimetric analysis is shown in Figure 7. There are two distinct major weight losses of 47.5% and 31.5% and approximately 21% of the original weight remained. The thermogravimetric curve altered slightly on exposing the compound to air.

Discussion

Although far from perfect the elemental analyses do tend to suggest that [PhNCOCONPh]Pd$(C_5H_5N)_2$ is formed. The infra red spectrum also suggests this with peaks corresponding to pyridine and CO stretching frequencies similar to those for the yellow solid obtained in reaction 3.1.4. The mass spectrum verifies the presence of some [PhNCOCONPh]Pd$(C_5H_5N)_2$, but also suggests that some of this may be present as a dimer. The thermogravimetric analysis is very interesting; the weight losses of 47.5% and 31.5% correspond closely to the percentage weights of [PhNCOCONPh] and $[C_5H_5N]_2$ in [PhNCOCONPh]Pd$[C_5H_5N]_2$,

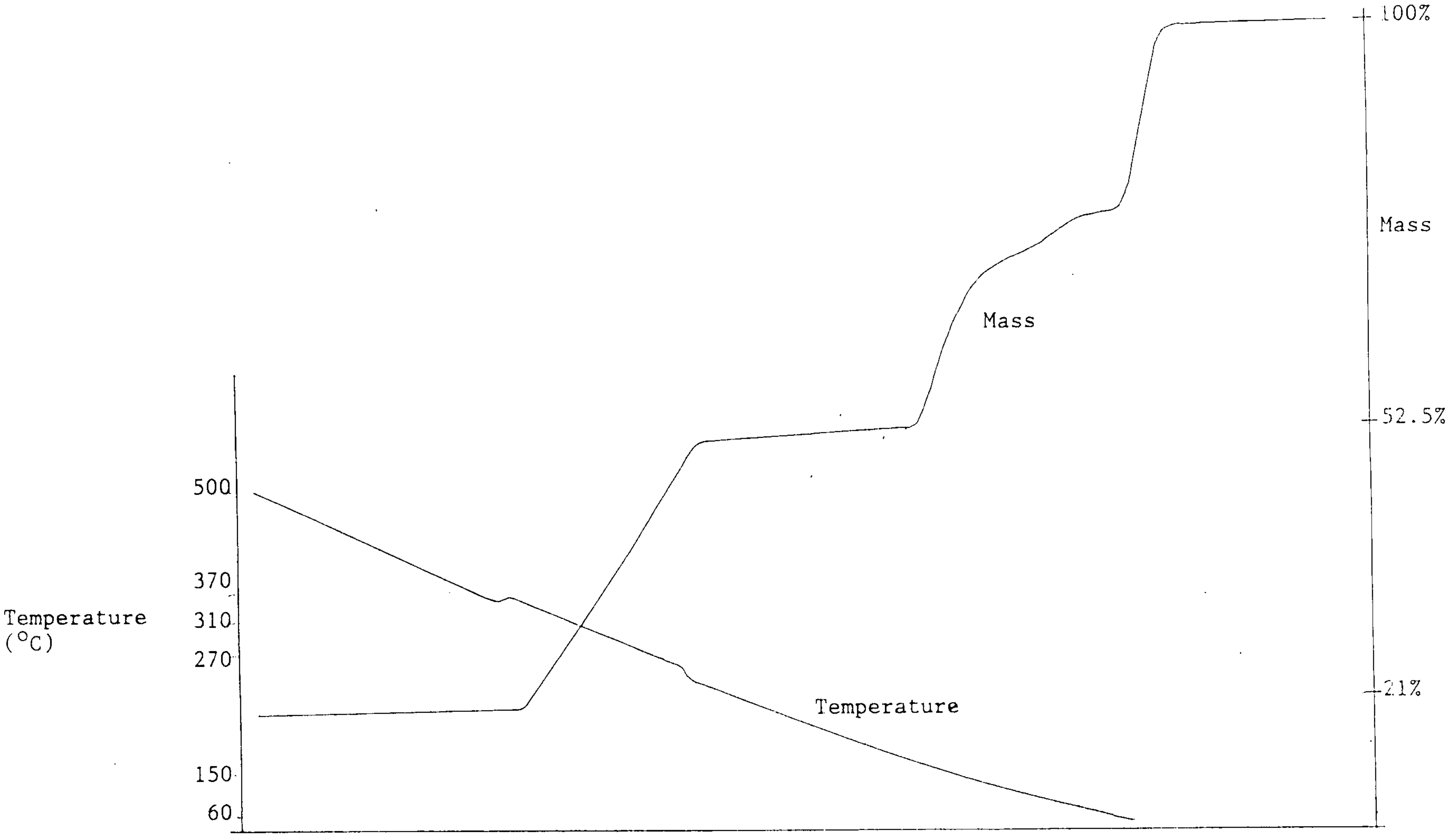
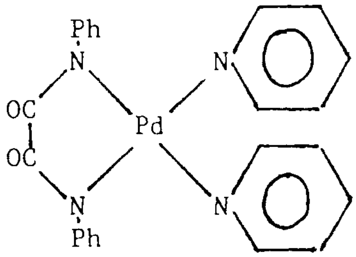
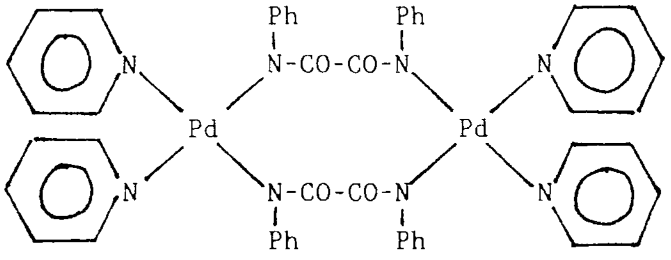


Figure 7. TGA of product from reaction 3.1.6.

but the oxanilide appears to be lost before the pyridine, and the loss of pyridine appears to be exothermic. To summarise the product is shown to contain pyridine, palladium, and the dianion of oxanilide. To determine the exact structure of the product would require further investigations but the following two empirical structures consistent with the data collected are tentatively suggested.





SECTION 2. REACTION OF RHODIUM AND IRIDIUM ALKENE COMPLEXES WITH AMINES

3.2.1 Introduction

In this section the known alkene complexes $[(PPh_3)_2RhCl(C_2H_4)]$,[4] $[CpRh(C_2H_4)_2]$,[5] $[(C_2H_4)_2RhCl]_2$[6] were synthesised and their reactions with amines investigated. The initial reactions with diethylamine and dimethylamine showed that elevated temperatures were often required, and this naturally led to the use of autoclave apparatus to contain the volatile amine. The complex $CpRh(C_2H_4)(PMe_3)$[7] was synthesised with only limited success, and the product decomposed before being converted to the target cationic complex $[CpRhH(C_2H_4)(PMe_3)]^{\oplus}$, for reaction with amines.

As mentioned in the literature survey the iridium complex $[Ir(CO)(PMe_2Ph)_2(C_2H_4)_2]^{\oplus}$ reacts with bromine, followed by nucleophiles to give complexes of the type $[Ir(CO)(PMe_2Ph)_2Br(C_2H_4Nuc)]^{\oplus}Br^{\ominus}$.[8] The intermediate complex $[Ir(CO)(PMe_2Ph)_2Cl]$[9] required for synthesis of the alkene complex was synthesised. Preliminary reactions of the alkene complex formed in situ, with bromine followed by diethylamine were promising, but materials were present in too small a quantity to carry out detailed investigations and obtain conclusive results.

3.2.2 Preparation of TrisTriphenylphosphine Rhodium(I) Chloride

This complex commonly known as Wilkinson's catalyst was prepared by the standard literature method.[4] Rhodium trichloride trihydrate (0.75 g, 2.8 mmoles), in absolute ethanol (20 ml), was added to a 250 ml round bottom 2 neck flask containing freshly recrystallised triphenylphosphine (4.5 g, 17.8 mmoles), in absolute ethanol (120 ml). The mixture was refluxed for 30 minutes and the burgundy red crystals produced on cooling were separated by filtration, washed with diethyl ether, and dried in vacuo. Typical yield 80%.

Elemental Analysis:

Found : C, 70.2; H, 4.98%

$C_{54}H_{45}ClP_3Rh$ requires: C, 70.1; H, 4.87%

3.2.3 Preparation of BisEthene Cyclopentadienyl Rhodium, $[CpRh(C_2H_4)_2]$

Bisethene cyclopentadienyl rhodium was prepared as described by King.[5] 0.7 g of $[RhCl(C_2H_4)_2]_2$[6] (1.8 mmoles), was placed in a 100 ml round bottom 2 neck flask with 10 ml of dry degassed THF. Approximately 4 equivalents of sodium cyclopentadienyl, (7.5 mmoles), in 15 ml of THF were added, the reaction refluxed for 30 minutes then left to stir for 24 hours. After removal of all the solvent under vacuum, the brown residue produced was transferred under nitrogen to a sublimation apparatus. Sublimation at 60°C and a pressure of 1 mm of Hg, gave the bright yellow product in 50% yield. The product melted at 72-73°C (lit. 73°C). N.B. The brown residue remaining after sublimation was found to contain excess cyclopentadienyl sodium and was pyrophoric.

3.2.4 Preparation of BisEthylene Rhodium Chloride Dimer, $[(C_2H_4)_2RhCl]_2$

$[(C_2H_4)_2RhCl]_2$ was prepared by the standard method as described by Cramer.[6] In a typical preparation, rhodium trichloride trihydrate, (2 g, 7.59 mmoles), was placed in a 250 ml round bottom 2 neck flask, water (4 ml), was added and complete solution achieved by warming with a steam bath. After addition of methanol (50 ml), the system was flushed with ethene. On slowly bubbling ethene through the stirred solution at room temperature for 7 hours, the product separated as a finely divided orange solid, which was filtered under an ethene atmosphere, washed with methanol and dried in vacuo.

Sodium hydroxide (0.3 g) was added to the filtrate to neutralise the HCl produced in the reaction which increases the solubility of the product. Bubbling ethene through the neutralised filtrate for a further 3 hours yielded a second crop of product. Yields were approximately 70%.

Typical Elemental Analysis:

Found : C, 24.70; H, 4.15%

$C_8H_{16}Cl_2Rh_2$ requires: C, 23.80; H, 4.45%

3.2.5 Reaction of $(PPh_3)_2RhCl(C_2H_4)$ with Diethylamine

Experimental

Tristriphenylphosphine rhodium(I) chloride (0.20 g, 0.23 mmoles) and dry degassed toluene (30 ml) were placed in a 100 ml round bottom 2 neck flask fitted with a bubbler and a reflux condenser. Ethene was bubbled through the solution with stirring until the initially burgundy red solution turned yellow, indicating the formation of $(PPh_3)_2RhCl(C_2H_4)$. Diethylamine solution in toluene (0.92 ml, 0.5M soln., 0.46 mmoles) was added and the reaction warmed to approximately 40°C with stirring. A very fine deep red solid was produced which was separated by filtration, washed with dry degassed toluene and dried under vacuum.

Results

Elemental Analyses:

Found :	C, 66.18;	H, 4.03;	N, 0.00;	Rh, 9.86%
$C_{42}H_{45}ClNP_2Rh$ requires:	C, 66.01;	H, 5.89;	N, 1.84;	Rh, 13.49%
$C_{40}H_{41}ClNP_2Rh$ requires:	C, 65.26;	H, 5.57;	N, 1.90;	Rh, 14.00%
$C_{54}H_{45}ClP_3Rh$ requires :	C, 70.09;	H, 4.87;	N, 0.00;	Rh, 11.14%
$C_{38}H_{34}ClP_2Rh$ requires :	C, 66.04;	H, 4.92;	N, 0.00;	Rh, 14.92%

Infra Red Spectrum:

The infra red spectrum of the red solid did not contain any N-H or C-N stretching frequencies. There was only a limited number of medium intensity peaks present, and these were all in the carbon-hydrogen or carbon-carbon stretching and bending regions.

Gas Liquid Chromatography

No higher amines were detected in the filtrate from the red solid, the only two major peaks in the gas liquid chromatograph corresponded to diethylamine and toluene.

Discussion

The lack of any nitrogen in the elemental analyses, or any N-H stretching frequencies in the infra red, suggest that the amine has attacked neither the alkene nor the metal. It is thought that the product is probably largely a mixture of $(PPh_3)_3RhCl$ and $(C_2H_4)Rh(PPh_3)_2Cl$. On attempting to recrystallise the red solid, the initially formed yellow orange solution slowly turned dark red, lending support to this theory. On attempting to repeat the whole reaction using diethylamine it was decided that these reactions should be performed in an autoclave in order to contain the volatile amine.

3.2.6 Autoclave Reactions

Reaction 1. $(PPh_3)_2RhCl + NEt_2H + C_2H_4$

The autoclave was flushed with dry nitrogen and charged with $(PPh_3)RhCl$ (0.46 g, 0.50 mmoles) in THF (45 ml), followed by NEt_2H (5.2 ml, 50 mmoles). It was then pressurised with 400 psi of ethene, (corresponds to approximately 250 mmoles), and heated to 60°C with stirring for 6½ hours. After allowing the reaction mixture to cool, a liquid sample was taken for qualitative GLC analysis. The reaction was then heated to 100°C for a further 4 hours before taking a further sample.

Reaction 2. $(PPh_3)_3RhCl + NEt_2H + C_2H_4 + H_2$

The autoclave was flushed with ethene and charged with $(PPh_3)_3RhCl$ (0.46 g, 0.50 mmoles), in THF (45 ml), and NEt_2H (5.2 ml, 50 mmoles). It was then pressurised with 400 psi of ethene and heated to 110°C for 4 hours with stirring. After allowing the reaction to cool a liquid sample was taken (2 ml) before adding 100 psi of hydrogen. The reaction was heated for another 4 hours at 100°C, cooled and another liquid sample withdrawn for GLC analysis.

Reaction 3. $CpRh(C_2H_4)_2 + NEt_2H + C_2H_4 + H_2$

The autoclave was flushed with ethene and charged with $CpRh(C_2H_4)_2$

(0.22 g, 1.0 mmoles), THF (45 ml) and NEt_2H (5.2 ml, 50 mmoles). After pressurising with 400 psi of ethene (∿ 250 mmoles), the reaction was heated to 100°C for 3½ hours with stirring. The reaction mixture was allowed to cool, a small liquid sample withdrawn, and 100 psi of hydrogen added before heating for a further 3½ hours at 100°C.

Qualitative Standardisation of the Chromatography Column

Samples of pure diethylamine, pure triethylamine and a mixture of the two in a 2:1 ratio respectively, were introduced to and separated by the column under varying conditions, until a consistent set of retention times were observed, with good separation of the two amines. These conditions were then kept as standard for all further analyses. The approximate concentration of amine in the reaction solutions was 1M. Prior to the analysis of any sample, a sample of standard 1 molar amine in THF was used for comparison purposes and to check that the retention time was unchanged.

Results and Discussion

No triethylamine nor any other alkylated amines apart from diethylamine were present in any of the final reaction mixtures. The gas liquid chromatograph registered only 2 main peaks, which corresponded to unreacted diethylamine and THF solvent. A very small peak due to a very volatile compound with a retention time approximately one third of that for diethylamine, was assumed to be due to a small amount of ethene or ethane dissolved in the reaction solution.

The final solution from reaction 1 was burgundy red in colour. If the bisphosphine ethene rhodium chloride complex had been formed as hoped one would expect a yellow solution. As the autoclave had been flushed with nitrogen, the catalyst had come into contact with amine before ethene. It was thought that the amine must have prevented coordination of the ethene. Consequently, the autoclave was flushed with ethene in the subsequent reactions, although this was found to make no difference to the end result.

In reaction 3 the final reaction solution was the same yellow colour as the starting solution. Concentration of the solution yielded a yellow solid. The infra red spectrum of this solid was very similar to that of an authentic sample of $CpRh(C_2H_4)_2$. The elemental analyses for the yellow solid were also in reasonable agreement with that required for $CpRh(C_2H_4)_2$.

Elemental Analyses:

Yellow solid, found: C, 49.02; H, 6.38; (N, 0.00)%

$C_9H_{13}Rh$ requires : C, 48.04; H, 5.82; (N, 0.00)%

3.2.7 Preparation of $CpRh(PMe_3)(C_2H_4)$

$CpRh(PMe_3)(C_2H_4)$ was synthesised with limited success using the method described by Werner et al.[7] Cooled trimethylphosphine (0.42 ml, 4.0 mmoles) was slowly syringed into a stirred solution of $[(C_2H_4)_2RhCl]_2$ (0.78 g, 2.0 mmoles) in THF (50 ml) contained in a 2-necked 100 ml round bottom flask. This initially gave a small amount of yellow precipitate, but this rapidly dissolved again to produce an orange solution which was stirred for 1½ hours. Cyclopentadienyl thallium (1.15 g, 4.2 mmoles) was added as a solid, and after stirring for 3½ hours the dark brown solution was filtered from the dark residue produced. All of the THF was removed under vacuo and the residue extracted with dry degassed pentane (50 ml). The extract was concentrated and cooled with solid CO_2 to produce light brown needle like crystals and dark brown residue. Yield ∿ 18%.

Typical Analyses:

Found : C, 44.14; H, 6.67%

$C_{10}H_{18}PRh$ requires: C, 45.52; H, 6.40%

N.B. The compound appeared to be very air and moisture sensitive.

On filtering the pentane extract prior to concentration, a dark residue precipitated even under dry nitrogen. The product also started to decompose in the glove box while being prepared for analysis. This occurred several times and it is now obvious that the use of white spot nitrogen is advisable with this preparation.

3.2.8 Preparation of $Ir(CO)Cl(PMe_2Ph)_2$

Iridium bisdimethylphenylphosphine carbonyl chloride was prepared as described in the literature.[9]

Iridium trichloride trihydrate (0.63 g, 1.79 mmoles), was placed in a 25 ml round bottom two neck flask along with concentrated HCl (2 ml), and absolute ethanol (10 ml). On bubbling carbon monoxide through the refluxing solution for 24 hours it turned from dark green to clear yellow. After allowing the reaction to cool below $60^{\circ}C$, dimethylphosphine (0.7 ml, ca. 8 mmoles) was added and a white precipitate immediately resulted. This was separated by filtration, washed several times with absolute ethanol, and washed back into the same flask with methanol (6 ml). (This was done to keep yields as high as possible.) Freshly made sodium methoxide in methanol (1.6 ml, 1.2M soln., 1.9 mmoles NaOMe) was added and the reaction mixture refluxed for a few minutes. This produced a clear yellow solution which on allowing to cool yielded yellow needles of crystalline product. Yield 56%.

Typical Analyses:

Found : C, 38.38; H, 4.17%

$C_{17}H_{22}ClIrOP_2$ requires: C, 38.27; H, 4.04%

APPENDIX A. General Experimental Details

A1. Handling Techniques

Most of the compounds were treated as being air and moisture sensitive. All operations were therefore performed in an atmosphere of dry nitrogen, or when appropriate an atmosphere of ethene. This was achieved using a vacuum line with 2 way taps enabling the system to be opened to vacuum or nitrogen. Solutions were stored under dry nitrogen and transferred by syringe against a counter current of dry nitrogen. Manipulation of air sensitive solids was done in a glove box containing dry nitrogen.

A2. Nitrogen Supply

Nitrogen was supplied to the bench as the boil off from the department's liquid nitrogen plant, having been passed through a deoxygenation plant. It was dried by passing through two drying columns containing molecular sieve and phosphorus pentoxide. Nitrogen in the glove box was continually recycled through a column of phosphorus pentoxide, and a dish of fresh phosphorus pentoxide was kept in the box at all times. A constant pressure of nitrogen was maintained in the apparatus by connection of the outlets to a bubbler containing heavy white oil.

A3. Solvents

Hydrocarbon solvents and diethylether were dried over freshly extruded sodium wire, whilst tetrahydrofuran was refluxed over potassium for several days before distilling onto sodium wire under nitrogen. Chlorocarbons were dried over molecular sieve types 4A or 13X. Solvents which had not been distilled under nitrogen were degassed when required by freezing with liquid nitrogen, then allowing to warm under vacuum until liquid again.

A4. Elemental Analyses

Carbon, hydrogen and nitrogen analyses were obtained using a Perkin Elmer 240 Elemental Analyser. Chlorine content was determined using the conventional method of oxygen flask combustion followed by potentiometric titration of the halide ion. Metal analyses were obtained using a Perkin Elmer 403 atomic absorption spectrometer.

A5. Infra Red Spectroscopy

Infra red spectra in the range 4000 cm^{-1} - 250 cm^{-1}, were recorded on Perkin Elmer 577 and 457 grating spectrophotometers. Spectra were mainly run as nujol mulls between KBr plates. A solution cell with calcium fluoride plates and 0.1 mm spacers was also used.

A6. Thermal Analysis

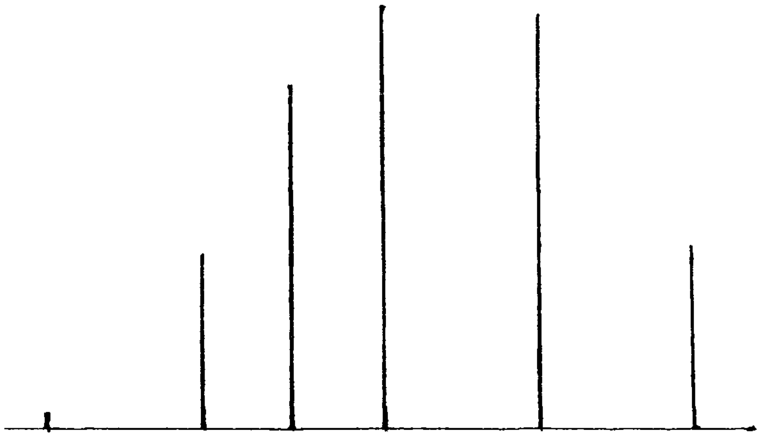
Thermogravimetric analyses traces were undertaken using a Stanton Redcroft TG 760 instrument. Moderately air sensitive compounds were transferred to the platinum crucible under a stream of nitrogen.

A7. Gas Liquid Chromatography

Amines were separated and detected using a five feet long glass column packed with Carbowax 20M 12%, and KOH 2%, supported on celite 100 - 120M, in conjunction with a Pye Unicam GCD machine.

A8. Mass Spectra

Mass spectra were obtained using a VG 7070E instrument; samples being introduced using a direct insertion probe. Electron impact spectra were run with an ion source temperature of 190°C, an ionising current of 70 eV and an accelerating potential of 8 kV. As well as electron impact, the technique of fast atom bombardment (FAB) ionisation was used. Mulls were made with thioglycerol and argon was used as the bombarding material. Mass spectra were mainly used for the characterisation of palladium compounds. Palladium has an atomic mass of 106.4 atomic units but occurs naturally as six stable isotopes with abundancies as shown in Figure 8. This makes palladium containing species relatively easy to identify, as they give clusters of peaks with a characteristic pattern, as shown in Figure 9. This pattern will be modified if other ions of the same mass are also present. Similarly, dimeric palladium species also give a characteristic pattern corresponding to species containing all the permutations of the six isotopes. This extends over a much greater mass range and is therefore much more frequently modified.



atomic mass	102	104	105	106	108	110
% natural abundance	1.0	11.0	22.2	27.3	26.7	11.8

Figure 8. Natural abundancies of palladium isotopes[10]

APPENDIX B. The Autoclave Apparatus

B1. Autoclave Section

The stainless steel autoclave has an internal volume of approximately 300 cm^3 and was pressure tested to 2000 psi. It was lined with a glass sleeve to help prevent contamination of the reaction mixture from any catalytic metals previously plated onto autoclave walls. The seal was obtained by screwing down the flat top onto a gasket, which was seated in a square cross-section channel around the rim of the vessel. The top is penetrated by a central thermocouple well, plus four inlet/exit pipes as illustrated in Figure 9. These were screwed into the top via Swagelock fittings.

Pipe 1, leads through valves T_3, T_4 and T_5 to the vent or either of 2 gas cylinders.

Pipe 2, gives access to the bottom of the autoclave, through valves T_1 and T_2.

Pipe 3, is connected to the pressure gauge and has a side arm capped with value T_6.

Pipe 4, contains the bursting disk rated at 800 psi, and leads into the catch pot which is also connected to the vent.

B2. Heating and Stirring

For rapid heating and for achieving higher temperatures, a band heater was fixed around the outside of the vessel. For more gentle heating a hot plate was placed underneath the vessel. In either case the heat source was controlled using a thermostat which monitored the reaction temperature via a thermocouple in the well. Stirring was achieved magnetically using a teflon coated follower. The heating equipment was plugged into the mains through a time switch. This enabled the system to be switched on and off automatically at the pre-set times.

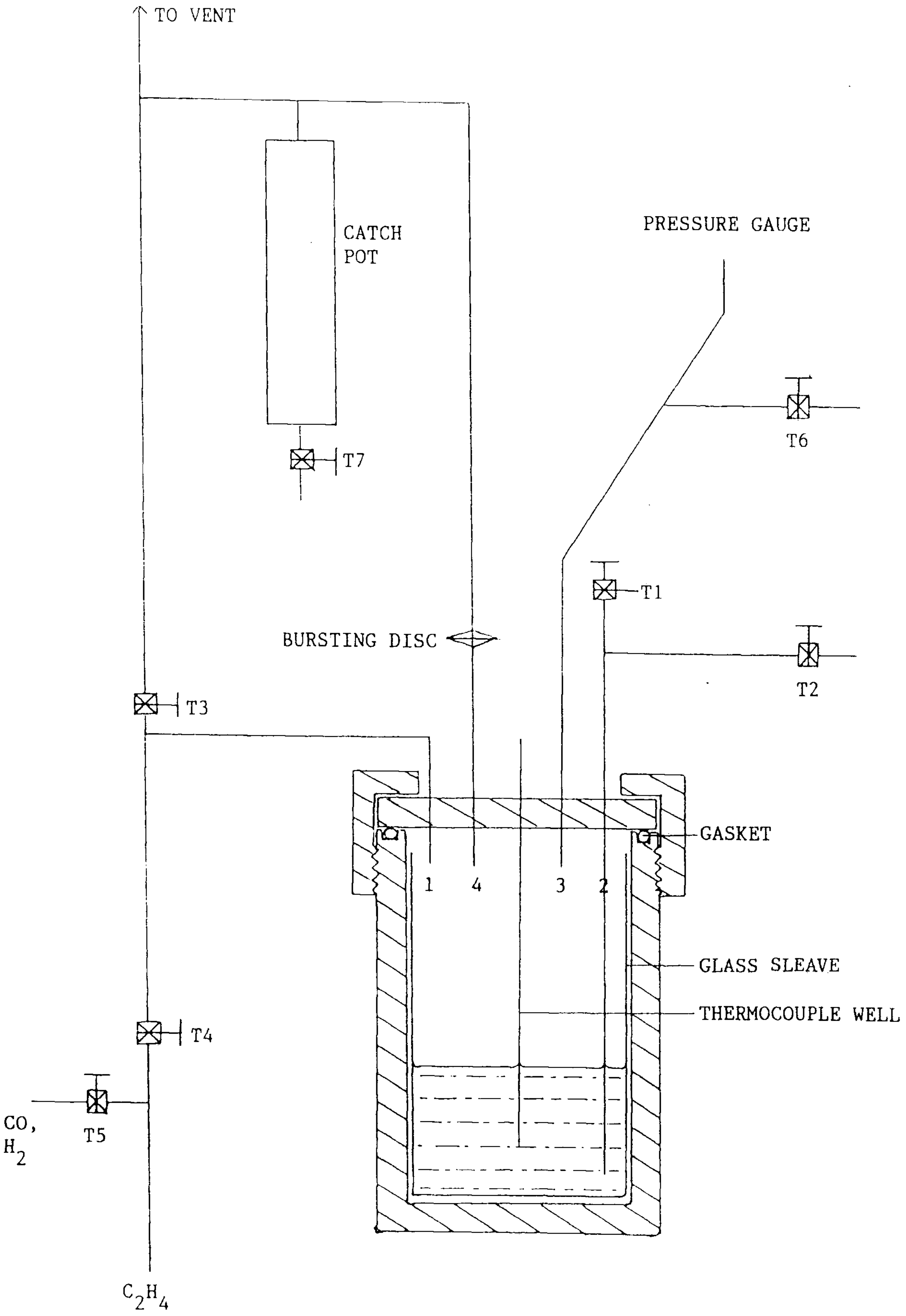


Figure 9. The Autoclave Apparatus.

B3. Use of the Apparatus

The basic common experimental procedures were achieved as follows.

Addition of catalyst

This was either added as a solid prior to closing and flushing out the system, or, if soluble, it was syringed in as a solution. The latter method was useful for air sensitive catalysts.

Addition of gases

Gases were allowed directly into the vessel from the supply cylinders via taps T_4 and T_5. It was important when introducing CO or H_2 into the reaction, to have the ethene cylinder head closed. This was to prevent transfer of the gases into the ethene cylinder which was invariably at a lower cylinder pressure.

Flushing the vessel:

This was done by allowing the appropriate gas to flow in through valve T_6 and out of the vent through valve T_3.

Obtaining reaction samples:

Liquid samples were obtained by opening valve T_2. This allowed the reaction mixture to be forced up line 2 which was connected to either a syringe or a cold trap. Gaseous samples could be obtained by opening valve T_6 to a cold trap and/or a sample cylinder.

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