The synthesis and metal complexes of some unusual phosphines

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THE SYNTHESIS AND METAL COMPLEXES

OF SOME UNUSUAL PHOSPHINES.

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To My Mother and Father

Cow Poetry: Distant Hills

"The distant hills call to me.
Their rolling waves seduce my heart.
Oh, how I want to graze their lush valleys.
Oh, how I want to run down their green slopes.
Alas, I cannot.
Damn the electric fence!
Damn the electric fence!"

G. Larson, '*Weiner Dog Art, A Far Side Collection*' (1990)

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ABSTRACT

The high temperature and pressure synthesis of chlorophosphines from an alkene, white phosphorus and phosphorus trichloride yielded both mono- and diphosphine products. Chain and cyclic alkenes, dienes and terpenes were used as substrates forming chain, ring and bicyclic mono- and diphosphines. Many novel, even unique, chlorophosphines were prepared in good yield and characterised using ^{31}P and ^{13}C NMR, mass spectroscopy and elemental analysis. Simple alkenes readily reacted forming mono- and 1,2-diphosphines. However 1,5-cyclooctadiene formed a 1,4-addition product after double bond conjugation. Butadiene dimerised prior to reaction, generating either a 2,2'-diphospholane or a 1,4-bridged phosphabicyclic alkane in addition to 1,2- and 1,4-diphosphines. Terpenoid dichlorophosphines were prepared but could not be isolated or characterised, because the substrate isomerised under the reaction conditions generating many similar products. Aromatic rings did not react, although the exocyclic double bond of styrene did undergo reaction. Chiral phosphines were readily produced from unsymmetric pro-chiral, alkenes.

Chlorophosphines are versatile precursors and, using standard organophosphorus techniques, were readily converted to phosphines, phosphites and other organophosphorus ligands suitable for chelation. Grignard reagents were used to prepare dimethyl derivatives, alcohols reacted with dichlorophosphines producing diethyl-, dimenthyl- or 1,4-butylphosphite derivatives. Piperazine also reacted although the products could not be fully characterised.

Electronic properties ($^{Mn}\chi$) of the phosphines in manganese carbonyl halide derivatives were measured as a function of the A_1 carbonyl stretching frequency. Substituent electronegativity was the most important factor in determining the π-acidity. Some dichloropalladium complexes were studied using ^{31}P NMR, although phosphine impurities complicated spectral interpretation. Iron and molybdenum hydrides reacted with dichlorophosphines to produce some unusual metal-phosphine compounds.

CONTENTS

ABBREVIATIONS

NMR	Nuclear magnetic resonance
DEPT	Distortionless enhancement by polarisation transfer
MS	Mass spectroscopy
FT-IR	Fourier transform infrared
EI	Electron impact
CI	Chemical ionisation
EA	Elemental analysis
Me	Methyl
Et	Ethyl
OEt	Ethoxy
Pr	Propyl
Bu	Butyl
Cy	Cyclohexyl
COD	1,5-Cyclooctadiene
Nb	2-Norbornyl
OMen	Menthoxy
Ph	Phenyl
Bz	Benzyl
Np	2-Naphthyl
AIBN	Azobis(isobutyronitrile)
LDA	Lithium diisopropylamide
DMPE	Bis-1,2-(dimethylphosphino)ethane
DPPE	Bis-1,2-(diphenylphosphino)ethane
DiPAMP	Bis-1,2-(phenyl-2-methoxyphenylphosphino)ethane
DCPE	Bis-1,2-(dichlorophosphino)ethane
PROPHOS	Bis-1,2-(diphenylphosphino)propane
CHIRAPHOS	Bis-2,3-(diphenylphosphino)butane
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
DIOP	2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenyl-phosphino)butane
NMDPP	Neomenthyldiphenylphosphine
NORPHOS	Bis-2,3-(diphenylphosphino)bicyclo[2.2.1]hept-1-ene
RENORPHOS	Bis-2,3-(diphenylphosphino)bicyclo[2.2.1]heptane
BPPFA	(S)-N,N-dimethyl-1-[(R)-1',2-bis(diphenylphosphino)-ferrocenyl]ethylamine

CHAPTER 1:

INTRODUCTION AND LITERATURE REVIEW

OF PHOSPHINE AND DIPHOSPHINE CHEMISTRY

INTRODUCTION

Phosphines and diphosphines are widely used in transition metal chemistry, bonding strongly to many different metals in a wide variety of oxidation states. A very large number of derivatives have been synthesised and structural studies undertaken. Steric and electronic properties of phosphines can be altered in a systematic and predictable way. Thus phosphines can stabilise, and facilitate the study of, many metal complexes. Additionally, the chemical reactivity of transition metal complexes can be modified by changing the coordinated phosphine, subtly altering the metal-ligand bonding interactions, and hence the reactivity. Phosphine ligands can also influence the rate of reaction at a metal centre, by stabilising the transition state or destabilising the ground state. Chiral phosphines will control the stereochemistry and subsequent reactions of the complex. Many phosphines and their transition metal complexes are commercially available.

Homogeneous catalytic processes often employ transition metal-phosphine complexes as the active (16 electron) catalyst, the phosphine ligands increase the selectivity of the reaction and hence the yield of pure products. Hydrogenation, isomerisation, carbonylation, hydroformylation, polymerisation, oxidation and metathesis reactions are all catalysed by transition metal-phosphine complexes. Phosphines often activate the catalyst system permitting milder reaction conditions, such as lower temperatures and pressures, to be used or they may stabilise the metal complex at higher temperatures, reducing the possibility of catalyst decomposition during the reaction. Phosphines also facilitate the reproducible generation, and stability, of the active catalytic species by electron density transfer. Diphosphines increase the stability of complexes compared with the corresponding monophosphines and order the coordination sites more effectively, as expected for the standard chelate effect. A recent development in the area of supported catalysts is the use of polymer supported catalysts, the polymers containing a phosphine group to bind the metal, thereby combining the high selectivity of a homogeneous catalyst with the ease of separation of the catalyst from the reaction mixture, one of the advantages associated with heterogeneous catalysts.

Chiral phosphines retain their chirality in transition metal complexes, therefore chiral complexes (and catalysts) can be readily prepared and applied to asymmetric syntheses. Enantiomerically pure hydrogenation products have been selectively synthesised from alkenes (eg. L-DOPA) and ketones using stereospecific chiral palladium, platinum or rhodium-diphosphine complexes.

This area of phosphine chemistry is expanding due to increasing interest in enantiomerically pure products.

Initial aims of this project involved the preparation of model transition metal-phosphine catalysts. Synthesis of (preferably chiral) chelating and bichelating phosphines and diphosphines was thus a necessary aspect of this work. Many methods for diphosphine synthesis have been devised, frequently using highly toxic reagents. A general method couples metal phosphides with haloalkanes producing α,ω-diphosphines. Another widely used method involves base catalysed addition of phosphorus-hydrogen bonds to vinyl phosphines, normally generating 1,2-disubstituted ethane derivatives. Longer chain derivatives (and polyphosphines) can be obtained in the presence of a free radical initiator. A method that had not been fully exploited prepared dichlorophosphines from alkenes, white phosphorus and phosphorus trichloride in a single step under high temperature and pressure conditions. This method was adopted and developed using many different mono-alkenes, dienes, terpenes and aromatic substrates. Chiral mono- and diphosphines could be synthesised from pro-chiral, unsymmetric alkenes.

Chlorophosphines are versatile precursors in organophosphorus chemistry, the highly reactive nature of phosphorus-chlorine bonds permitting many different derivatives to be readily formed. Grignard or lithium organometallic reagents react with chlorophosphines at low temperature forming tertiary phosphines; protic hydrogen compounds, such as alcohols and amines, react at ambient temperatures producing phosphites and aminophosphines. Chiral derivatives may be synthesised using chiral reagents.

Analysis of the chlorophosphines and their derivatives was achieved using ^{31}P and ^{13}C NMR, mass spectroscopy and elemental analysis. NMR provided an insight into the nature of phosphorus substitution; ^{31}P-^{13}C coupling constants yielding detailed structural information concerning the alkyl substituents. Structures could often be confidently assigned using the NMR data alone. Although mass spectroscopy and elemental analysis generated valuable information, these techniques were generally used to prove the NMR-based assignments.

Electronic properties of phosphines can be assessed using the carbonyl stretching frequency of transition metal-carbonyl-phosphine complexes. Reactions of many novel mono- and diphosphines with manganese pentacarbonyl bromide were investigated using FT-IR spectroscopy, to determine the electronic

properties and trans-effect of each phosphine. Other transition metal complexes were also synthesised, Palladium-phosphine complexes were prepared from palladium dichloride and examined using ^{31}P NMR spectroscopy. Additionally, dichlorophosphines reacted with other transition metal compounds producing some interesting complexes, although no products containing unusual metal-phosphine interactions were isolated.

Many new and unusual phosphines and diphosphines were synthesised from inexpensive, readily available starting materials. Phosphorus, phosphorus trichloride and chlorophosphines are hazardous materials, however the phosphine syntheses involved fewer stages, a controlled environment and less toxic reagents than other literature methods. This study concentrates on the synthesis and characterisation of chlorophosphines and their derivatives. Transition metal-phosphine complexes were also prepared and analysed, although some of these results were inconclusive.

LITERATURE REVIEW

1.1. Introduction

The nature of the transition metal-phosphine bond is an important feature of both transition metal and phosphorus chemistry. Electron density transfer occurs from the phosphine to the metal centre and from the metal to the phosphine ligand, therefore the phosphine significantly affects the electronic properties of the complex. The steric size of the phosphine will also affect the properties of the complex. Thus the influence of the metal-phosphine interaction has widespread implications on the reactivity of the complex. The first part of this review describes the nature of the transition metal-phosphine bond and the associated modifications to the physical and chemical properties of the metal complex.

Diphosphines (and polyphosphines) confer greater stability on metal complexes than the analogous monophosphines, and have been widely used as ligands in homogeneous catalysis. Many methods for the synthesis of diphosphines are known, however most involve many stages and toxic reagents. These methods are described, the aim being to provide an overview of the synthetic routes normally used rather than to review the detailed preparation of specific diphosphines.

Chlorophosphines, such as those synthesised in this work, are very reactive materials and can be readily converted into a wide range of organophosphorus compounds. These reactions are well known and are not extensively reviewed here; only those reactions relevant to this work are described. Additionally, some recent unusual reactions of chlorophosphines with transition metal complexes are included.

1.2. Bonding in Metal Phosphine Complexes

The nature of the metal-phosphorus bond has been well documented[1-3], and is determined by both electronic and steric effects[4]. This section contains an account of metal-phosphorus bonding theory and the practical implications.

In his landmark review, Tolman[4] showed electronic and steric properties of phosphine ligands were important in understanding the chemistry of transition metal-phosphine complexes, and in determining the relative reactivity of each

ligand. The electronic parameter (χ) consists of both σ-donor and π-acceptor bonding effects and can be measured quantitatively, based on the carbonyl stretching frequencies of the metal complex. Phosphine cone angles (θ) were used as a measure of the spatial volume required by the ligand in the complex. Steric effects can have important electronic consequences and vice versa, affecting the nature of the metal-phosphine interaction. Therefore the σ-donor, π-acceptor and steric components of the metal-phosphorus interaction cannot be easily separated and quantified, although theoretical QALE (quantitative analysis of ligand effects) calculations[3] provide convenient and accurate approximations.

Conventionally[2] the bonding between a metal and the phosphine ligand is thought to consist of synergic σ- and π-components (Dewar-Chatt model[5-7]). The σ-bond is formed by donation of electrons from the ligand lone-pair orbital to an empty orbital on the metal centre, the ligand behaving as a Lewis base (σ-base). A d_π-d_π backbond is formed by electron donation from a full metal d-orbital to an empty 3d phosphorus orbital of similar symmetry, the ligand behaving as a Lewis acid (π-acid):

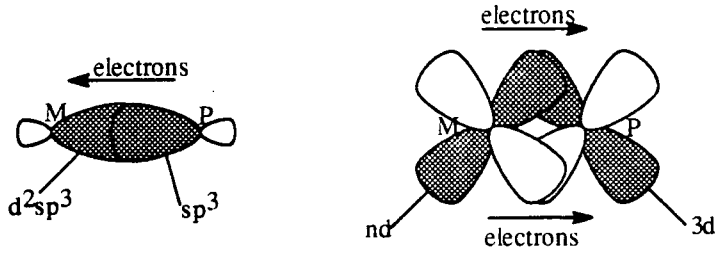


Figure 1.1: Bonding in Metal-Phosphine Complexes

Hybrid orbitals are involved in the σ-bond, on coordination the sp^3 hybrid phosphorus orbitals are tetrahedral. Similarly, splitting of the crystal field generates d^2sp^3 hybrid metal acceptor orbitals, of σ-pseudo-symmetry. Crystal and ligand field theory[8,9] show the effect on the energy of a metal atomic orbital (AO) in an electrostatic or ligand field. Field strength is dependant on the ligand basicity. Splitting of the d-orbital energy levels is caused by the spatial arrangement of the ligands about the metal, and affects the kinetic, thermodynamic and electronic properties of the metal[10]. Metal d-orbital degeneracy will be destroyed by the incoming ligands, because each orbital interacts with the ligands differently. In octahedral complexes, the $d_{x^2-y^2}$ and d_{z^2} orbitals point directly at the incoming ligands, interacting with the ligand lone-pair (bonding) electrons. d_{xy}, d_{xz} and d_{yz} orbitals point between the axes of ligand approach so their energy level is little affected by the incoming ligands. Thus the

field is split into t_{2g} (d_{xy}, d_{xz} and d_{yz}) and e_g ($d_{x^2-y^2}$ and d_{z^2}) energy levels, with the metal electrons preferentially populating the lower (t_{2g}) energy level and leaving the e_g levels vacant. The difference between the two energy levels is the crystal field splitting energy (Δ_o). In octahedral transition metal complexes[11] the hybrid d-orbitals, of correct symmetry for σ-bonding with the ligand, are the vacant e_g atomic orbitals (also forming the LUMOs). The populated t_{2g} atomic orbitals are not significantly affected by the ligand's approach, becoming non-bonding molecular orbitals (HOMOs), and available for π-bonding[12]. The difference between HOMO and LUMO energies is a measure of the 'hardness' of the system. Hardness[13] is a unifying concept for identifying shells and subshells in atoms and molecules. It is a measure of the resistance of the metal centre to the change in electron density distribution. For CO, alkenes and phosphines π-bonding occurs when the ligand possesses low-lying vacant atomic orbitals of the correct π-symmetry. Non-bonding electrons from the t_{2g} level (produced during σ-bond formation) are stabilised by donation to a vacant orbital on the phosphorus ligand. A schematic molecular orbital diagram for σ- and π-bond formation is shown below:

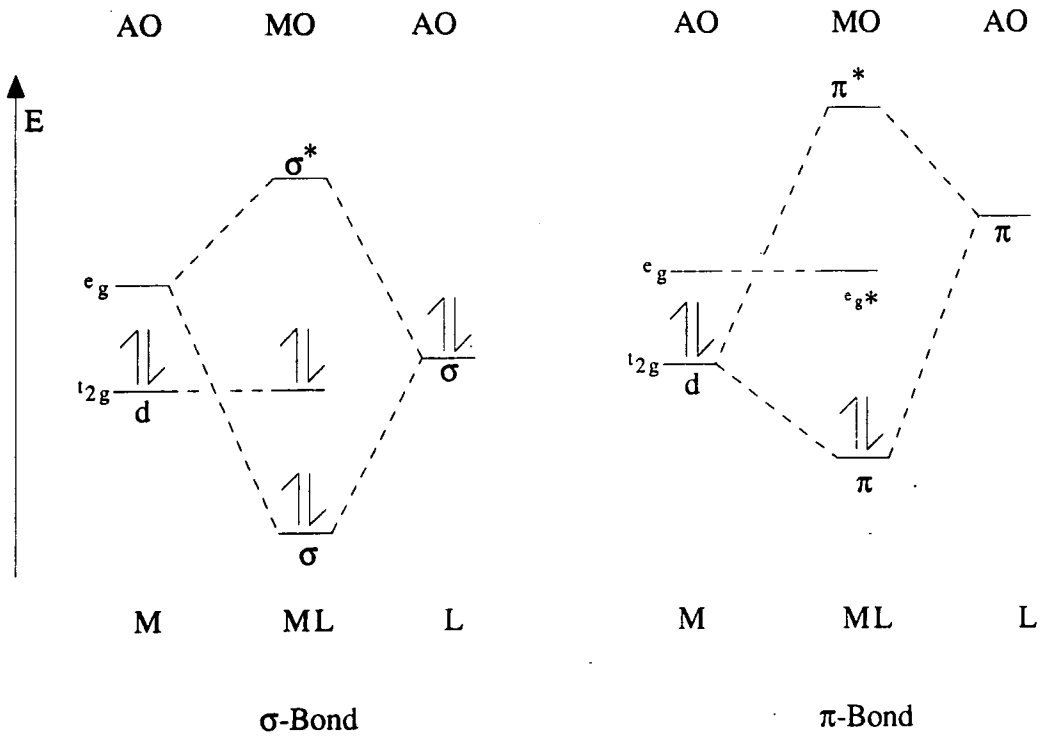


Figure 1.2: Molecular Orbital-Energy Diagram for Metal-Phosphine Bonding

Low oxidation state metals are stabilised by π-bonding, the phosphine accepting the metal atom's excess electron density and thus lowering its

reactivity. However the σ-donor and complimentary π-acceptor properties determine the overall electronic effect of the ligand.

Theoretically[8] the order of nickel d-orbital energies in 5-coordinate Ni^{II} low-spin square pyramidal complexes, based on σ-bonding considerations only, is $xz, yz < xy < z^2 < x^2-y^2$; however experimental evidence[2] shows the order is $xy < xz, yz < z^2 < x^2-y^2$. The order of d_{xy} and d_{xz} is the reverse to that expected from simple crystal-field considerations, but is explained in terms of optimum L-M-L bond angles and metal-ligand backbonding[2].

Recently the nature of the π-bond has been rigorously investigated[14,15] using molecular orbital calculations. It was argued that the 3d phosphorus orbitals were too diffuse and energetically unsuitable to significantly interact with the metal d-orbitals. These calculations, supported by some experimental evidence, have shown that the phosphine LUMOs are doubly degenerate having σ* and 3d character, as shown below. The σ* anti-bonding orbital is from the phosphorus-substituent bond. These σ*-3d hybrid orbitals are excellent π-acceptors, having the correct symmetry[16] to interact with metal d-orbitals. The degree of hybridisation is determined by the relative energies of the σ* and 3d orbitals.

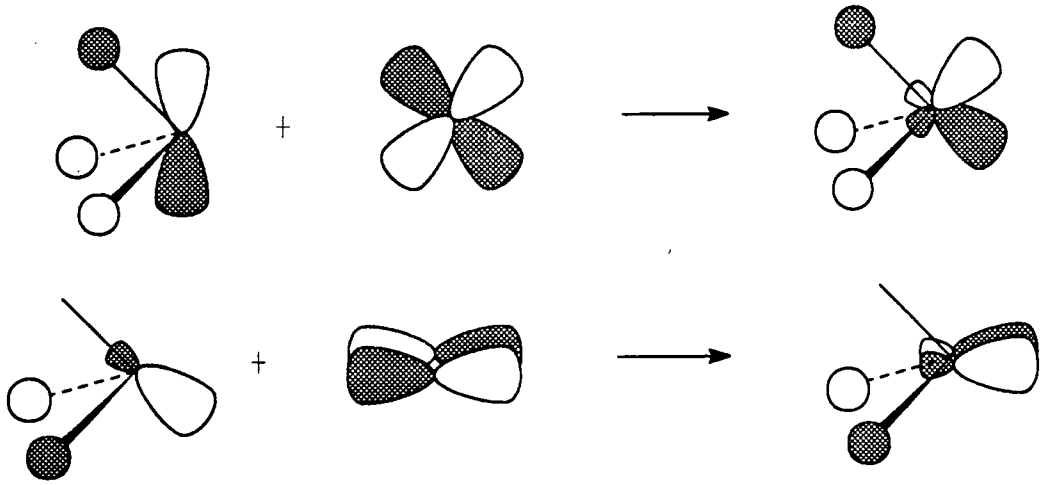


Figure 1.3: Doubly Degenerate Phosphine LUMOs (from reference 17)

Quantum mechanical calculations[11] of the frontier orbitals of trimethylphosphine have shown that the ligand LUMO also contains significant phosphorus 3p character. Generally, electronegative phosphorus substituents increase 3p character in σ*, lowering its energy and allowing more σ*-3d mixing, thus enhancing the π-acceptor character of the phosphine. Orpen[17,18] has

demonstrated this theory by correlating the charge on the metal centre with the metal-phosphorus and phosphorus-substituent bond lengths.

Taft[19] developed Hammett's free energy relationship to describe steric and electronic terms in organic chemistry. Similar relationships have been developed in organometallic chemistry, although they are less frequently used. Different electronic and steric factors are associated with every phosphine and these affect the resulting properties of the metal-phosphine complex. Generally[20] the attractive term in metal-phosphorus bonding is related to electronic factors and the repulsive component to steric factors, as described below.

1.2.1. Electronic factors

Electronic effects of ligands theoretically consist of: field effects (dipole effects), electronegativity effects, polarisability effects and electron-transfer effects[21]. For phosphines these are usually divided into σ-donor and π-acceptor components, which are difficult to separate experimentally since only the overall effect of both can be measured. More emphasis is normally placed on the magnitude of the π-bond, rather than the σ-bond[2]. Some workers[22] believe it is possible to characterise pure σ-donor phosphines in addition to those with the normal σ-donor/π-acceptor properties, every phosphine belonging to one of the two groups. The concept of an electronic threshold (π_t) as a measure of the metal valence orbital energy was introduced to account for metal-phosphorus multiple bonding[3]. This work, however, is disputed[23] due to the difficulty in separating the σ- and π-effects in bonding.

σ-basicity (donor ability) is reflected in the ionisation potential of the metal-phosphine bond and generally shows the ability of the ligand to split the t_{2g} orbitals of the metal into the e (doubly degenerate) and b_2 (non-degenerate) components[24]. Electropositive phosphorus substituents increase the electron density at phosphorus, therefore the σ-basicity of the phosphine is increased (as measured by the pK_a of the phosphine[22]). Some studies[23] suggest the σ-donation is only slightly smaller in trifluorophosphine (regarded as a poor σ-donor) than trimethylphosphine (a good σ-donor), arguing that pK_a values are an inappropriate measure of phosphine σ-basicity. Other methods[25] of determining the phosphine donor ability measure the enthalpy of protonation of the free ligand (ΔH_{HP}) and the metal complex (ΔH_{HM}). Correlation of the metal complex and phosphine basicity determines the σ-donor effect of the phosphine. Sterically bulky phosphines significantly affect metal-complex basicity. Table 1.1. (on page

14) shows the pK_a and electronic parameters of some common phosphines, the recognised order of σ-basicity is:

$$PMe_3 > P(OMe)_3 > P(NMe_2)_3 > PF_3$$

Interestingly the lone-pair donor orbital of aminophosphines contains significant nitrogen character (at least in the free ligand) caused by mixing of the phosphorus and nitrogen lone-pair orbitals[24]. However the oxygen lone-pair orbitals in phosphites do not significantly interact with the phosphorus lone-pair orbital. Therefore the σ-donor trend (reverse of π-acceptor trend below) does not always exactly parallel the electronegativity of the phosphorus substituents, as indicated by the reversed[24] order of σ-donor ability of aminophosphines and phosphites when compared to their π-acceptor ability. Thus σ-donor strengths are influenced by the direct interaction of the substituents' lone-pair orbitals, although to a lesser extent than substituent electronegativity.

Generally a poor phosphorus σ-donor is a good π-acceptor, because both effects normally reflect the electronegativity of the phosphorus substituents. Thus, as the substituents become more electronegative the orbital used in the phosphorus-substituent bond decreases in energy and becomes more stable, implying the σ* orbital becomes more stable[26]. Additionally because this σ-bond is polarised towards the substituent, the σ*-bond must be polarised towards the phosphorus. Therefore, as the phosphorus contribution to the anti-bonding σ* orbital increases, the size of the σ* orbital that points towards the metal also increases, making it more accessible for back donation. Molecular orbital theory describing backbonding shows that the energy of the ligand LUMO determines bond strength[11]. Bagus[23] has shown the phosphorus 3d orbitals need not be directly involved in metal-phosphine bonding, since the anti-bonding σ* orbitals can form π-bonds in the absence of 3d orbitals[14,15]. However the 3d orbitals dictate bond strength by enhancing metal-phosphine backbonding, thus shortening and strengthening the bond. Therefore metal complexes formed with π -acidic phosphines generally possess shorter, stronger metal-phosphorus bonds[22]. The order of π-acid character is[11,22,24]:

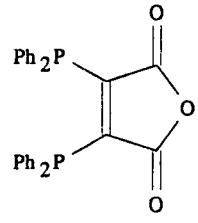
good π-acceptor: $CO \approx PF_3 > PCl_3 > PCl_2OR > PCl_2R > PCl(OR)_2 > PClR_2 > P(OAr)_3 > ArP(OAr)_2 > RP(OAr)_2 > Ar_2P(OAr) > R_2P(OAr) \approx ArP(OR)_2 > Ar_2POR \approx P(OR)_3 > PAr_3 > P(NR_2)_3 > PR_3 >> RNH_2$ good σ-donor

Trifluorophosphine compares favourably with CO as a coordinating ligand[27] because their σ-donor and π-acceptor properties are very similar, both

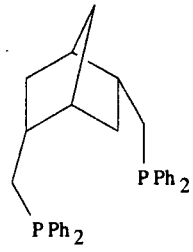
forming strong π-bonds. The small cone angle of trifluorophosphine also contributes to its excellent coordinating properties. Using CSOV computer simulation[23], even trimethylphosphine has been shown to possess significant π-acidity.

Although oxygen atoms can donate a lone-pair to the π* orbitals of aromatic rings, no similar donation to the σ* orbitals on phosphorus is possible. Therefore different effects of the same alkoxy group on aromatic and phosphorus compounds[26] are observed.

Interestingly bis-2,3-[diphenylphosphino]maleic anhydride [1] can stabilise supposedly 19-electron complexes[12]. 18-electron complexes are very stable because the nine lowest energy molecular orbitals (formed from interaction of the ligand with the metal s-, p- and d-orbitals) are bonding orbitals. These filled MOs are never anti-bonding[8] and therefore the complex is very stable. In complexes with more than 18 electrons some of the anti-bonding MOs will be populated, destabilising the complex. However, for complexes of [1], the vacant π* ligand orbital is of lower energy than a metal-ligand anti-bonding σ*-orbital, and hence accepts the unpaired electron. Thus these complexes exist as 18-electron complexes with a reduced ligand[12].



[1]



[2]

Metal-phosphine bond formation involves significant σ (phosphorus to metal) and π (metal to phosphorus) electron density transfers[27] but only a small net electron density transfer between the two atoms results. Thus the relative σ-donor (σ-basic) and π-acceptor (π-acidic) properties of the phosphine ligand significantly affect the electron density at the metal centre. More basic phosphines increase the electron density at the metal, stabilising electron-deficient transition metals and transition states formed during dissociative processes. Similarly π-acidic phosphines lower the electron density, stabilising electron-rich transition metals and transition states formed during associative processes[22,28]. Most phosphines show this latter π-acidic stabilising property. Cyclic voltametry and IR spectroscopy have been utilised[29] to determine the relative charge density at chromium and molybdenum centres in various bidentate

phosphine complexes. Triphenylphosphine ligands are significantly distorted on interaction with transition metals[30]. σ-Donation to the metal results in a smaller phosphorus-ring bond length and a greater Ph-P-Ph bond angle. Analogously, π-acceptance from the metal generates longer phosphorus-ring bond lengths and smaller Ph-P-Ph bond angles. The net electronic effects of σ-donation and π-acceptance tend to balance. However the properties are difficult to separate, although the overall effect on the metal centre can be measured using the carbonyl stretching frequencies (υ_{CO}) of transition metal-carbonyl-phosphine complexes. Widely used methods for determining the σ- and π- characteristics of ligands are based on a Graham analysis[31] of carbonyl force constants and Cotton-Kraihanzel[32,33] force constants. Tolman[4] measured the A_1 carbonyl mode of $Ni(CO)_3L$ to determine the electronic effect (υ) of the phosphine, the relative electron density at the metal centre[34] and hence the relative electronic effects of various phosphines. Unfortunately metal-carbonyl π-bonds can release electron density into a metal as the acceptor ability of the trans-phosphorus ligand increases. This effect is discussed later. An alternative method of measuring electronic effects involves Bodner's electronic parameter (δ)[35] and is obtained from the difference in ^{13}C NMR chemical shift of $Ni(CO)_3L$ relative to $Ni(CO)_4$.

1.2.2. Steric Effects

Electronic factors alone are insufficient to explain the ability of phosphine ligands to compete for coordination on $Ni(CO)_4$[4]. Steric effects describe both the molecular volume of the ligand and the repulsive forces generated on bonding to a metal centre. Bulky phosphines distort the positions of surrounding ligands, shielding the metal centre and thus affecting its chemistry. Tolman[4] introduced the cone angle concept (θ) to measure the steric size of ligands, although the 'steric effect' and 'cone angle' are not identical. The cone angles of some phosphines are shown in Table 1.1. To determine the (minimum) cone angle, in degrees, for symmetric ligands, a cone is constructed around the ligand, centred on the phosphorus atom with a metal atom at the apex, which just touches van der Waals radii of the outermost atoms. This is shown schematically below:

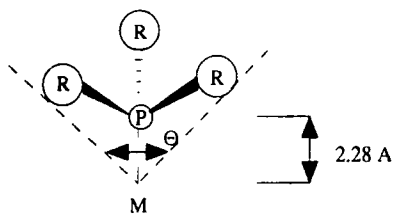


Figure 1.4: The Cone Angle in Phosphines

There is a mathematical relationship between the nature of the substituent and the cone angle. Therefore addition of the contribution from each substituent will produce a fairly accurate value for the cone angle[4]. For example, the cone angle of $PMePh_2$ (136°) is approximately two-thirds between PMe_3 (118°) and PPh_3 (145°). For non-symmetric ligands the cone angle can be determined using the sum of the half-angles ($\theta_i/2$; where θ_i is the cone angle of each substituent):

$$\theta = 0.66 \Sigma \theta_i/2 \quad (°)$$

However the theoretical cone angle does not account for steric compression around the phosphorus centre caused by its interaction with the metal and so is not necessarily the dominant consideration in ligand behaviour. For example, a ring in tricyclohexylphosphine is known to adopt a twist conformation on complex formation[20] thus changing the effective cone angle. Therefore experimentally determined cone angles are often slightly smaller than those calculated using molecular models, although even for bulky phosphines the differences are small. Cone angles thus provide a reliable measure of the steric effects of a phosphine in a metal complex. Table 1.1 overleaf shows the cone angle, basicity and electronic parameter for some simple phosphines.

Phosphites have a smaller cone angle than the analogous phosphine because they are more flexible, rotation around the P-O-C bond relieving steric strain in both the free ligand and the complex. Cone angles can also be used to describe some of the steric properties of diphosphines (and polyphosphines). However, bite angles (the P-M-P bond angle) provide a better measure of the steric effects of bi-chelating ligands[11] because they have smaller steric requirements than two analogous monodentate ligands. Since the oxidation state determines the size of a metal centre, the steric strain enforced by the ligand backbone depends on the oxidation state of the metal[25]. The natural bite angle (β_n) of diphosphines[36] is the preferred chelation angle, and is determined only by ligand backbone constraints and not by metal valence angles. It is therefore independent of the electronic preference of the metal centre and is based solely on steric considerations. Metal-chelate rings are usually non-planar, therefore the experimentally determined bite angle is usually smaller than the theoretical value. For example, the bite angle[36] of endo,endo,bis-2,5-[(diphenylphosphino)methyl]norbornane [2] is 122.6° although the experimental value is slightly below 120°.

Table 1.1: Ligand Properties of Phosphorus (III) Compounds[3,11,22]

Phosphine	Cone Angle, θ (°)	pK_a	Electronic Parameter, χ (cm^{-1})
$PPhH_2$	106	-2.0	20.85
$P(OMe)_3$	107	2.6	24.10
$P(OEt)_3$	109	3.31	21.60
PMe_3	118	8.65	8.55
$P(OMe)_2Ph$	120	2.64	19.45
$P(OEt)_2Ph$	121	3.1	18.10
PMe_2Ph	122	6.5	10.60
PPh_2H	126	0.03	17.35
$P(OPh)_3$	128	-2.00	30.20
$P(O^iPr)_3$	130	4.08	19.50
$P(OMe)Ph_2$	132	2.69	16.30
PEt_3	132	8.69	6.30
PBu_3	132	8.43	5.25
$P(OEt)Ph_2$	133	2.91	15.60
$PMePh_2$	136	4.57	12.10
$P(O\text{-}o\text{-}tol)_3$	141	-1.83	27.7
$P(OCy)_3$	141	---	18.00
$P(^iBu)_3$	143	7.97	5.70
PCy_2H	143	4.55	9.10
PPh_3	145	2.73	13.25
$P(p\text{-}MePh)_3$	145	3.84	---
$P(p\text{-}MeOPh)_3$	145	4.59	10.50
$P(p\text{-}ClPh)_3$	145	1.03	16.80
$P(p\text{-}FPh)_3$	145	1.97	15.70
$PBzPh_2$	152	---	12.30
$PCyPh_2$	153	5.05	---
$P(^iPr)_3$	160	---	3.45
PBz_3	165	---	10.35
$P(m\text{-}tol)_3$	165	3.30	---
PCy_3	170	9.70	1.40
$P(^tBu)_2Ph$	170	---	4.95
$P(^tBu)_3$	182	11.40	0.0

Physical properties of many metal complexes are influenced by the steric size of phosphine ligands. Metal-phosphine bond lengths have been found to increase linearly as the phosphine cone angle increases[20]. Multiple terminal

carbonyl absorptions, caused by steric effects of the phosphine, in (η^5-Cp)FeL(CO)Me (L = PR_3 or $P(OR)_3$) complexes were observed[22] when the phosphine cone angle exceeded 152°. Complexes with π-acidic ligands (eg. carbonyls) are apparently more sensitive to the steric bulk of the phosphine, as shown by studies of the terminal carbonyl stretching frequency of iron complexes[22], because the metal-ligand bonds of π-acids are shorter[3] and more susceptible to ligand steric effects. Bulky phosphine ligands also affect the equilibria of ligand dissociation in palladium (0) phosphine complexes[37], PdL_4 = PdL_3 + L = PdL_2 + 2L. The extent of ligand dissociation decreases in the order:

$$PMe_3 \approx PMe_2Ph \approx PMePh_2 > PEt_3 \approx PPh_3 > P^iPr_3 > PCy_3 > PPh(^tBu)_2$$

Ligand exchange reactions[38] on nickel (0) phosphine complexes allowed semi-quantitative measurements of ligand steric effects to be made. These steric effects, related to the cone angle, were apparently more important than the associated electronic effects on the exchange equilibria, and determined the degree of substitution. However electronic and chelation effects will also affect the stability of the complexes formed.

Steric interactions cause many phosphine complexes to deviate from their expected geometries. For example, a 'tilting' of the phosphine ligand, with respect to the metal-phosphine bond axis, to relieve the steric repulsions between phosphorus substituents, occurs in $Cr(CO)_5PR_3$ complexes[20]. It is caused by the three phosphorus substituents adopting different orientations relative to the carbonyl groups in the $Cr(CO)_4$ plane. One alkyl group occupies a staggered conformation, the others are eclipsed by Cr-CO bonds. In the tricyclohexylphosphine complex additional steric repulsions between the carbonyl groups and cyclohexyl rings result in one of the rings adopting a twist conformation[20], as the complex assumes a minimum-strain configuration. The long metal-phosphine bond length in the tri-t-butylphosphine complex indicates the steric effects of the ligand, which prevents formation of a 'normal' metal-phosphine bond. Thus as the phosphorus substituents become more branched their repulsive interactions with each other and the metal ligands increases. These effects cause the donor atoms in Wilkinson's catalyst [$RhCl(PPh_3)_3$] to adopt a non-planar conformation[39]. Similar subtle steric interactions, exerted by chiral phosphines, control the stereoselectivity of asymmetric homogeneous catalysts[11,37].

In the metal clusters $[Cu_2Ru_4(\mu^3\text{-}H)_2(CO)_{12}(PR_3)_2]$ (R = alkyl or aryl)[40], the cone angle of the phosphine ligand affects the metal framework structure.

Tri-i-propylphosphine generated two isomers that interconverted at ambient temperature, whereas the tricyclohexylphosphine complex contained a previously unobserved Cu_2Ru_4 metal core structure, in which a Ru_4 tetrahedron with one edge bridged by a $Cu(PCy_3)$ unit is mono-capped on a non-adjacent face by a second $Cu(PCy_3)$ unit. At ambient temperatures the two $Cu(PCy_3)$ units interchange, although the ground structure is observed spectroscopically at -100° C.

Free ligands substituted at the β-carbon, such as $P(^iBu)_3$, are able to adopt a sterically favourable conformation. However, on coordination, the resulting M-P-C_α-C_β dihedral angle (ϕ) indicates a significant repulsive interaction between the metal and the β-carbon. 2-Norbornylphosphines, synthesised during this study, would be expected to show similar effects on coordination. This torsional strain is known as the β-effect[21] or phosphine backstrain[41].

Recently new measures of ligand steric effects have been introduced, namely the ligand profile[42-4] and the ligand repulsive energy (E_R)[21]. Experimental evidence has shown that the cone angle is generally a reliable indicator of the steric effects of the ligand. However bulky or non-symmetric phosphines do not behave as regular cones, and are better described using the concept of a ligand profile. This is obtained by plotting the maximum semi-cone angle ($\theta/2$) of each hydrogen atom of the phosphine during rotation around the M-P bond[42]. By evaluating a 'solid angle' (Ω), an estimate of the angular parameter (Θ') can be obtained, which is comparable with the cone angle. Ω decreases as crowding around the metal centre increases. Therefore Θ' values are always lower than the cone angle because the ligand profile incorporates steric compression effects of the metal complex on the phosphorus centre, whereas the cone angle is usually determined for an idealised system or a free ligand.

T.L. Brown[21] has recently calculated the ligand repulsive energy (E_R) for various phosphines from the van der Waals repulsive force acting between the ligand and metal centre along the metal-phosphorus axis, at the equilibrium metal-phosphorus distance (r_e):

$$E_R = [\delta E_{vdW}/\delta r_{(M\text{-}P)}]r_e \text{ (kcal mol}^{-1}\text{)}$$

Unlike cone angles, E_R values are calculated for each ligand in the conformation adopted in the complex. The calculations show phosphites respond differently to phosphines during complex formation because phosphites are more flexible, the increase in steric strain being absorbed by the P-O-C bond rather

than in bond stretching modes[21]. A close correlation between cone angle and E_R is observed, discrepancies being due to non-symmetry of the ligands causing tilting of the ligand with respect to the metal-phosphorus bond. This correlation showed an absolute steric threshold (≈82°), corresponding to the minimum angle necessary for significant repulsive ligand-metal interaction. Below this threshold angle the ligand exerts no repulsive or steric effect. However the exact angle depends on the characteristics of the metal centre.

1.2.3. The Trans-Effect

First recognised by Werner as a labilising effect, and originally described[45] as the tendency of a coordinated group to direct an incoming group into the position trans- to itself, the trans-effect is now[46] defined as 'the effect of a coordinated group on the rate of substitution reactions of ligands trans to itself' or[47] 'the effect of one ligand on another caused by electronic transmission through a central metal atom'. It is a kinetic effect affecting the transition state only. In contrast the trans-influence of a ligand is a thermodynamic effect[48] affecting the ground state properties of the complex[49] and is measured spectroscopically. Frequently, though erroneously, the two terms are used interchangeably. However, both are very significant in square planar complexes such as platinum (II) compounds[50,51], a factor of 10^6 difference in the rate of substitution between a complex containing a good trans- labilising ligand and one with a poor labilising ligand may be observed. For example[52], the rate of pyridine substitution of trans-$PtClL(PEt_3)_2$ complexes shows a rate of $k_1 = 10^{-2}$ s^{-1} for hydride ligands and 10^{-6} s^{-1} for chloride ligands. Similarly the rhodium-phosphine bond trans- to chlorine in Wilkinson's catalyst is shorter than those cis- to chlorine[37]. The trans-effect is much less important in octahedral complexes. An isotopic trans-effect has been recognised[53] in platinum hydrides, explained by the difference in internuclear M-H and M-D distance. For platinum (II) complexes the trans-effect decreases in the order[52,54]:

$$CO \approx CN^- \approx C_2H_4 > PR_3 \approx H^- > Me^- \approx SC(NH_2)_2 > Ph^- \approx NO_2^- \approx I^- \approx SCN^- > Br^- \approx Cl^- > \text{pyridine} \approx RNH_2 \approx NH_3 \approx OH^- \approx H_2O$$

Initial work[55] suggested that backdonation of electron density from the metal to the ligand explained the trans-effect. More recently, molecular orbital calculations[48] have shown that the two trans- ligands form σ-bonds with metal orbitals of the same symmetry. Therefore a strongly bonding orbital to one ligand will only be weakly bonding to the trans- ligand, a strong σ-donor ligand forming a stronger bond at the expense of the trans- ligand. Similarly, strong π-acids will

draw more electron density from the metal than weaker π-acids. Thus both the σ- and π-electronic factors contribute to the trans-effect. A transition state stabilisation theory[48] has been used to explain the trans-effect of ligands of negligible trans-influence. Trans- electron withdrawing ligands on the metal stabilise the electron rich transition state in associative reactions of square planar complexes[28], thus accelerating the reaction rate.

Potential energy calculations[52] have shown the reaction rate increases with increasing σ-strength, π-acidity and polarisability (softness) of the entering ligand, or decreasing σ-strength (trans-labilising effect) of the trans- ligand. Increasing σ-strength of cis- ligands (the so-called 'cis-effect') also increases the rate.

1.3. Diphosphine Chemistry

1.3.1. Introduction

Diphosphines are widely used in transition metal chemistry because of their great versatility. Many transition metal complexes are known, and their chemistry has been extensively reviewed[56-61]. Diverse applications of diphosphines are possible because of their predictable and systematic electronic and steric properties. Comparison with monodentate phosphines shows that alkyl bidentate (and polydentate) ligands offer several advantages[62], including an increase in the nucleophilicity (basicity) towards the metal centre. Thus more control of the coordination number, stoichiometry and stereochemistry in the metal complex is possible. Additionally intra- and intermolecular exchange reactions are slower and more controlled. When phosphines in general are used as ligands, ^{31}P NMR provides detailed structural and bonding information derived from the metal-phosphorus and phosphorus-metal-phosphorus coupling constants. Of special interest in this work, ^{31}P NMR can also be used in synthetic studies of chiral phosphines[63]. Some common chiral phosphines and diphosphines are shown on page 35.

1.3.2. Catalytic Asymmetric Synthesis

Many diphosphines contain chiral centres, which may occur at the phosphorus atom, in the backbone or in the substituents; for example S,S-DiPAMP, R,R-(-)-DIOP or NMDPP respectively (the abbreviations are listed on page ix). Axial and planar chiral phosphines such as BINAP and BPPFA are also

known[64], and shown at the end of the chapter. Metal complexes containing chiral ligands are themselves chiral and are frequently used to mediate asymmetric reactions[65]. Stereoselective transformations can readily be performed, for example the homogeneous hydrogenation of prochiral alkenes produces enantiomerically enriched products because the chiral catalyst controls the reaction route[66]. Chiral rhodium, palladium and platinum complexes are the most widely used[67] asymmetric catalysts.

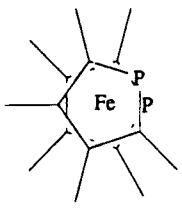
An early diphosphine used to induce stereospecific catalysis was DIOP[68], producing an effective asymmetric hydrogenation catalyst in conjunction with a rhodium or palladium centre[69]. Another efficient and widely used chiral auxiliary is BINAP[70], the phenyl substituents on phosphorus normally dictate the precise conformation of the catalytic complex. Rhodium-BINAP complexes catalyse the asymmetric hydrogenation of alkenes and ketones, and allylic hydrogen shifts[70]. However, 1,2-[diphosphino]ethanes with either phosphorus or backbone chirality are the most efficient ligands in asymmetric syntheses and catalysis. Some diphosphines, such as DiPAMP, contain chiral phosphorus centres supported on an achiral carbon framework. Rhodium-DiPAMP complexes are very active asymmetric hydrogenation catalysts[71]. DIOP and DiPAMP hybrids[72] have also been prepared and possess a similar catalytic activity.

Chiral auxiliaries containing a C_2 axis of symmetry, such as DIOP, CHIRAPHOS and DiPAMP, provide more stereochemical control in the metal complex than ligands lacking symmetry[73]. The axis of symmetry reduces the number of theoretically competing diastereomeric transition states in catalytic reactions. Similarly, the high activity of metal-NORPHOS catalysts is caused by the rigidity of the norbornene ring conformation[66].

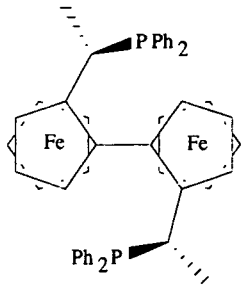
Recently a 'respective control concept' has been introduced[74], stating that one phosphine group of a diphosphine ligand oriented cis- to the prochiral group of the substrate controls the enantioselectivity and the second group oriented trans- to the prochiral group increases the reaction rate, especially in asymmetric hydrogenation processes. Frequently this second group is electron rich, accelerating the rate of oxidative addition, leading to higher catalytic activity. Rigid chelation of the metal centre with olefins, by backdonation, thus leads to higher enantioselectivity.

Chiral ferrocenylphosphine ligands, such as BPPFA[75-7], 2,2',3,3',4,4',5,5'-octamethyl-1,1'-diphosphaferrocene[78-80] [3] and the trans-

chelating bis-2,2'-[1-(diphenylphosphino)ethyl]-1,1'-biferrocene[81] [4] have been synthesised, and modified using crown ether substituents[82]. They show high enantioselectivity in palladium catalysed allylation reactions[75-82]. Other chiral trans-spanning ligands, such as endo,endo,bis-2,5-[(diphenylphosphino)methyl]-norbornane [2] (β_n=120°)[83], have also been produced and various metal complexes studied. Water soluble diphosphines, such as [1] or those containing aromatic sulphonic acid substituents are of interest for hydroformylation catalysis[84,85].



[3]



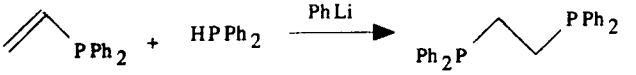
(R,R)-(S,S)-[4]

1.3.3. Diphosphine Synthesis

The synthesis of monophosphines has been extensively documented[86-92], and will not be described in this review. Early syntheses of diphosphines were restricted to general coupling reactions of haloalkanes with alkali metal phosphides to produce α,ω-diphosphines in good yield. An alternative method couples primary or secondary phosphines (containing a phosphorus-hydrogen bond) with vinyl phosphines. These reactions are usually initiated either photolytically or with radical initiators, such as AIBN, and provide a facile route for α,ω-diphosphine synthesis. Many chiral phosphines have been produced by this method, although the starting materials must be carefully prepared. Bis[dichlorophosphino]alkanes can be readily synthesised from simple starting materials, and are versatile intermediates in phosphine chemistry. Phosphorus-chlorine bonds are very reactive, and are readily converted to a wide range of derivatives[92]. Many other chiral phosphines have been prepared from alkaloid starting materials[69].

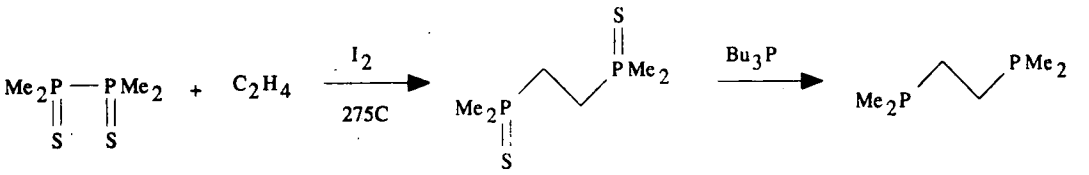
One of the most commonly used and easily prepared diphosphines is bis-1,2-[diphenylphosphino]ethane (DIPHOS, DPPE). This was prepared[93] by metal phosphide coupling. Sodium cleaves triphenylphosphine generating sodium diphenylphosphide, which reacts with 1,2-dichloroethane forming DPPE in good

yield. DPPE is also readily synthesised[94] by coupling diphenylvinylphosphine with diphenylphosphine in the presence of a base, usually phenyl lithium.



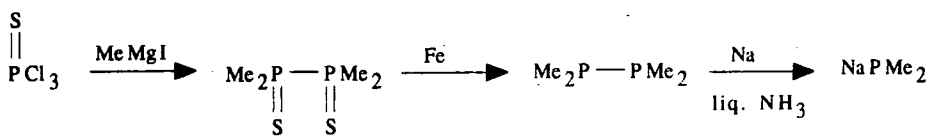
Transition metal complexes formed with alkyl diphosphines, such as bis-1,2-[dimethylphosphino]ethane (DMPE), have higher electron density at the metal centre than DPPE complexes because alkylphosphines are less π-acidic and better σ-donors than the corresponding arylphosphines. Therefore the metal-phosphine complexes are more reactive towards electrophilic attack at the metal centre. Diphosphines may act as monodentate, chelating bidentate or bridging bidentate ligands. Unfortunately the syntheses of these versatile diphosphine ligands often involves highly toxic reagents and many intermediate stages, as described below.

The first synthesis of DMPE involved the addition of tetraalkyldiphosphanes to ethene under high pressure. Parshall reported[95] the synthesis of DMPE in 66% yield from tetramethyldiphosphane disulphide and ethene in the presence of iodine. The reaction was performed at 275°C for 48 hours in a Carius tube. Tributylphosphine was used to remove sulphur from, and reduce, the resulting diphosphine disulphide:

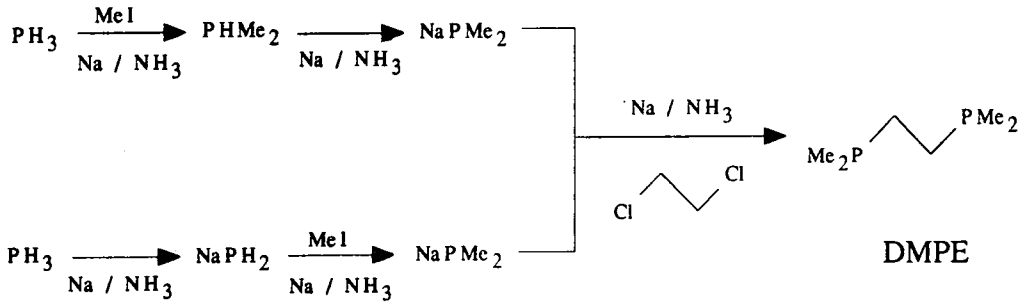


Metal Phosphide Coupling

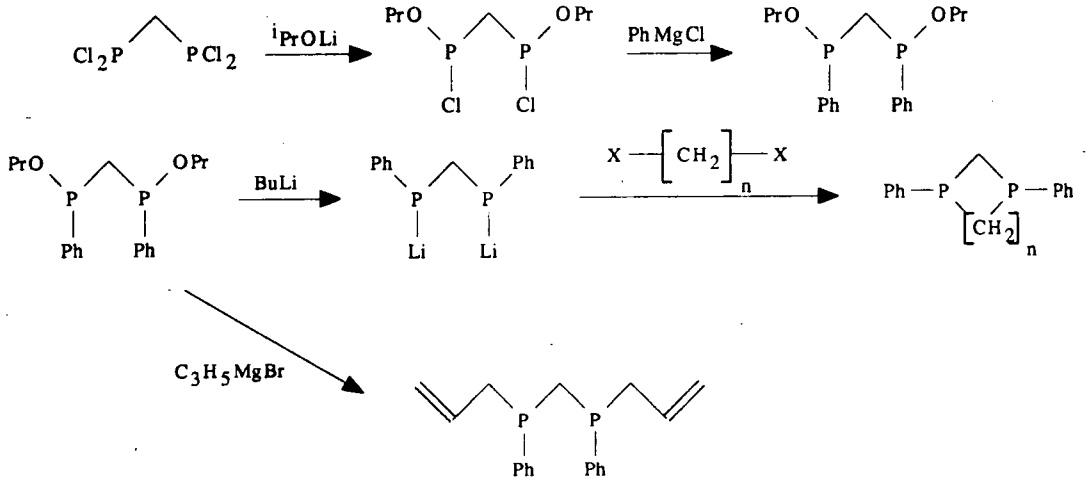
A later synthesis[96] of DMPE also involves the apparent insertion of methylene groups into a diphosphane. Tetramethyldiphosphane is formed by methylating thiophosphoryl chloride. Sulphur is removed from the product with iron. Sodium in ammonia cleaves the resulting diphosphane forming sodium dimethylphosphide, which reacts with 1,2-dichloroethane producing DMPE:



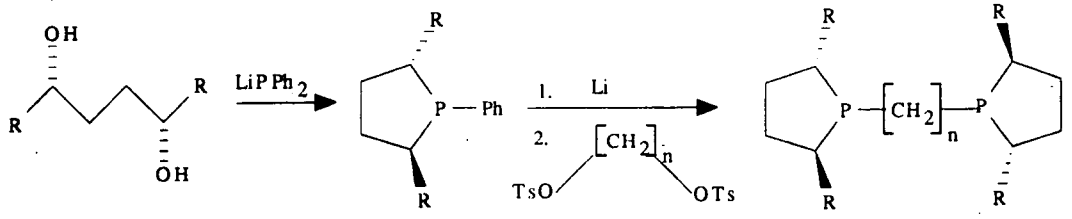
An alternative method[97] of forming the metal phosphide is from phosphine. The literature suggests phosphine is alkylated by methyl iodide; however, the alkylation of sodium phosphide[96] is the more likely reaction:



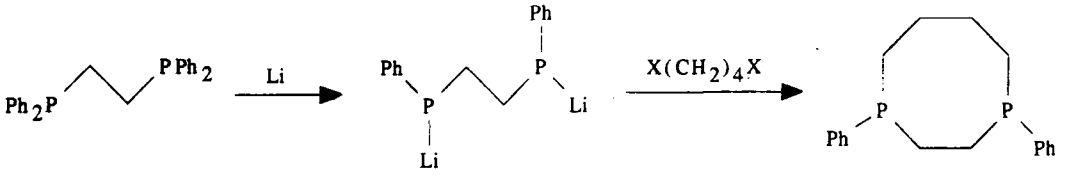
Metal phosphide coupling provides a general method for diphosphine synthesis. The multi-step metallation of phosphorus halides by alkyl or alkoxy lithium reagents[98] provides a synthetic route to chiral methylene diphosphines and diphosphorus heterocycles:



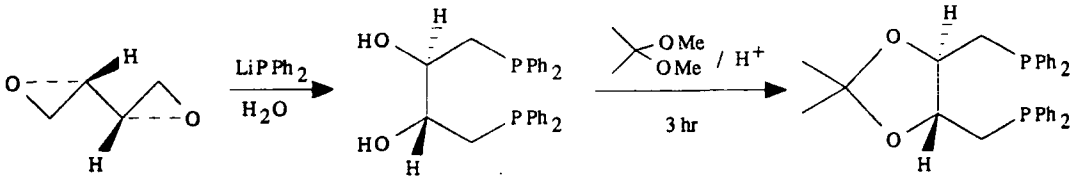
Chiral mono- and bidentate 2,5-disubstituted phospholanes have been prepared[99] by lithium phosphide coupling of alcohols and tosylates:



Other stereochemically pure diphosphorus heterocycles have been prepared by the cleavage of phenyl groups from bis[diphenylphosphino]alkanes with lithium[100,101] (Issleib's Method).



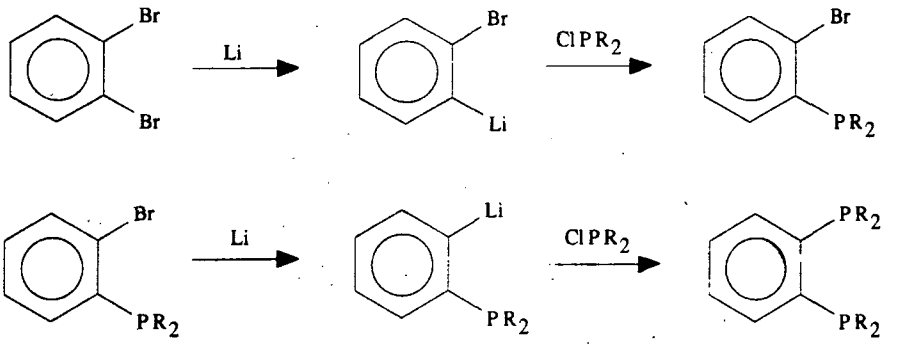
DIOP has recently been prepared[102] from the reaction between (-)-1,2,3,4-diepoxybutane and lithium diphenylphosphide, followed by ketal formation using 2,2-dimethoxypropane:



(-)-DIOP

The relative ease of formation of metal phosphides, especially with lithium, provides a facile synthesis of diphosphines. In theory the versatility of the reaction is limited only by the ease of dihaloalkane synthesis. Metal phosphides, however, are very toxic, air-sensitive materials and must be handled with extreme caution.

The synthesis of bis-1,2-[dialkylphosphino]benzene[103], coupling chlorophosphines with lithiated bromobenzenes, avoids using metal phosphides but is not a generally applicable method. However, this method gave a better yield than the analogous Grignard route.



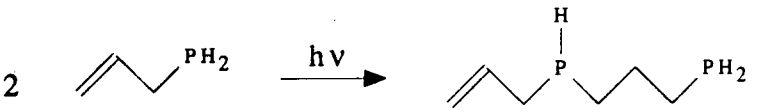
Other aromatic diphosphines have also been prepared[104,105] and their interaction with transition metal complexes investigated. Ring size and

conformation of the bichelate phosphine significantly affects the coordination chemistry of these diphosphines.

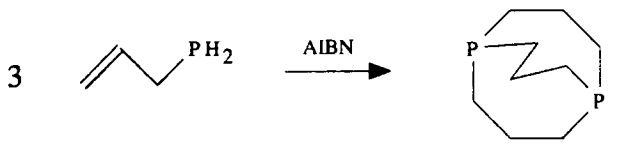
These methods, although producing diphosphines in good yield, involve laborious stages and very toxic reagents and intermediates. Generally the most favoured products have been α,ω-diphosphines, with short (C_2 to C_6) chain lengths.

Vinylphosphine Coupling

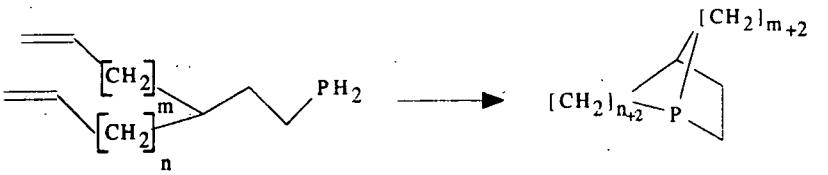
A less hazardous method, developed by Diel and Norman[106], couples vinyl phosphines by photolysis in the gas phase:



By distilling the product from the reaction zone formation of higher oligomers is minimised. However, further reaction is possible if the diphosphine is not removed from the UV source. This reaction readily produces a diphosphine, though for metal chelation a tertiary alkyl diphosphine is generally preferred rather than the parent phosphine. Some chain phosphine polymers are also reported. If AIBN is used as a radical initiator the major product is 1,5-diphosphabicyclo[3.3.3]undecane:



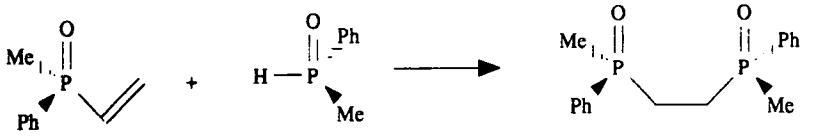
Similar bicyclic phosphines with a single bridgehead phosphorus atom have also been produced[107] from divinyl phosphines:



m = n = 1,2,3

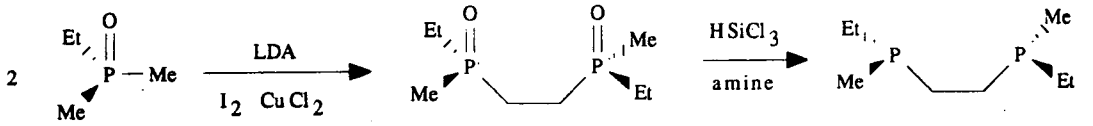
Another synthesis of bridgehead phosphorus compounds involves intramolecular Friedel-Crafts alkylation of 1-benzylphospholane oxides producing 1-phosphabicyclo[3.2.1]octane systems in high yield[108].

Other di- or polyphosphines, usually containing phenyl substituents, can be prepared by the addition of phosphorus-hydrogen bonds across the carbon-carbon double bond of vinyl phosphines in the presence of a base catalyst such as phenyl lithium[95]. The method was developed[109] into a chiral synthesis by coupling non-equivalent phosphine oxides, one possessing a vinyl group:



The diphosphine is readily obtained from the diphosphine dioxide using trichlorosilane and an amine to reduce the phosphorus centre. Optically pure starting materials must be prepared to ensure enantiomerically pure products are obtained. Therefore, although the coupling reaction is straightforward the total synthesis is a lengthy process.

Phosphine oxides may also be oxidatively coupled [71,110] using a copper (II) chloride catalyst. A methyldialkylphosphine oxide is necessary to produce bis[dialkylphosphino]ethanes. Chiral diphosphines may be obtained from chiral starting materials only if they are of high optical purity.



Diphosphine dioxides are easily reduced using trichlorosilane and an amine. The products of both syntheses may contain chiral phosphorus centres, rather than chirality along the backbone or in the substituents. These methods may be used for producing achiral phosphines, but still require very high purity starting materials, which must be synthesised prior to coupling, increasing the complexity of the synthetic route.

Chlorophosphine Synthesis

A convenient method for synthesising dichlorophosphines and bis-[dichlorophosphino]alkanes was patented by the Stauffer company[111,112] and later reported by Leigh[113]. White phosphorus, phosphorus trichloride (or other phosphorus trihalides) and ethene are heated at 260°C under high pressure in an autoclave to produce bis-1,2-[dichlorophosphino]ethane:

$$6\,C_2H_4 + P_4 + 8\,PCl_3 \rightarrow 6\,Cl_2PCH_2CH_2PCl_2$$

The reaction proceeds in good yield (up to 70% conversion from ethene). Other chain alkenes may also be used. However, as the molecular mass of the alkene increases, the yield of diphosphine drops significantly (20% conversion from 1-octene). Terminal alkenes were found to give the best yields: for example[113] 1-butene reacts to form bis-1,2-[dichlorophosphino]butane (40% yield); cis- or trans-2-butene reacts at 200°C to form bis-2,3-[dichlorophosphino]butane (10% yield) and at 260°C producing bis-1,2-[dichlorophosphino]butane (23% yield).

The reaction was developed by M.L.H. Green[114,115] to include the reaction with cyclic alkenes, forming trans,bis-1,2-[dichlorophosphino]cycloalkanes. The enantiomers were resolved using nickel (II) bromide.

An important and useful side product of these reactions is the alkyldichlorophosphine ($RPCl_2$). This is produced in varying amounts, but usually in higher yield than the diphosphine. The other major side-product is a black solid, the mass being reduced by increasing the volume of phosphorus trichloride used. The source of the black polymer material is not discussed, but is believed to result from decomposition of the starting materials.

The method appears to be very general, with several different alkenes reacting under similar conditions. Readily made from commercially available, inexpensive, materials the chlorophosphine products are versatile synthetic intermediates. Chiral phosphines and diphosphines are synthesised from unsymmetric alkenes, which contain a pro-chiral centre. Because only simple, selected alkenes had been used, the range of alkene substrates and diversity of the products was investigated in this work.

An iodine catalyst in a stainless steel autoclave was employed[111] in the reactions claimed in the original patent. A subsequent method[113] using a Hastalloy autoclave and glass liner showed that iron may act as a catalyst although halogens had no apparent affect. The active form of the catalyst may be iron (III) chloride[116]. However iron in any form may be added to the autoclave.

Several possible mechanisms have been postulated for the reaction. Unambiguous determination of the reaction route is complicated by the nature of the reagents and high temperature and pressure conditions. Previous

studies[112,117] have concentrated on the reaction with ethene, and do not explain the formation of alkyldichlorophosphines.

Radical addition of phosphorus trichloride across the carbon-carbon double bond to form a 2-chloroalkyldichlorophosphine may be the first step. This reaction is known to occur under UV conditions[118] but the thermal initiation has not been reported. However 2-chloroethyldichlorophosphine has been observed[112] in small amounts in the reaction product mixture. Further reaction of this phosphine with phosphorus and phosphorus trichloride may result in diphosphine formation. This latter reaction has been reported to proceed between 200 and 300°C[119]. Similarly[120] methyl chloride reacts with red phosphorus at high temperature in the presence of copper powder producing methyldichlorophosphine and dimethylchlorophosphine.

$$6\ C_2H_4 + 6\ PCl_3 \rightarrow 6\ ClCH_2CH_2PCl_2$$
$$6\ ClCH_2CH_2PCl_2 + P_4 + 2\ PCl_3 \rightarrow 6\ Cl_2PCH_2CH_2PCl_2$$

A similar reaction to the first step, involving perfluoroalkenes, has been reported[122]. Dialkylphosphine reacts with trifluoroethene in UV light giving the addition products 1,2,2- and 1,1,2-trifluoroethyldialkylphosphines.

In the presence of aluminium trichloride and phosphorus pentoxide, haloalkanes react with phosphorus (III) halides[121] at elevated temperature and pressure forming alkylphosphinic and phosphonic products of the type $R_nP(O)X_{(3-n)}$.

This reaction scheme contains known chemistry, and the phosphine intermediate has been detected. However formation of the alkyldichlorophosphines is not explained. Hydrogen chloride may be eliminated from the intermediate generating the hydrogen source needed to saturate the alkene. The carbon-chlorine bond must be broken, eliminating the chlorine atom, to produce the observed major products.

A second postulated reaction route involves the reaction of phosphorus and phosphorus trichloride forming diphosphorus tetrachloride (P_2Cl_4). This species has been observed in the reaction products[123]. Subsequent reaction of diphosphorus tetrachloride with ethene may form bis[dichlorophosphino]ethane:

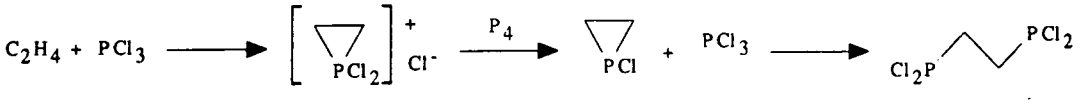
$$8\ PCl_3 + P_4 \rightarrow 6\ P_2Cl_4$$
$$6\ P_2Cl_4 + 6\ C_2H_4 \rightarrow 6\ Cl_2PCH_2CH_2PCl_2$$

Diphosphorus tetrachloride is very unstable, decomposing at room temperature to phosphorus trichloride and a non-volatile solid. It is normally prepared by electric discharge in the vapour above a solution of white phosphorus in phosphorus trichloride[124].

Monophosphines may be produced by the reaction of diphosphorus tetrachloride with excess alkene, in a radical mechanism. The intermediate formed could then react with a hydrogen radical from hydrogen chloride or alkene forming alkyldichlorophosphines. However the expected intermediate radical would be a secondary rather than primary radical. Thus the predicted product would be a 1-alkyldichlorophosphine not the observed 2-alkyldichlorophosphine. Intramolecular hydrogen transfer is unlikely to occur because the less stable intermediate would be generated. If the hydrogen radical adds to the double bond before diphosphorus tetrachloride then the intermediate would be a secondary radical, and the observed and predicted products would be the same. Thermal initiation of hydrogen radical formation would be required for this reaction to occur.

Another postulated reaction pathway involves the free radical addition of phosphorus dichloride moieties to ethene. Phosphorus trichloride is known to undergo homolytic fission in UV[125]. In the presence of cyclohexane cyclohexyldichlorophosphine is formed by radical addition[126], but no diphosphine is detected. Methyldichlorophosphine reacts in UV to generate Me(Cl)P· and chlorine radicals[125]. As in the other theories, formation of 2-alkyldichlorophosphines is not readily explained. A simple free-radical mechanism is therefore unlikely to be operating, although free-radicals are probably the active species.

A polar mechanism has also been suggested, involving a cyclic phosphirane intermediate, although this is thought unlikely to be the reaction route. This type of species has been reported[127] and may account for the observed products. The postulated reaction between phosphorus trichloride and ethene is:



The original patent[111] also reported the synthesis of bis-1,2-[dichlorophosphino]ethane from the diphenyl analogue (DPPE) and phosphorus trichloride at 280°C using an aluminium trichloride catalyst. Ethene was also

reported[117] to react with phosphorus pentasulphide and thiophosphoryl chloride or phosphorus trichloride to produce bis-1,2-[dichlorothiophosphino]ethane $Cl_2P(S)CH_2CH_2P(S)Cl_2$ in good yield. Other alkenes reacted at higher temperature.

1.4. Chlorophosphine Chemistry

1.4.1. Introduction

Alkyldichlorophosphines ($RPCl_2$) are generally known either as dichlorophosphines or as phosphonous dichlorides. Similarly dialkyl-chlorophosphines (R_2PCl) may be referred to as monochlorophosphines or phosphinous chlorides. For consistency the standard 'phosphine' nomenclature is preferred here.

During this project many dichlorophosphines and bis[dichloro-phosphino]alkanes were produced. They are clear viscous liquids and soluble in most organic solvents. Although having high boiling points they possess a characteristic, musty odour. Storage under a dry, inert atmosphere is necessary to prevent aerial hydrolysis and oxidation of phosphorus (III) to the phosphorus (V) oxide. Because of the very reactive nature of the phosphorus-chlorine bond, dichlorophosphines are useful synthetic intermediates and many derivatives can be prepared. These reactions have been documented by Corbridge[92], although only the reactions of relevance to this work will be described.

1.4.2. Metal Mediated Coupling

The most generally used phosphorus ligands are trialkyl- and triarylphosphines. These can be readily synthesised from alkyldichlorophosphines using a metal coupling reaction. Alkali or alkaline earth metals, such as organolithium or Grignard reagents, are preferred:

$$RPCl_2 + 2\ MeMgI \rightarrow RPMe_2 + 2\ MgICl$$
$$RPCl_2 + 2\ PhLi \rightarrow RPPh_2 + 2\ LiCl$$

The reactions, though usually proceeding smoothly at low temperatures in an organic solvent precipitating the metal chloride, are not very selective because every phosphorus-chlorine bond usually reacts with the reagents. However bulky

alkyl groups may reduce the degree of substitution; for example, the reaction of phosphorus trichloride with 2-norbornylmagnesium chloride[128] produces 2-norbornyldichlorophosphine exclusively.

Less reactive organometallic reagents, such as those containing cadmium or mercury, can be used to partially substitute dichlorophosphines with alkyl groups. Thus two different alkyl substituents can be coupled to an alkyldichlorophosphine. Using this method a phosphine containing phosphorus chirality can be produced:

$$RPCl_2 + MeHgI \rightarrow RPMeCl + HgICl$$
$$RPMeCl + EtHgI \rightarrow RPMeEt + HgICl$$

Usually simple metal alkyl or aryl metal compounds are used. However a chiral centre can be introduced into the phosphine using chiral reagents, such as l-menthylmagnesium chloride[129,130].

Most alkali and alkaline earth organometallic reagents will react with phosphorus-chlorine bonds; for example, stannylphosphines[131] can be prepared from sodium triphenyltin and a chlorophosphine:

$$NaSnPh_3 + Ph_2PCl \rightarrow Ph_3Sn\text{-}PPh_2 + NaCl$$

However, only a low yield of dialkyl- or diaryl[triphenylstannyl]phosphine can be isolated due to a competing reaction producing hexaphenylditin:

$$NaSnPh_3 + Ph_2PCl \rightarrow Ph_3Sn\text{-}Cl + NaPPh_2$$
$$NaSnPh_3 + Ph_3Sn\text{-}Cl \rightarrow Ph_3Sn\text{-}SnPh_3$$

If lithium replaces sodium reagents[132] the dimerisation reaction is suppressed, although the products can still only be isolated in low yield.

1.4.3. Reaction with Active Hydrogens

Protic hydrogen compounds, such as alcohols (and water), thiols and amines, readily react with alkyldichlorophosphines and dialkylchlorophosphines forming phosphites, thiophosphines or aminophosphines. Unless a base is present, the reaction is accompanied by oxidation of phosphorus (III) by hydrogen chloride.

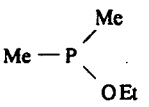
$$R_2PCl + R'OH \rightarrow R_2P(O)OR'$$
$$RPCl_2 + 2\ R'OH \rightarrow RPH(O)OR'$$

Tertiary nitrogen bases, such as pyridine or triethylamine, are generally used to neutralise and remove hydrogen chloride as the ammonium salt, to prevent phosphine oxidation:

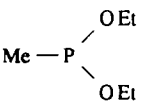
$$R_2PCl + R'OH + Et_3N \rightarrow R_2POR' + Et_3NHCl$$
$$RPCl_2 + 2\ R'OH + Et_3N \rightarrow RP(OR')_2 + 2\ Et_3NHCl$$

Note on Nomenclature

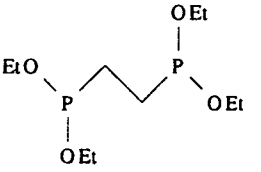
These monophosphine derivatives may be named either as alkyl phosphites or phosphonites[133]. For consistency, in this work the 'phosphite' terminology will be used. Diphosphines will be named systematically, from the dichlorophosphine starting material.



Dimethyl ethylphosphite

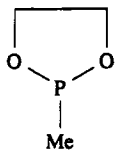


Methyl diethylphosphite

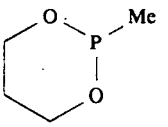


Bis-1,2-[diethoxyphosphino]ethane

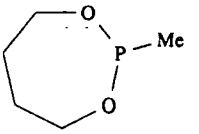
The reaction of diols with dichlorophosphines and bis[dichlorophosphino]alkanes may form cyclic and bridged alkyl phosphites. Dutasta[134-7] named these phosphite rings as:



methyl-2-dioxa-1,3-2-phospholane

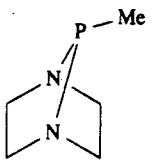


methyl-2-dioxa-1,3-2-phosphorinane

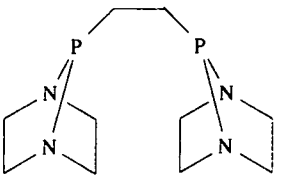


methyl-2-dioxa-1,3-2-phosphepane

Other protic hydrogen compounds of elements from group V or VI react analogously to alcohols. For example dichlorophosphines react with primary and secondary amines forming a phosphorus-nitrogen bond. With piperazine bicyclic compounds may be synthesised from dichlorophosphines:

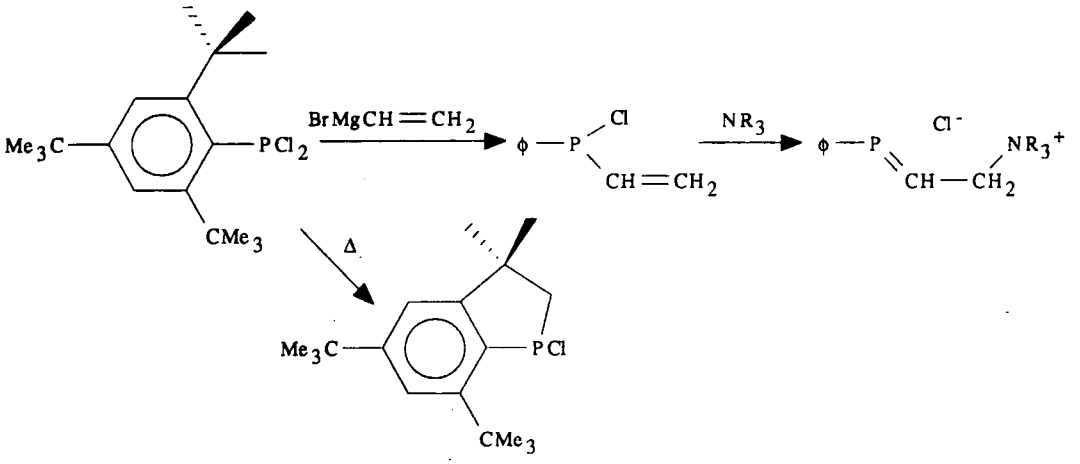


7-methyl-7-phospha-
1,4-diazanorbornane

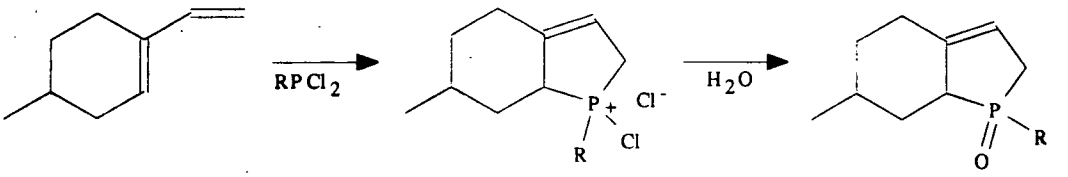


bis-1,2-[7-phospha-1,4-
diazanorbornyl]ethane

Many reactions of alkyldichlorophosphines and dialkylchlorophosphines with organic reagents are known. For example, 2,4,6-(tri-t-butylphenyl)dichlorophosphine reacts with Grignard reagents and nucleophilic amines[138] forming phosphaalkenes. The same chlorophosphine undergoes thermolysis in refluxing toluene[139] producing 2,3-dihydro-1H-phosphindole derivatives:



Stereoselective cycloaddition[140] of methyldichlorophosphine to 4-alkyl-1-vinylcyclohexene in refluxing hexane produces a phosphonium salt. Hydrolysis of this adduct forms a phosphine oxide:



Corbridge[92] provides a useful review of general chlorophosphine chemistry, summarised below:

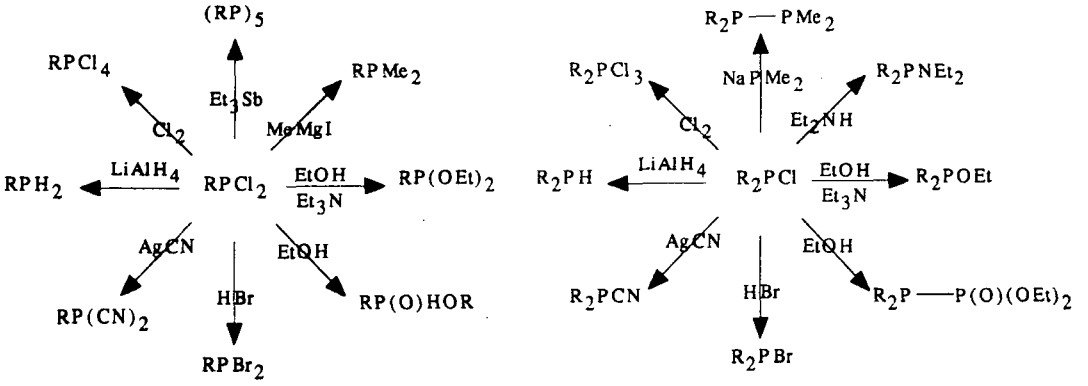
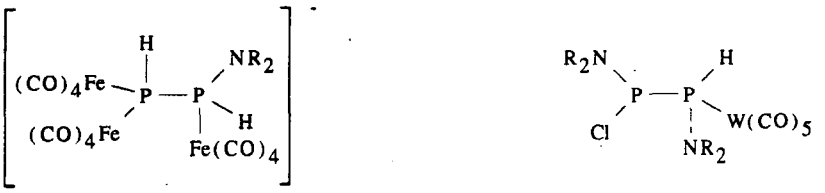


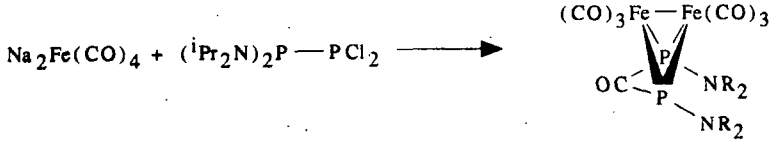
Figure 1.5: The Reactions of Chlorophosphines (from reference 92)

1.4.4. Reaction with Metal Complexes

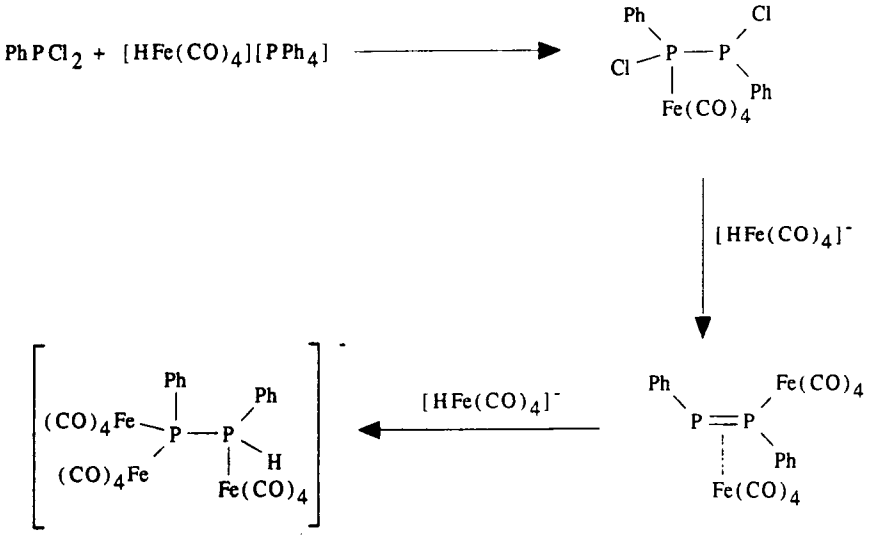
Recently some novel dihalophosphine reactions have been reported[141-4]. The 1,1-dichlorodiphosphine $(^iPr_2N)_2P\text{-}PCl_2$ reacts with anionic hydrido tetracarbonyliron(0) and hydrido pentacarbonyltungsten(0) to form unusual metal complexes[144]:



Using the same chlorophosphine, phosphorus bridging carbonyl derivatives of disodium iron tetracarbonyl have been synthesised[145]. Various complexes containing the cleaved diphosphine have also been detected, for example:

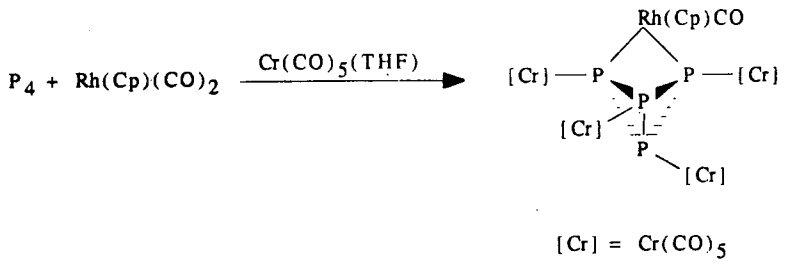


Similarly hydrido tetracarbonyliron(0) anions reacted with chlorophosphines forming some non-classical complexes:



Different alkyldichlorophosphines react forming slightly different products, the steric size of the dichlorophosphine substituent being an important factor in determining the nature of the product.

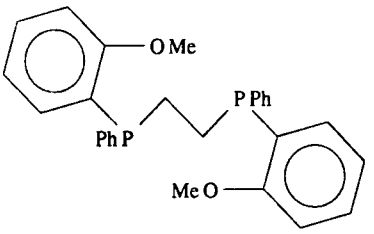
In an interesting aside, rhodium complexes[146] may cap a white phosphorus tetrahedron in the presence of chromium carbonyls, inserting into a phosphorus-phosphorus bond.



1.5. Phosphine Structures

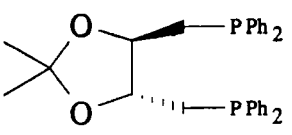
A diverse range of chiral phosphines and diphosphines are known, some common ones are shown below:

DPPE[93]



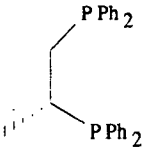
S,S-DiPAMP[71]

(phosphorus chirality)

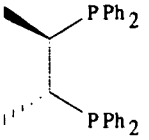


(R,R)-DIOP[68]

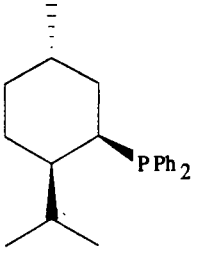
(backbone chirality)



R-(+)-PROPHOS[147]

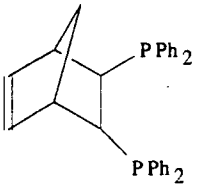


(R,R)-(+)-CHIRAPHOS[148]

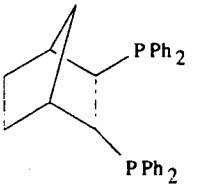


NMDPP

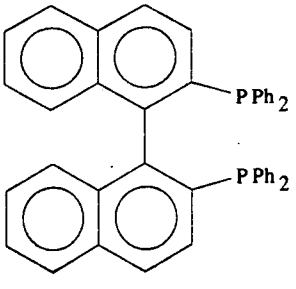
(substituent chirality)



(R,R)-(-)-NORPHOS[149-51]

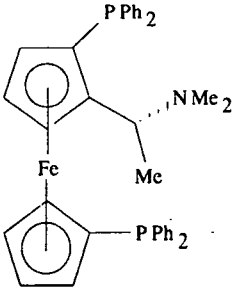


(R,R)-(-)-RENORPHOS[149-51]



(S)-(-)-BINAP[70]

(axial chirality)



(S,R)-BPPFA[75-7]

(planar chirality)

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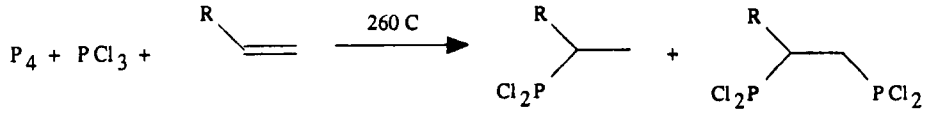
CHAPTER 2:

THE HIGH TEMPERATURE AND PRESSURE SYNTHESIS OF DICHLOROPHOSPHINES FROM MONO-ALKENES

2.1. Introduction

Alkyldichlorophosphines and bis-1,2-[dichlorophosphino]alkanes were synthesised following the method of Uhing and Toy[1,2] and Green[3]. White phosphorus, phosphorus trichloride and a mono-alkene were heated in an autoclave at 260°C for 40 hours. The products were isolated as colourless liquids by distillation under reduced pressure.



Alkenes used as substrates can be categorised as chain alkenes *eg.* ethene, perhaloethenes, 1-butene, trans-2-butene and 1-hexene; or cyclic alkenes *eg.* cyclopentene, cyclohexene and 2-norbornene. Control experiments, in the absence of alkene or phosphorus, were also performed.

NMR, mass spectroscopy and elemental analysis were used to characterise the products. ^{31}P NMR identified the substitution pattern around the phosphorus atom[4,5], while the alkyl substituent structure was examined by ^{13}C NMR. The magnitude of the ^{31}P-^{13}C coupling constant helped in determining the position of the carbon atoms relative to phosphorus, the NMR data often being sufficiently detailed to assign the structure of the phosphine. Very little additional structural information could be determined from the fragmentation pattern in the mass spectrum. However the mass of the parent ion was used as a proof in confirming the nature of the phosphine produced.

2.2. Experimental

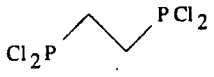
2.2.1. Synthesis of Bis-1,2-[dichlorophosphino]ethane [5]

A dry stainless steel autoclave fitted with a 600 atm pressure gauge and a 270 atm stainless steel bursting disk was flushed with nitrogen. The autoclave was charged with freshly distilled, degassed phosphorus trichloride (180 ml, 2.06 mol) and dry white phosphorus (16g, 0.13 mol). After being sealed using a freshly annealed copper gasket the autoclave was evacuated, closed and connected to a high pressure gas line. The line was flushed with nitrogen (2 x 50 atm) and ethene (2 x 30 atm) before the autoclave was opened and charged with ethene (60 atm). An essential operation during this process was gently shaking the autoclave to dissolve the gas in the phosphorus trichloride. A diagram of the

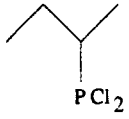
autoclave is shown in Figure 2.1. After being closed the autoclave was heated in a rocking furnace at 260°C for 40 hours. During this time the pressure increased to a maximum of 180 atm. However at an internal temperature of 240°C the pressure began to fall gradually to 50 atm as ethene was consumed by the reaction. When, after 40 hours, the pressure had fallen to 20 atm the reaction was considered to be complete.

The autoclave was cooled to ambient temperature and any excess pressure vented. Immediately the liquid contents of the autoclave were poured into a 500 ml round bottom flask against a slow counter-current of nitrogen. All the black residue was washed with dry, degassed diethyl ether (3 x 50 ml) and these washings combined with the supernatant liquid. Under reduced pressure the volatile components were removed at ambient temperature to give a dark brown/black viscous liquid. This was distilled under reduced pressure to isolate a colourless fraction at 61±1°C (0.1 mmHg). A yield of 40g (25% from phosphorus) of bis-1,2-[dichlorophosphino]ethane was obtained.

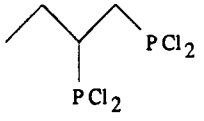
A similar method was used to synthesise 2-butyldichlorophosphine [6] and bis-1,2-[dichlorophosphino]butane [7] from 1-butene and trans-2-butene (70g, 1.25 mol). The gas was vacuum transferred to the autoclave, so an accurate mass of the alkene was known.



[5]



[6]



[7]

Data

i. Bis-1,2-[dichlorophosphino]ethane [5]

distillation temperature: 61±1°C (0.1 mmHg).

yield: 40g (25% from phosphorus).

NMR (neat); ^{31}P (ppm): 190.4 singlet

^{13}C (ppm): 38.74 dd ^{1}J [^{31}P-^{13}C] = 50.1 Hz

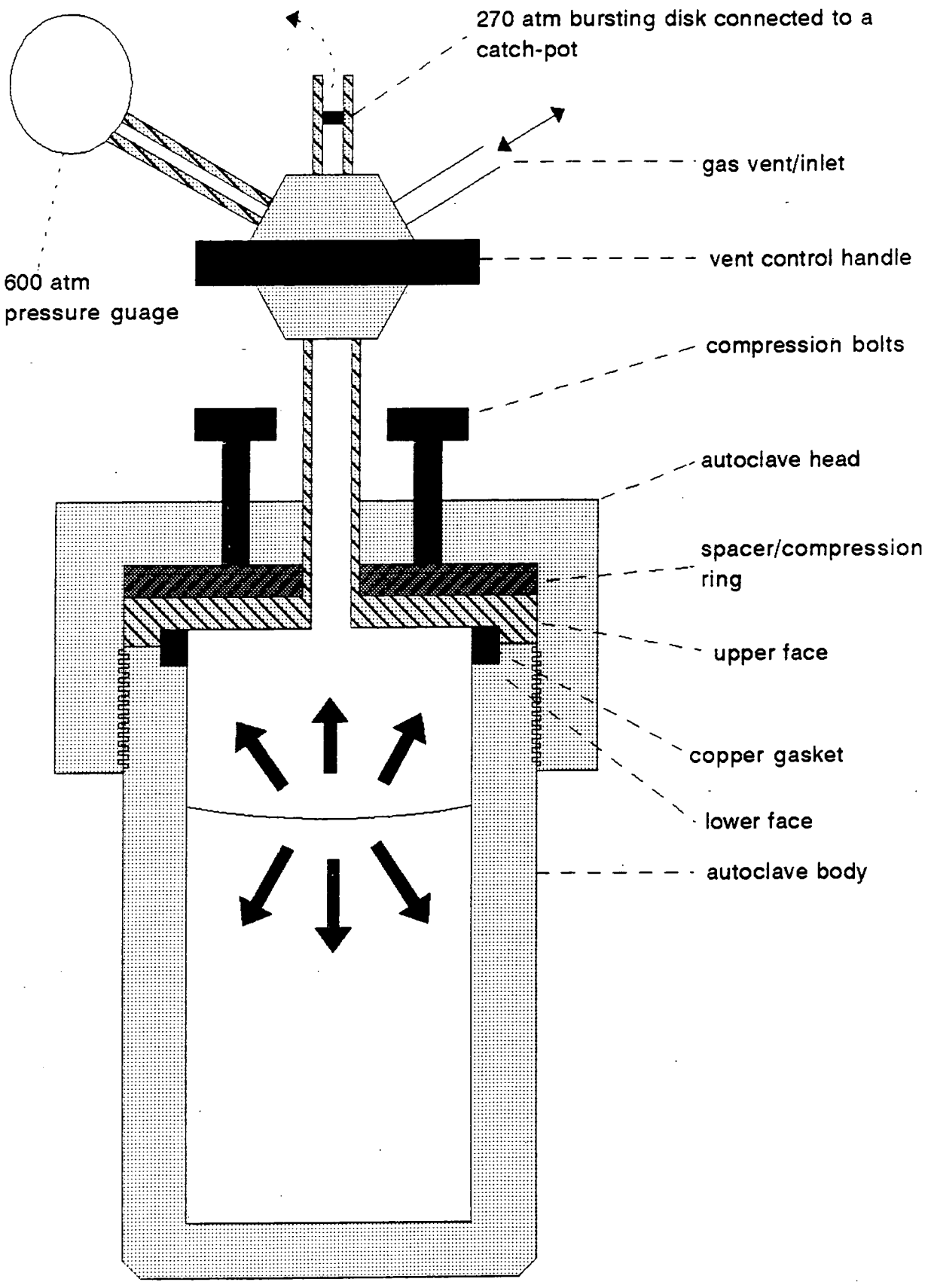
^{2}J [^{31}P-^{13}C] = 8.7 Hz

EA: found (required)

%C 12.7 (10.8); %H 2.0 (1.7); %P ♦; %Cl 55.6 (61.2).

MS; EI: 230 $[M]^+$; 202 $[P_2Cl_4]^+$; 129 $[M\text{-}PCl_2]^+$; 101 $[PCl_2]^+$.

Figure 2.1: Diagram of a High Pressure Autoclave



ii. 2-Butyldichlorophosphine [6]

distillation temperature: 33±1°C (0.9 mmHg).

yield: 57g (24% from 1-butene).

26g (11% from trans-2-butene)

NMR (neat); ^{31}P (ppm): 200.5 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	12.29	d	^2J = 19.1
C_2	45.31	d	^1J = 45.4
C_3	23.58	d	^2J = 19.2
C_4	12.25	d	^3J = unres.

EA: found (required)

%C 38.3 (30.2); %H 7.2 (5.7); %P 19.3 (19.5); %Cl ♦.

MS; EI: 158 $[M]^+$; 123 $[M\text{-}Cl]^+$; 57 $[M\text{-}PCl_2]^+$.

iii. Bis-1,2-[dichlorophosphino]butane [7]

distillation temperature: 85±1°C (0.1 mmHg);

yield: 39g (12% from 1-butene).

13g (4% from trans-2-butene)

NMR (neat); ^{31}P (ppm): 196.9 singlet,

192.2 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	39.83	dd	^1J = 46.6
			^2J = 9.5
C_2	43.08	dd	^1J = 46.6
			^2J = 6.9
C_3	23.54	d	^2J = 13.2
C_4	12.94	d	^3J = 14.0

EA: found (required)

%C 28.2 (18.6); %H 4.8 (3.1); %P ♦; %Cl 40.8 (54.6).

Figure 2.2: NMR Spectra of 2-Butyldichlorophosphine

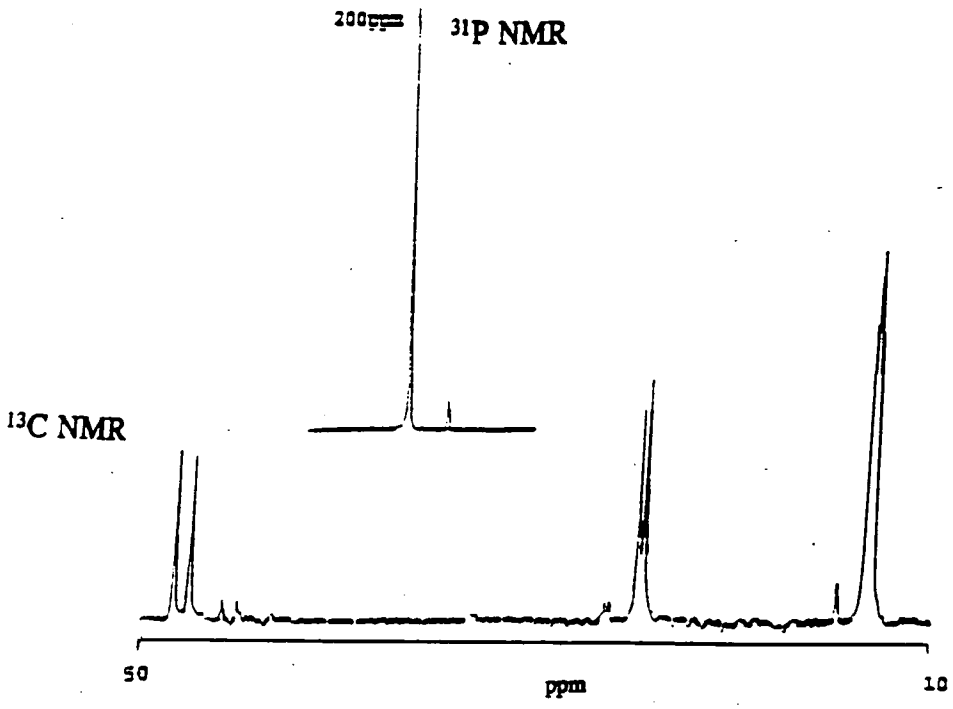
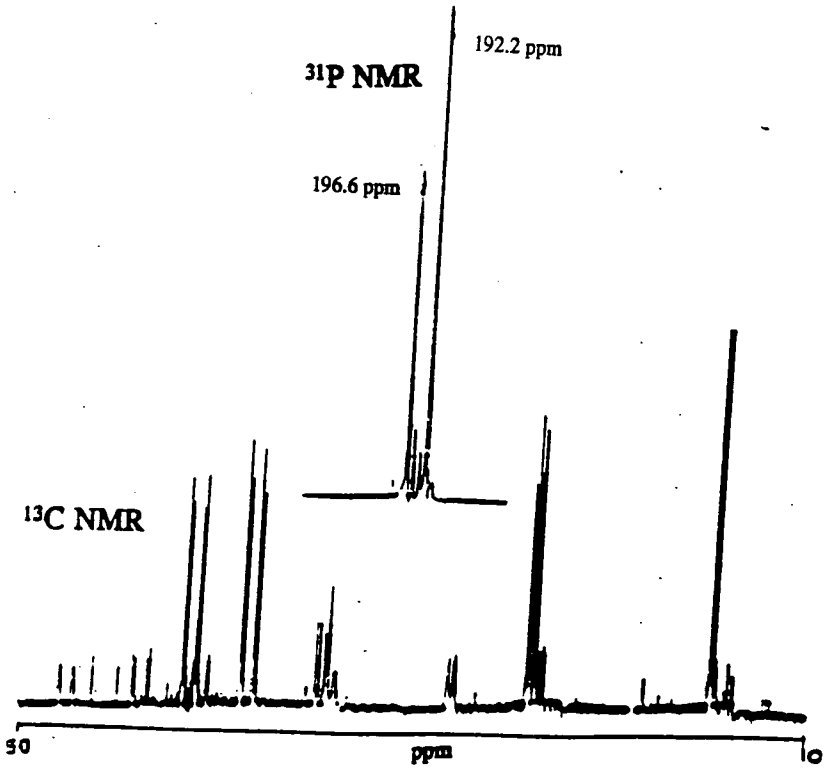


Figure 2.3: NMR Spectra of Bis-1,2-[dichlorophosphino]butane

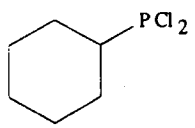


2.2.2. Synthesis of Trans,bis-1,2-[dichlorophosphino]cyclohexane [9]

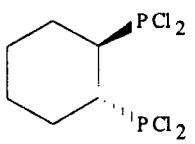
A dry stainless steel autoclave fitted with a 600 atm pressure gauge and a 270 atm stainless steel bursting disk was flushed with nitrogen. The autoclave was charged with freshly distilled, degassed phosphorus trichloride (180 ml, 2.06 mol), freshly distilled, degassed cyclohexene (85 ml, 1.25 mol) and dry white phosphorus (16g, 0.13 mol). After being sealed using a freshly annealed copper gasket the autoclave was evacuated, closed and heated in a rocking furnace at 260 °C for 40 hours. During this time the pressure increased to a maximum of 100 atm. When, after 40 hours, the pressure had fallen to 20 atm the reaction was considered to be complete.

The autoclave was cooled to ambient temperature and any excess pressure vented. Immediately the liquid contents of the autoclave were poured into a 500 ml round bottom flask against a slow counter-current of nitrogen. All the black residue was washed with dry, degassed diethyl ether (3 x 50 ml) and these washings combined with the supernatant liquid. Under reduced pressure the volatile components were removed at ambient temperature to give a dark brown/black viscous liquid. This was distilled under reduced pressure to give cyclohexyldichlorophosphine [8] as the major fraction at 66±1°C (0.1 mmHg) and a second fraction at 109±4°C (0.9 mmHg). This higher boiling fraction was redistilled to give trans,bis-1,2-[dichlorophosphino]cyclohexane [9] as a colourless liquid at 107±2°C (0.1 mmHg); yield of 30g (9% from cyclohexene).

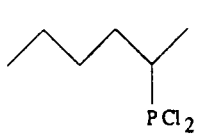
Using the same method 2-hexyldichlorophosphine [10] and bis-1,2-[dichlorophosphino]hexane [11] from 1-hexene (156 ml, 1.25 mol); cyclopentyl-dichlorophosphine [12] and trans,bis-1,2-[dichlorophosphino]cyclopentane [13] from cyclopentene (99.5 ml, 1.25 mol); exo- and endo-2-norbornyldichloro-phosphine [14a/b] (exo:endo, 3:1) and trans,bis-2,3-[dichlorophosphino]-norbornane [15] from 2-norbornene (norbornylene, bicyclo[2.2.1]hept-2-ene; 100g, 1.25 mol) were prepared.



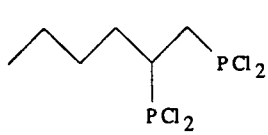
[8]



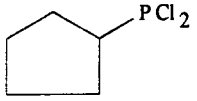
[9]



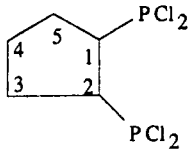
[10]



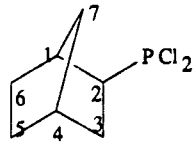
[11]



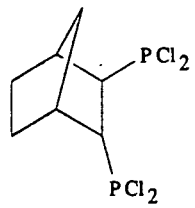
[12]



[13]



[14]



[15]

Data

i. Cyclohexyldichlorophosphine [8]

distillation temperature: 66±1°C (0.1 mmHg).

yield: 58g (32% from cyclohexene).

NMR (neat); ^{31}P (ppm): 193.8 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	47.67	d	$^1J = 45.6$
$C_{2/6}$	34.02	d	$^2J = 9.0$
$C_{3/5}$	26.77	s	---
C_4	18.05	s	---

MS; EI: 83 $[M\text{-}PCl_2]^+$; CI: 150 $[MH\text{-}Cl]^+$.

ii. Trans,bis-1,2-[dichlorophosphino]cyclohexane [9]

distillation temperature: 107±2°C (0.1 mmHg).

yield: 30g (9% from cyclohexene).

NMR (neat); ^{31}P (ppm): 195.7 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/2}$	51.22	dd	$^1J = 47.4$ $^2J = 8.6$
$C_{3/6}$	29.18	d	$^2J = 15.3$
$C_{4/5}$	29.82	d	^3J = unres.

MS; CI: 215 $[MH\text{-}Cl_2]^+$; 114 $[MH\text{-}Cl_4P]^+$.

iii. 2-Hexyldichlorophosphine [10]

distillation temperature: 46±1°C (0.03 mmHg).

yield: 76g (35% from 1-hexene).

NMR (neat); ^{31}P (ppm): 200.4 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	12.71	d	^2J = 12.2
C_2	43.49	d	^1J = 45.6
C_3	29.84	d	^2J = 8.9
C_4	29.89	d	^3J = 3.9
C_5	22.59	s	---
C_6	13.87	s	---

EA: found (required)
%C ♦; %H 5.7 (7.0); %P 17.3 (16.6); %Cl 33.6 (37.9).

MS; EI: 186 $[M]^+$; 151 $[M\text{-}Cl]^+$; 85 $[M\text{-}PCl_2]^+$.
CI: 152 $[MH\text{-}Cl]^+$.

iv. Bis-1,2-[dichlorophosphino]hexane [11]

distillation temperature: 115±1°C (1.5 mmHg).
yield: 6g (2% from 1-hexene).
NMR (neat); ^{31}P (ppm): 194.8 singlet
191.3 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	38.12	dd	^1J = 39.5 ^2J = 9.3
C_2	49.76	dd	^1J = 39.1 ^2J = 8.6
C_3	32.64	d	^2J = 12.1
C_4	31.31	s	---
C_5	22.21	s	---
C_6	13.79	s	---

v. Cyclopentyldichlorophosphine [12]

distillation temperature: 52±1°C (1.0 mmHg);
yield: 37g (15% from cyclopentane).
NMR (neat); ^{31}P (ppm): 193.1 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	53.44	d	^1J = 44.2
$C_{2/5}$	31.95	d	^2J = 18.6
$C_{3/4}$	30.96	d	^3J = 5.5

vi. Bis-1,2-[dichlorophosphino]cyclopentane [13]

distillation temperature: 107±2°C (0.9 mmHg);

yield: 30g (9% from cyclopentene).

NMR (neat); ^{31}P (ppm): 191.4 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/2}$	51.22	dd	$^{1}J = 47.4$
			$^{2}J = 8.5$
$C_{3/5}$	29.18	d	$^{2}J = 15.2$
C_4	29.91	d	^{3}J = unres.

vii. 2-Norbornyldichlorophosphine [14]

distillation temperature: 81±1°C (0.5 mmHg).

yield: 20g (27% from 2-norbornene).

MS; EI: 95 $[M\text{-}PCl_2]^+$.

CI: 162 $[MH\text{-}Cl]^+$; 127 $[MH\text{-}Cl_2]^+$; 96 $[M\text{-}PCl_2]^+$.

NMR (neat);

Exo-Phosphorus [14a]

^{31}P (ppm): 185.7 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	38.09	d	$^{2}J = 18.0$
C_2	53.99	d	$^{1}J = 46.0$
C_3	32.74	d	$^{2}J = 14.4$
C_4	36.50	s	---
C_5	28.19	s	---
C_6	30.99	d	$^{3}J = 7.3$
C_7	36.68	d	$^{3}J = 3.4$

Endo-Phosphorus [14b]

^{31}P (ppm): 194.5 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	38.92	d	$^2J = 11.5$
C_2	52.89	d	$^1J = 43.8$
C_3	34.64	d	$^2J = 8.8$
C_4	33.23	s	---
C_5	29.24	s	---
C_6	24.50	d	$^2J = 27.3$
C_7	40.13	d	$^3J = 3$

viii. Trans,bis-2,3-[dichlorophosphino]norbornane [15]

distillation temperature: 110±1°C (0.59 mmHg).

yield: 6g (2% from 2-norbornene).

NMR (neat); ^{31}P (ppm): 193.5 singlet

192.9 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	38.67	d	$^2J = 18.6$
$C_{2/3}$	55.17	dd	$^1J = 48.3$
			$^2J = 6.9$
C_5	28.53	d	$^3J = 17.3$
C_6	27.32	d	$^3J = 6.1$
C_7	33.89	d	$^3J = 6.2$

♦ = Elemental analysis was performed, however the percentages obtained for these components differed by more than 5% from the theoretical values, and were too inaccurate for use in characterisation.

2.3. Discussion

2.3.1. Experimental

Optimum yields of dichlorophosphines required pure, dry starting materials. Phosphorus trichloride was distilled under nitrogen to remove decomposition and hydrolysis products such as hydrogen chloride, phosphorus oxychloride, phosphoric acid and other phosphorus (V) compounds. Surface water was removed from white phosphorus with acetone in a schlenk tube under reduced pressure at ambient temperature. This dry white phosphorus was immediately immersed under dry, degassed phosphorus trichloride and poured into the reaction autoclave. Liquid alkenes were dried over molecular sieve and distilled to remove any impurities or stabilisers. An approximate molar ratio of alkene to phosphorus trichloride of 1.25:1.8 maximised dichlorophosphine yield. Phosphorus trichloride also acts as a solvent in the reaction.

The external temperature of the autoclave was slowly raised to 260°C over 2 hours, and maintained at this temperature using feedback control through two independent thermocouples. A temperature gradient existed across the autoclave walls since the reactant temperature was measured as 237°C through a thermocouple-well in a similar, smaller autoclave. It was vital to agitate the reaction vessel during heating, otherwise very low yields of dichlorophosphines were obtained. No products were obtained from gaseous alkenes without thoroughly mixing the reactants during heating. After the autoclave had cooled to ambient temperature only a very low pressure (<10 atm) remained. Although not analysed, any vented gas contained significant amounts of hydrogen chloride. Characterisation of the products was achieved using ^{31}P, ^{13}C NMR, MS and elemental analysis, the instrumental parameters for each technique are shown in appendix 1.

The crude reaction products were screened using ^{31}P NMR, using 1% H_3PO_4 as an external reference, showing many dichlorophosphines were present with up to ten peaks being observed. However, invariably, there were only one or two major products, which were isolated by fractional distillation. The ^{31}P chemical shift of alkyldichlorophosphines ($RPCl_2$) is normally between 185-210 ppm, the chemical shift of dialkylchlorophosphines (R_2PCl) normally lies in the range 110-135 ppm and phosphine oxides (hydrolysis and oxidation products) are detected between 35-60 ppm[4,5]. A reduction in spectral resolution, due to peak broadening, was sometimes observed, caused by the nature of the products.

Chemical shifts of chlorophosphines observed in the ^{13}C NMR spectra only differed slightly from those of the parent alkane, except for the α-carbon, these similarities being attributable to the similar electronegativities of phosphorus and hydrogen[6]. Inductive rather than steric effects normally dictate the observed chemical shift; the latter effects can be determined from the magnitude of the ^{31}P-^{13}C coupling constant. Thus the chemical shift of the α-carbon is deshielded by the dichlorophosphine unit and is detected at a much lower field than in its parent alkane. Other changes in the chemical shift are mainly due to the C-C-H and C-C-P bond angle differences and the related steric factors. Spectra were normally recorded in the proton decoupled mode, but the ^{31}P-^{13}C coupling constants provided detailed structural information. The coupling constant magnitude helped in determining the position of the carbon atom relative to, and its interaction with, phosphorus and hence its position in the alkyl group. The instrument was sufficiently accurate to quote the ^{13}C chemical shift to 2 decimal places, and the coupling constant to ±0.3 Hz. Overlap of multiplets occasionally complicated spectral interpretation. For example, in Figure 2.2 both methyl groups resonate at 12.2 ppm. Therefore identification of each doublet is difficult. High resolution instruments would separate the multiplets and permit accurate calculation of the coupling constants, proving the assignment. However these experiments were only performed when absolutely necessary.

One-bond ^{31}P-^{13}C coupling constants (^{1}J) were found between 40-50 Hz. This is a large value for trivalent phosphorus and has been related to the significant s content in the phosphorus hybridised orbitals[7]. Normally the chemical shift of this α-carbon is between 40-50 ppm. Values of the ^{2}J coupling constant are normally 10-20 Hz and the ^{3}J coupling constant is normally in the range between 5-15 Hz. Occasionally the ^{3}J coupling constant is greater than the ^{2}J coupling constant because both values are not only determined by the proximity of the carbon atom to phosphorus through the alkyl chain but also by the carbon-phosphorus dihedral angle (ϕ)[8,9]. Since this angle is under strong steric control, a wide range of values occur.

All NMR spectra were recorded as neat liquid samples to maximise the signal-to-noise ratio, although decreasing the resolution. Therefore the ^{13}C NMR spectra were sufficiently resolved and intense to allow accurate calculation of the coupling constants. Differences of up to 1 ppm from previously reported data were sometimes observed in ^{31}P NMR spectra. These could arise from the use of an external reference in this work, shown in appendix 1, because the magnetic susceptibility of phosphoric acid is solvent dependent. The NMR magnet employed may also lead to small differences in the observed spectra,

superconducting magnets polarise the sample along the axis of the NMR tube whereas an electromagnetic field is applied across the NMR tube. However, the wide sweep width employed experimentally sigificantly reduces the resolution of the spectra and will have the greatest effect on the observed chemical shift, compared with previously reported data. An internal standard and deuterium solvent, to provide a secondary reference, would reduce these systematic instrumental errors.

The phosphine products were isolated by fractional distillation, giving a sample sufficiently pure for NMR and MS analysis. However small amounts of other dichlorophosphines and decomposition products were detected by ^{31}P NMR. Although not significantly interfering with NMR and MS, these impurities prevented accurate and precise elemental analysis. Typically, a large discrepancy between the theoretical and experimentally determined percentages was observed, sometimes in excess of 5% (marked ♦). The experimental values for %C and %H were generally more accurate than the %P and %Cl analyses. Analytically pure samples could be obtained by several redistillations of the phosphine, with the associated loss of product. Elemental analysis of these purified samples was more accurate, but still subject to significant error. Each analysis was usually only performed once so the precision of the result is unknown.

Alkyldichlorophosphine yields were much higher than those of bis-1,2-[dichlorophosphino]alkanes in every high pressure reaction. As the molecular mass and steric hindrance of the alkene increased the overall yields decreased. Chiral phosphines and diphosphines were readily produced from unsymmetric alkenes. A pro-chiral carbon atom in the alkene was converted into a chiral centre (at the α-carbon) by the addition of the phosphorus group.

In addition to the phosphine products, a polymeric side-product was also formed in every high pressure reaction. This polymer varied from a very viscous dark brown liquid to a black solid. The mass of polymer produced also varied, more being made in the reaction with ethene. Analysis showed the material contained Fe, P, C and H in varying ratios. Typical values were: %Fe 3-6; %P 9-14; %Cl 12-22; %C 39-41; %H 2-6. No information was obtained from MS. Mechanistic implications arising from the formation and nature of this product are discussed in the next chapter.

A control experiment was performed to determine the reaction between white phosphorus and phosphorus trichloride under high temperature and pressure conditions. After 40 hours at 260°C the autoclave contained red

phosphorus and phosphorus trichloride. No polymeric material was observed, and no phosphorus products, such as diphosphorus tetrachloride (P_2Cl_4) were detected by ^{31}P NMR. A second blank experiment, the reaction of phosphorus trichloride and 1,5-cyclooctadiene, was studied under high temperature and pressure conditions. Black polymer material was isolated from the autoclave at the end of the reaction. ^{31}P NMR of the liquid product mixture showed alkyldichlorophosphines were present, suggesting phosphorus trichloride adds across the carbon-carbon double bond. Mechanistic implications of these experiments are discussed in the next chapter.

2.3.2. Reaction with Chain Alkenes

No monophosphine product was isolated from the reaction with ethene, although the crude products were not screened by ^{31}P NMR before distillation. Ethyldichlorophosphine probably formed but was vented or removed under reduced pressure at ambient temperature with the other volatile components, such as phosphorus trichloride. The triple point of ethene is 9.9°C and 50.5 atm, therefore above 10°C ethene is a gas. The maximum cylinder and autoclave pressure was approximately 40 atm at ambient temperature. Thus if the autoclave was not gently agitated during charging very little ethene dissolved in the phosphorus trichloride so the ethene concentration was low. Therefore only a low yield of dichlorophosphines was obtained. Too much agitation saturated the phosphorus trichloride with ethene and on heating, pressures in excess of 350 atm were reached at 240°C, exceeding by at least 150 atm the safe working limit of the autoclave! A better yield was sometimes obtained by cooling the autoclave after a 24 hour reaction period, recharging with ethene then heating for another 24 hours. However this procedure resulted in a significant increase in the amount of polymer formed, which complicated distillation of the products.

Perhaloalkenes such as 1,1,2-trichloroethene and 1,1-difluoroethene reacted very vigorously in the autoclave, generating pressures in excess of 600 atm before escaping from the autoclave around the copper gasket. This suggests that at least 3.5 mols of volatile materials were present. No products, other than a polymer material, were obtained. The very high pressures generated suggest competing reactions were occurring to those of the intended reaction, generating gas. It is possible either halogen, hydrogen halide or hydrogen gases were displaced or eliminated from the alkene under these reaction conditions, accounting for the high pressures observed. Other possible competing reactions may involve abstraction of halogen from the alkene by phosphorus or phosphorus trichloride. Phosphorus is known to react with haloalkanes[10] giving

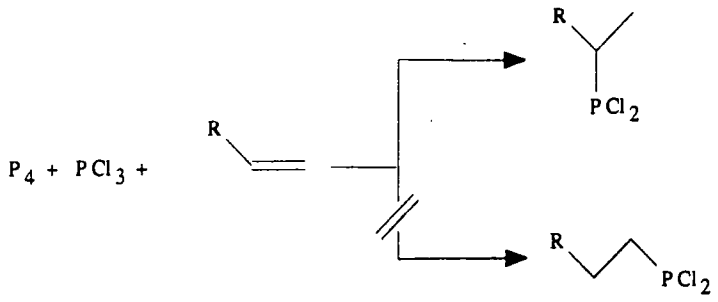
alkyldichlorophosphines and dialkylchlorophosphines. Of relevance here, trichloromethyldichlorophosphine and a red phosphorus polymer are obtained[10] at 160°C from carbon tetrachloride and phosphorus. However such phosphorus halide products are unlikely to result in such a high pressure being generated. Surprisingly, some workers[1,2] claim inert halogen solvents such as carbon tetrachloride can be used as a solvent in the high temperature and pressure reaction.

Slight corrosion of the copper gasket was usual during all the high pressure reactions, however the gasket was severely damaged after the experiments with perhaloalkenes. On one occasion a hole had been punched laterally through the gasket, with some apparent signs that the copper had melted around the hole.

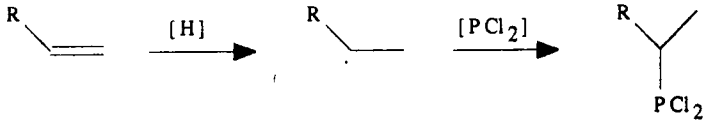
The obvious safety implications of the reaction with perhaloalkenes prevented any further studies. To contain any further accidental leaks a stainless steel bursting disk was fitted to the autoclave (see Figure 2.1). A teflon disk protected the face of the bursting disk, this was regularly checked for damage and routinely replaced.

1-Butene, trans-2-butene and 1-hexene reacted to form the expected products, 2-alkyldichlorophosphine and bis-1,2-[dichlorophosphino]alkane, only. No 2,3-diphosphine was detected from the reaction with 2-butene. Both types of products consist of an enantiomeric pair (d and l configuration)[11], caused by the introduction of a chiral centre at C_2. However each enantiomeric pair will have identical physical properties, including ^{31}P and ^{13}C NMR chemical shifts, and were not separated. 1-Butene began to react when the internal temperature of the autoclave reached 180°C, generating a maximum pressure of 130 atm. The terminal double bond in 1-butene reacted more readily than the internal double bond of 2-butene, generating a higher yield of chlorophosphines. Consistently a very low yield of bis-1,2-[dichlorophosphino]hexane was produced.

The monophosphine obtained from all the alkenes was the Markownikoff type product, 2-alkyldichlorophosphine. None of the anti-Markownikoff-type product, 1-alkyldichlorophosphine, was detected by ^{31}P and ^{13}C NMR[12]:

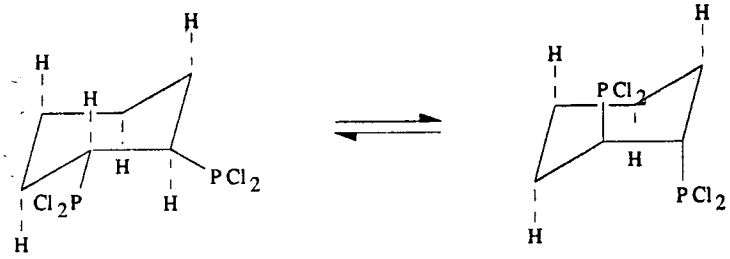


This suggests the hydrogen atom is added to the alkene before the phosphorus group, generating the more stable secondary intermediate. Both ionic and radical intermediates prefer secondary to primary reactive, trivalent, carbon atoms. Therefore the hydrogen atom source is of prime importance in maximising the diphosphine yield and determining the reaction mechanism.



2.3.3. Reaction with Cyclic Alkenes

Cyclopentene and cyclohexene react to form cycloalkyldichlorophosphines and trans,bis-1,2-[dichlorophosphino]cycloalkanes, identical products to those reported by M.L.H. Green[3]. The ring conformation in trans,bis-1,2-[dichlorophosphino]cyclohexane is probably similar to that in trans,bis-1,2-[dichlorophosphino]cyclopentane[13]. This trans,diequatorial conformation is the only one that avoids 1,3-diaxial interactions between hydrogen and phosphorus:



trans,diequatorial trans,diaxial

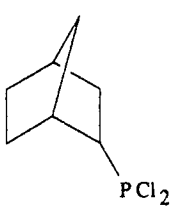
1,3-diaxial interactions in the diaxial conformer will drive the equilibrium towards the diequatorial conformer. The free energy changes between the two conformers will involve a very high energy transition state as the phosphorus groups become very close during interconversion. Thus interconversion will not be favoured and most of the molecules will preferentially adopt the diequatorial conformation. Studies of 1,4-disubstituted cyclohexyl phosphorus

compounds[8,14,15] show the diequatorial conformation is favoured. Only one resonance was observed in the experimental ^{31}P NMR spectrum suggesting only one conformer was present, confirming the literature theories. Cyclohexyldichlorophosphine, however, exists as a pair of rapidly interconverting axial and equatorial conformers[8].

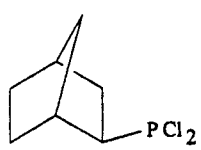
Bis-1,2-[diphenylphosphino]cyclopentane, DPCP, has recently been synthesised from the dichloro- analogue[16] and some rhodium complexes investigated. Two diphosphine ligands coordinate to the rhodium centre, generating a bis[diphosphine] square planar complex, which is an active catalyst.

The equatorial position is favoured by phosphorus in 2-norbornyldichloro-phosphine. No conformational changes are possible because the norbornane ring system is rigid, consequently both axial (endo) and equatorial (exo) phosphines are detected, Figure 2.4. These products are diastereoisomers. Peak integration of the ^{31}P NMR spectrum shows the ratio of endo:exo isomer is approximately 1:3. Comparison with literature ^{31}P NMR data[17] shows formation of, or rearrangement to, 7-norbornyldichlorophosphine has not occurred.

Substitution at the 2-position in norbornene generally leads to the exo-substituted derivatives, which are lower in energy than their endo-diastereoisomers[18]. Although in norbornane the 2,3 and 5,6 bonds are eclipsed, a slight twist may occur in endo-substituted 2-norbornanes to reduce the steric hindrance.



Endo-adduct



Exo-adduct

Figure 2.4: Endo- and Exo-2-Norbornyldichlorophosphine

The experimental NMR data, shown in Figure 2.5, are compared with published data for 2-norbornyldichlorophosphine[8] in Tables 2.1, 2.2 and 2.3. The literature compound was synthesised from phosphorus trichloride and 2-chloronorbornane using Grignard methods. In both syntheses the diastereoisomers could not be separated and so mixtures were used in determining the structures[8].

Table 2.1: ^{31}P NMR Data for 2-Norbornyldichlorophosphine Isomers

^{31}P	Experimental (ppm)	Literature[8]
Exo	185.8	187.5
Endo	194.5	196.8

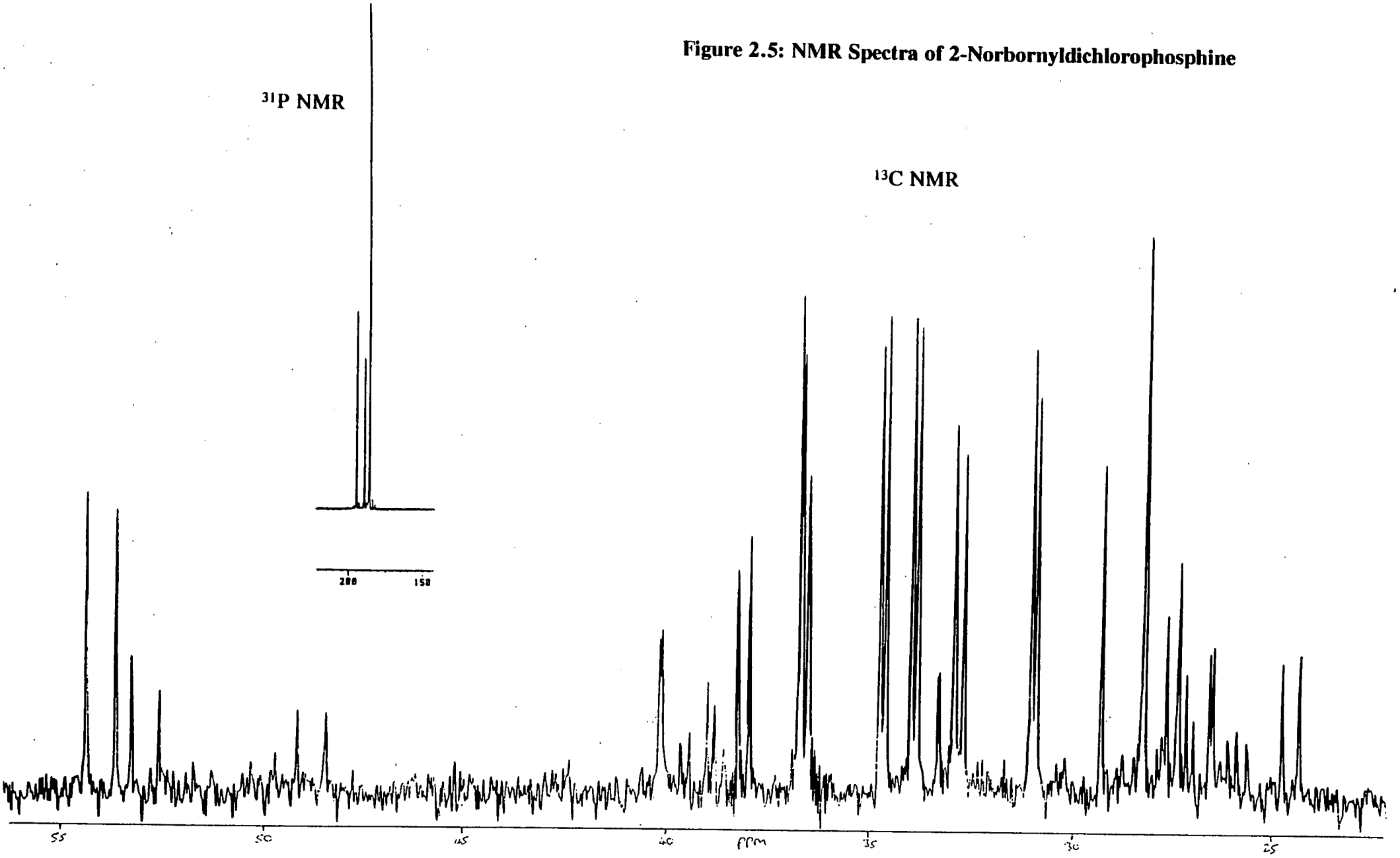
Table 2.2: ^{13}C NMR Data for Exo-2-Norbornyldichlorophosphine

^{13}C	Experimental		Literature[8]	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	38.09	18.0	38.5	17.3
C_2	53.99	46.0	54.5	46.5
C_3	32.74	14.4	33.1	14.8
C_4	36.50	s	37.0	s
C_5	28.19	s	28.4	s
C_6	30.99	7.3	31.2	7.5
C_7	36.68	3.4	37.0	4.7

Table 2.3: ^{13}C NMR Data for Endo-2-Norbornyldichlorophosphine

^{13}C	Experimental		Literature[8]	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	38.92	11.5	39.4	12.3
C_2	52.89	43.8	53.4	44.0
C_3	34.64	8.8	33.3	28.0
C_4	33.23	s	---	---
C_5	29.24	s	29.5	s
C_6	24.50	27.3	24.8	28.0
C_7	40.13	3	40.5	3.5

Figure 2.5: NMR Spectra of 2-Norbornyldichlorophosphine



Because of the greater intensity of the exo- signal, the structures are easily resolved. For both diastereoisomers there is good agreement between the experimental and literature data. ^{31}P NMR signals for the exo-derivatives occur at higher frequency than the endo-derivatives because the non-bonded interactions of the exo-phosphorus group with the β-CH at C_1 apparently shields the signals more than the steric crowding in the endo-adducts[17]. The structural influence of the exo-phosphorus group with the β-CH depends on subtle molecular differences related to parameters such as bond and torsion angles and bond lengths, which must overcome the effect of steric compression caused by the proximity of the endo-hydrogen atoms at C_3 and C_6 in the endo-derivative.

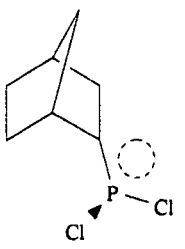
Few differences are observed between the ^{13}C NMR spectra. Experimental ^{31}P-^{13}C coupling constants in the exo- adduct differ slightly from those reported in the literature, these are probably due to the differences in resolution of the spectrometers used. The experimental data was acquired at 62.896 MHz, the literature data at 25.03 MHz, so the experimental data reported here is of higher resolution.

More importantly the ^{31}P-^{13}C coupling constant at C_3 in the endo- adduct is very different in the two sets of data. The previously reported constant[8] of ^2J [^{31}P-$^{13}C_3$] = 28.0 Hz is large but, interestingly, is similar to the expected value for a sterically hindered two-bond coupling constant; although this doublet was only assigned tentatively owing to peak overlap. Differences between the reported data[8] and the experimental data may be caused by an interpretation error or be due to slight differences in the two compounds caused by the orientation of the lone-pair orbital on the phosphorus atoms.

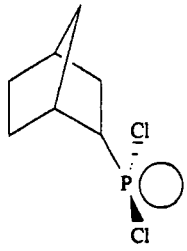
^2J coupling constants are controlled by the dihedral angle (ϕ) between the lone-pair orbital on phosphorus and the β-carbons ($C_1$and C_3). In rigid systems, such as 2-norbornanes, substitution in the endo- or exo-orientation leads to different ^2J values[19]. The larger the value of the coupling constant, the smaller the dihedral angle and the closer the lone-pair orbital is to the β-carbon[20]. Therefore the lone-pair orbital may be regarded as being cis- to the β-carbon in restricted systems. The experimental constant of ^2J [^{31}P-$^{13}C_3$] = 8.8 Hz obtained in this study suggests a large dihedral angle, so the lone-pair orbital is more remote from C_3 than in the literature compound.

Thus, using this argument, the lone-pair orbital on phosphorus is predicted to be closer to C_3 than C_1 in the literature compound (^2J [^{31}P-$^{13}C_3$] > ^2J [^{31}P-$^{13}C_1$]); whereas the lone-pair orbital on phosphorus is apparently

approximately equidistant from both C_1 and C_3 (^2J [^{31}P-$^{13}C_3$] ≈ ^2J [^{31}P-$^{13}C_1$]) in the compound prepared in this work. Thus steric crowding in the endo-isomer may cause a preferred population of rotameric forms, with either the phosphorus substituents or lone pair orbital projecting away from the ring framework:



reference



experimental

This surprisingly suggests rotation around the carbon-phosphorus bond is partially restricted at ambient temperature, questioning the validity of the reported data. An error in the original reference or an error in calculating the coupling constants seems to be the most likely reason for the discrepancy. The relationship of dihedral angle to ^3J coupling constants (Karplus relationship) also explains the large value of ^3J [^{31}P-$^{13}C_6$] = 27.3 Hz in the experimental endo-adduct[17]. Qualitatively, transannular interactions between the endo-phosphorus group and the endo-hydrogen attached to C_6 generate the large observed coupling constant.

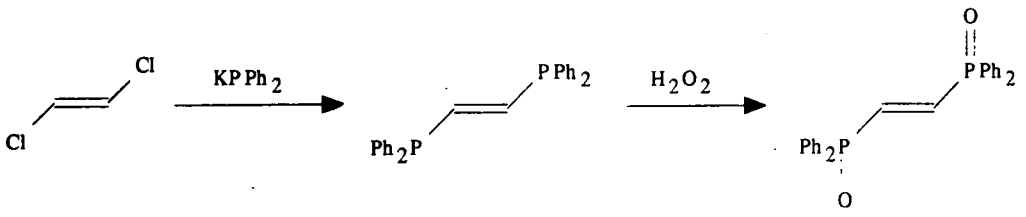
Bis-2,3-[dichlorophosphino]norbornane, which is a precursor for RENORPHOS (see Figure 2.6), was isolated in a very low yield, probably because of the steric and electronic reasons outlined above. Two peaks are observed in the ^{31}P NMR spectrum showing the phosphorus atoms are non-equivalent. Thus the conformation will probably be endo,exo- (trans-) to reduce the steric interactions between the two phosphorus groups. Similarly both the related compounds, NORPHOS and RENORPHOS (Figure 2.6), exhibit the 2R,3R (P_{endo},P_{exo}) conformation[21,22]. Therefore both ligands can be considered to possess pseudo-C_2-symmetry[23], and are very active in asymmetric hydrogenation catalysis[24].

NORPHOS and RENORPHOS are conveniently prepared by the Diels-Alder reaction of cyclopentadiene with trans,bis-1,2-[diphenylphosphano]ethene[25-7]. After resolving the enantiomers[21] the phosphine oxide (NORPHOSO) is reduced with trichlorosilane to yield NORPHOS. Alternatively the carbon-carbon double bond may be reduced by diimide[28], generated in situ by the thermal decomposition of ρ-

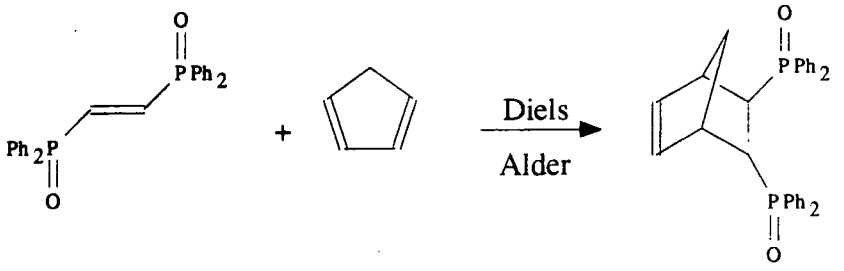
toluenesulphonhydrazide in boiling glyme, prior to reduction of the phosphine oxide to yield RENORPHOS.

Figure 2.6: Synthesis of NORPHOS and RENORPHOS

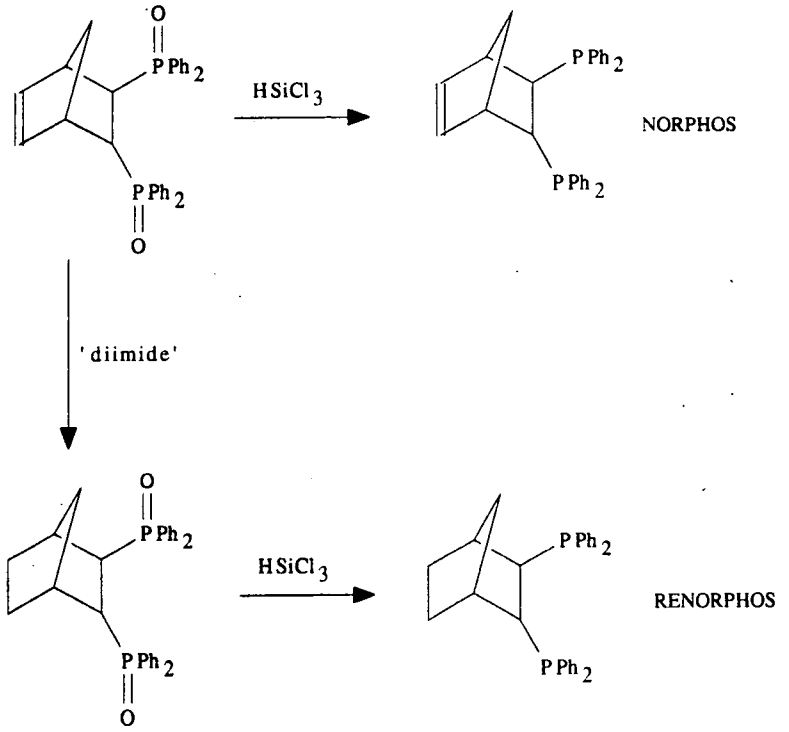
i. Synthesis of trans,bis-1,2-[diphenylphosphano]ethene



ii. Synthesis of trans,bis-2,3-[diphenylphosphano]norbornane (NORPHOSO)



iii. Reduction to NORPHOS and RENORPHOS



This elegant synthesis generates a high yield (70-80%) of enantiomerically pure diphosphine from cyclopentadiene using an established method. However the main drawback of using this route involves handling toxic reagents during the synthesis of trans,bis-1,2-[diphenylphosphano]ethene, and resolving the phosphine oxide enantiomers. Protection of the phosphine groups as the oxides increases the number of reaction stages required to isolate the free diphosphine ligands, lowering the overall yields.

2.4. Conclusion

Simple alkenes react under high temperature and pressure with phosphorus and phosphorus trichloride to produce alkyldichlorophosphines and bis[dichloro-phosphino]alkanes in moderate yield. Haloalkenes also react, but in a dangerous manner to give other types of products which generated dangerously high pressures preventing further studies of the reaction. More sterically restricted alkenes, such as trans-2-butene and 2-norbornene, react but the yield of both the mono- and diphosphine is low. Thus, although the precursor to RENORPHOS was prepared by this route, it is less convenient than the higher yielding synthesis by Diels-Alder addition. However trans,bis-2,3-[dichlorophosphino]norbornane, made under high pressure conditions, is a versatile precursor and can be readily converted to the diphenyl- derivative (RENORPHOS) or other derivatives.

Alkyldichlorophosphines were isolated in a higher yield than bis-1,2-[dichlorophosphino]alkanes in every high pressure reaction. As the molecular mass and steric hindrance of the alkene increased the overall yields decreased. Thus a yield of 32% of bis-1,2-[dichlorophosphino]cyclohexane but only 2% of bis-2,3-[dichlorophosphino]norbornane were obtained. Pro-chiral carbon atoms in the alkene are readily converted into a chiral centre by the addition of the phosphorus group, generating chiral phosphines. However the enantiomers were not separated.

Isolation of the products was achieved by fractional distillation under reduced pressure. ^{31}P and especially ^{13}C NMR analysis were sufficiently detailed to unambiguously characterise the phosphines without further purification. Interpretation of the chemical shift and the ^{31}P-^{13}C coupling constants in the ^{13}C NMR provided valuable information; the magnitude of the coupling constants being directly related to the position of the carbon atom in the alkyl chain. MS proved the structure, but did not provide any structural information.

Elemental analysis was complicated by sample impurity, although analytical samples were prepared by several redistillations and accurately analysed. Usually each phosphine was analysed only once because reproducible results were rare, caused by slow decomposition of the phosphine. Some results, especially %P and %Cl analyses, were occasionally very inaccurate, these rogue results being discarded (♦). The significance of elemental analysis was surpassed by the value of the NMR data.

This series of reactions with mono-ene substrates gave an insight into the variables, conditions and problems associated with the high pressure synthesis, including the handling and analysis of dichlorophosphines. Although some of the alkyldichlorophosphines and bis-1,2-[dichlorophosphino]alkanes prepared had been previously made by this method[1,3], by repeating these literature experiments the method was developed to optimise the conditions and maximise the yield. These experiments also provided the background knowledge and a foundation for high pressure reactions with more complex and sterically hindered alkenes. permitting the range of alkenes known to react with phosphorus and phosphorus trichloride under the high temperature and pressure conditions to be extended. These reactions are described in the next chapter.

2.5. References

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CHAPTER 3:

THE HIGH TEMPERATURE AND PRESSURE SYNTHESIS OF DICHLOROPHOSPHINES FROM DIENES AND TERPENES

3.1. Introduction

The preceding chapter describes the synthesis of alkyldichlorophosphines and bis[dichlorophosphino]alkanes from mono-alkenes. In this chapter the work is extended to the reaction of white phosphorus and phosphorus trichloride with dienes, terpenes and aromatic substrates under high temperature and pressure conditions.

Dienes such as 1,3-butadiene, cyclopentadiene, 2,5-norbornadiene and 1,5-cyclooctadiene were used as substrates. Changing the ratio of phosphorus trichloride to the number of carbon-carbon double bonds was also studied. Product nature, extent of reaction and dichlorophosphine yields were determined as the ratio varied. Terpene substrates such as α-pinene, β-pinene, camphene and limonene were also used. These natural products contain at least one stereocentre so optical purity of the enantiomers is important. Addition of the phosphorus group across the unsymmetric double bond retains the chiral configuration of the starting material in the product, and generates a new stereocentre. Addition of a dichlorophosphine unit to the aromatic ring of benzene, toluene and styrene, under the forcing reaction conditions, was also attempted.

3.2. Experimental

3.2.1. Synthesis of Bis-1,4-[dichlorophosphino]cyclooctane [17]

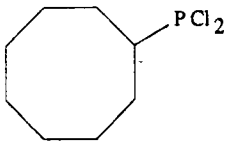
The method using cyclohexene, described in the previous chapter, was employed to produce cyclooctyldichlorophosphine [16] and bis-1,4-[dichlorophosphino]cyclooctane [17] from 1,5-cyclooctadiene (86 ml, 0.7 mol; 150 ml, 1.25 mol; 300 ml, 2.45 mol). Similarly cyclopentyldichlorophosphine [12] and trans,bis-1,2-[dichlorophosphino]cyclopentane [13] were prepared from freshly distilled cyclopentadiene (83g, 1.25 mol) or dry dicyclopentadiene (cyclopentadiene dimer; 100 ml, 0.75 mol), endo- and exo-2-norbornyl-dichlorophosphine [14a/b] and trans,bis-2,3-[dichlorophosphino]norbornane [15] were prepared from 2,5-norbornadiene (bicyclo[2.2.1]hepta-2,5-diene; 100 ml, 0.93 mol).

2-Butyldichlorophosphine [2], bis-1,2-[dichlorophosphino]butane [3], bis-1,4-[dichlorophosphino]butane [18] and either dichloro-2,2'-diphospholane [19] or 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane [20] were synthesised

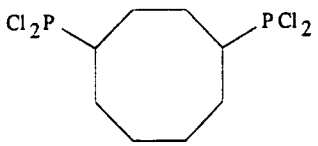
from 1,3-butadiene (40g, 0.74 mol; 70g, 1.3 mol; 100g, 1.85 mol) using a similar method.

In an analogous reaction with styrene (140 ml, 1.25 mol) ^{31}P NMR showed six resonances at low frequency compatible with the dichlorophosphine structural unit. However none of these products could be isolated in sufficient purity for further analysis.

The many reaction products derived from the terpenes (1R)-(+)-α-pinene (100 ml, 0.63 mol); (1S)-(-)-β-pinene (180 ml, 1.14 mol); (+)-camphene (170g, 1.25 mol) and (1S)-(-)-limonene (80g, 0.6 mol) were screened by ^{31}P NMR. However they could not be separated, even by distillation using a high resolution Fischer Spaltrohr spinning column system.

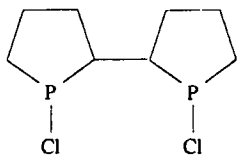


[16]

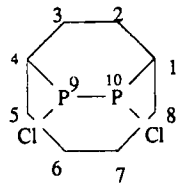


[17]

[18]



[19]



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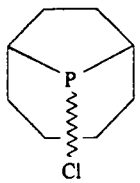

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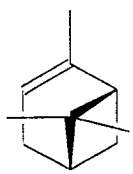
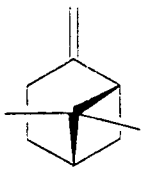
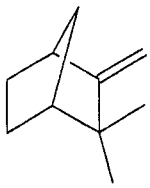


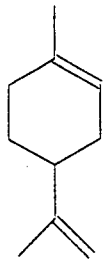
α-pinene



β-pinene



camphene



limonene

Data

i. Cyclooctyldichlorophosphine [16]

distillation temperature: 70±1°C (0.04 mmHg).

yield: 51g (21% from cyclooctadiene).

NMR (neat); ^{31}P (ppm): 195.2 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	57.40	d	^1J = 45.5
$C_{2/8}$	36.34	d	^2J =20.0
$C_{3/7}$	34.06	s	---
$C_{4/6}$	32.53	s	---
C_5	25.83	s	---

EA: found (required)
%C 46.4 (45.1); %H 6.6 (7.0); %P 13.1 (14.6); %Cl 27.1 (33.3).

MS; EI: 109 $[M-PH_2Cl_2]^+$.
CI: 178 $[MH-Cl]^+$; 143 $[MH-Cl_2]^+$.

ii. Bis-1,4-[dichlorophosphino]cyclooctane [17]

distillation temperature: 108±2°C (0.05 mmHg).
yield: 33g (9% from cyclooctadiene).
NMR (neat); ^{31}P (ppm): 191.0 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	56.15	d	^1J = 45.2
$C_{2/3}$	47.53	dd	^2J = 17.5
			^3J = 5.2
$C_{5/8}$	30.30	d	^2J = 18.6
$C_{6/7}$	34.22	d	^3J = 5.4

EA: found (required)
%C 33.1 (30.6); %H 4.35 (4.5); %P 14.3 (19.7); %Cl 42.8 (45.2).

MS; CI: 142 $[MH-PCl_4]^+$; 111 $[MH-P_2Cl_4]^+$.

iii. Bis-1,4-[dichlorophosphino]butane [18]

distillation temperature: not isolated.
yield: not isolated.
NMR (neat); ^{31}P (ppm): 194.2 singlet

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	41.58	d	^1J = 45.7
$C_{2/3}$	23.27	d	^2J = 11.8

iv. Dialkylchlorophosphine Synthesised from 1,3-Butadiene

The identity of this product could not be unambiguously determined, however two different compounds may be proposed using the available data:

distillation temperature: 78±2°C (0.05 mmHg).
yield: 14g (6% from butadiene).

EA: found (required for $C_8H_{14}P_2Cl_2$)
%C 45.2 (39.5); %H 5.7 (5.8); %P 25.5 (17.5); %Cl 27.6 (29.2).

MS; EI: 141[M-PCl_2]$^+$; 110 [M-P_2Cl_2]$^+$.
CI: 177 [MH-PCl]$^+$; 142[MH-PCl_2]$^+$; 111 [MH-P_2Cl_2]$^+$.

^{31}P NMR (neat); (decoupled, ppm): 125.9 singlet
(^{1}H coupled, ppm): 126.2 singlet

a. ^{13}C NMR for Dichloro-2,2'-diphospholane [19] (postulated)

Bruker AC250 (neat liquid sample):

^{1}H decoupled	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{2/2'}$	50.20	dd	$^1J = 49.1$ $^2J = 4.9$
$C_{3/3'}$	35.38	dd	$^2J = 26.8$ $^3J = 8.1$
$C_{4/4'}$	28.45	dd	$^2J = 20.6$ $^4J = 4.6$
$C_{5/5'}$	35.85	dd	$^1J = 33.9$ $^4J = 12.4$

^{1}H coupled	δ (ppm)	multiplicity	J (Hz)
$C_{2/2'}$	50.17	dd	$J_{C-H} = 135.0$ $^1J_{P-C} = 48.7$
$C_{3/3'}$	35.49	t	$J_{C-H} = 133.4$
$C_{4/4'}$	28.45	dt	$J_{C-H} = 133.8$ $^2J_{P-C} = 20.2$
$C_{5/5'}$	35.61	td	$J_{C-H} = 131.8$ $^1J_{P-C} = 33.5$

Bruker AMX 500 (Sample dissolved in $CDCl_3$):

^{13}C; ^{1}H decoupled	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)	DEPT135
$C_{2/2'}$	50.31	d	^{1}J = 46.5	CH
$C_{3/3'}$	36.08	dd	^{2}J = 27.9	CH_2
			^{3}J = unres.	
$C_{4/4'}$	29.21	d	^{2}J = 20.2	CH_2
$C_{5/5'}$	36.67	dd	^{1}J = 33.9	CH_2
			^{4}J = 12.4	

^{1}H ($CDCl_3$)	δ (ppm)	multiplicity	J [^{1}H-^{1}H] (Hz)
$C_{2/2'}$	2.179	t	15.9
$C_{3/3'}$	1.244	td	8.2
			unres.
$C_{4/4'}$	1.636	t	unres
$C_{5/5'}$	1.987	d	7.8

b. ^{13}C NMR data for 9,10-Dichloro-9,10-diphosphabicyclo[4.2.2]decane [20] (postulated)

Bruker AC250 (neat liquid sample):

^{1}H decoupled	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	50.20	dd	^{1}J = 49.1
			J = 4.9
$C_{2/3}$	35.85	dd	^{2}J = 33.9
			^{3}J = 12.4
$C_{5/8}$	35.38	dd	^{2}J = 26.8
			^{3}J = 8.1
$C_{6/7}$	28.45	dd	^{3}J = 20.6
			J = 4.6

^{1}H coupled	δ (ppm)	multiplicity	J (Hz)
$C_{1/4}$	50.17	dd	$J_{C-H} = 135.0$ $^{1}J_{P-C} = 48.7$
$C_{2/3}$	35.61	td	$J_{C-H} = 131.8$ $^{2}J_{P-C} = 33.5$
$C_{5/8}$	35.49	t	$J_{C-H} = 133.4$
$C_{6/7}$	28.45	dt	$J_{C-H} = 133.8$ $^{3}J_{P-C} = 20.2$

Bruker AMX500 (Sample dissolved in $CDCl_3$):

^{13}C; ^{1}H decoupled	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)	DEPT135
$C_{1/4}$	50.31	d	$^{1}J = 46.5$	CH
$C_{2/3}$	36.67	dd	$^{2}J = 33.9$ $^{3}J = 12.4$	CH_2
$C_{5/8}$	36.08	dd	$^{2}J = 27.9$ ^{3}J = unres.	CH_2
$C_{6/7}$	29.21	d	$^{3}J = 20.2$	CH_2

^{1}H ($CDCl_3$)	δ (ppm)	multiplicity	J [^{1}H-^{1}H] (Hz)
$C_{1/4}$	2.179	t	15.9
$C_{2/3}$	1.987	d	7.8
$C_{5/8}$	1.244	td	8.2 unres.
$C_{6/7}$	1.636	t	unres

Figure 3.1: NMR Spectra of Dichloro-2,2'-diphospholane or 9,10-Dichloro-9,10-diphosphabicyclo[4.2.2]decane

(recorded on Bruker AC250 NMR Spectrometer)

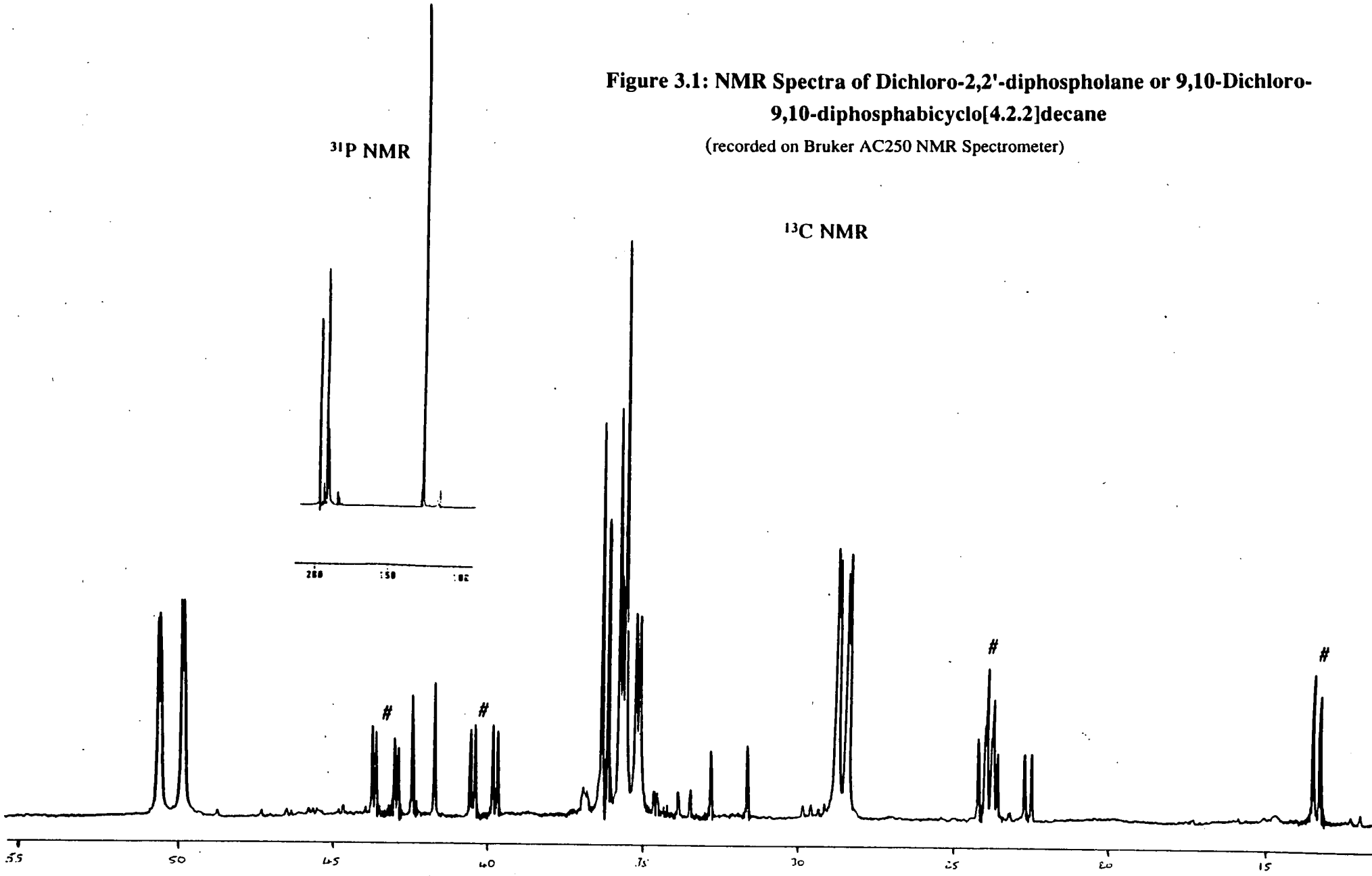
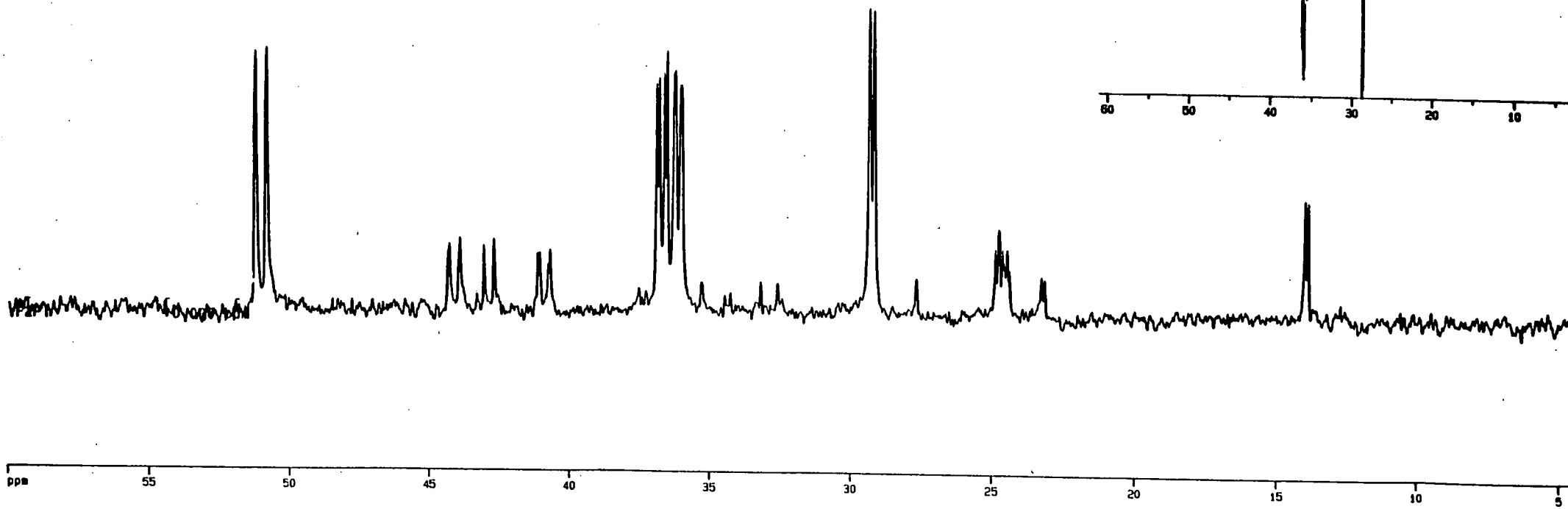


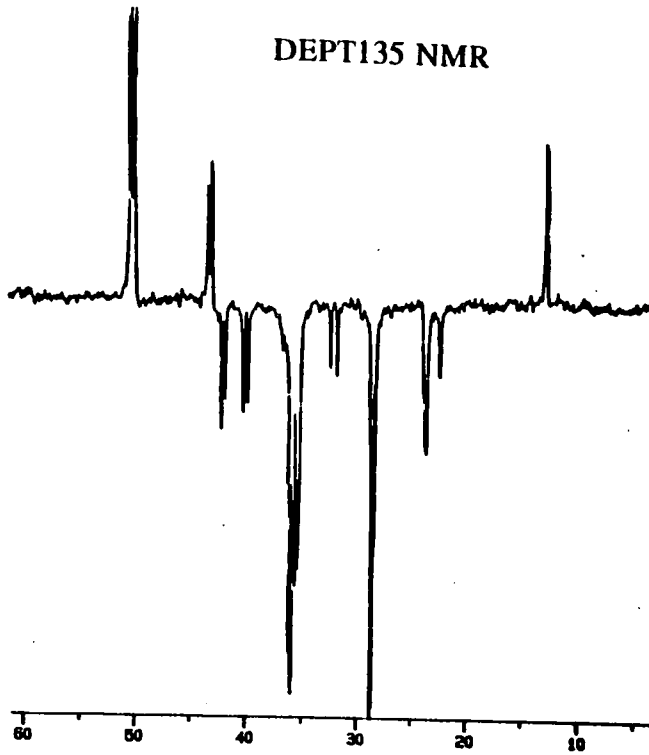
Figure 3.2: NMR Spectra of Dichloro-2,2'-diphospholane or 9,10-Dichloro-9,10-diphosphabicyclo[4.2.2]decane

(recorded on Bruker AMX500 NMR Spectrometer)

^{13}C NMR



DEPT135 NMR



v. Reaction with Styrene

distillation range: 92-108°C (1.2 mmHg).

yield: not calculated.

^{31}P NMR (neat):

δ (ppm)	Possible assignment*
201.6 194.0 185.9	$RPCl_2$, probably cyclohexyl derivatives
177.5	$RPCl_2$, may be $PhCH(Me)PCl_2$ (major component)
162.1	$ArPCl_2$, phosphorus attached to ring
114.0	R_2PCl

vi. Reaction with (1R)-(+)-α- and (1S)-(-)-β-Pinene

distillation range: 80-96°C (1.0 mmHg).

yield: not calculated.

^{31}P NMR (neat):

δ (ppm)	Possible assignment*
196.5 196.0 194.6 194.1 192.8 189.7	$RPCl_2$
178.4 161.6	? ?
103.2	R_2PCl

vii. Reaction with (+)-Camphene

distillation range: 83-96°C (1.0 mmHg).

yield: not calculated.

^{31}P NMR (neat):

δ (ppm)	Possible assignment*
197.8	$RPCl_2$
161.5	?
103.4	R_2PCl

viii. Reaction with (1S)-(-)-Limonene

distillation temperature: 82-94°C (1.0 mmHg).

yield: not calculated.

^{31}P NMR (neat):

δ (ppm)	Possible assignment*
196.0	$RPCl_2$
104.1	R_2PCl

*Based on CRC Handbook of ^{31}P NMR Data[1,2].

3.3. Discussion

3.3.1. Experimental

Isolation of the products was achieved by fractional distillation under reduced pressure. As the molecular mass of the alkene, and hence the products, increased the distillation temperature of the products also rose. Therefore the products, especially the diphosphines, often distilled at very high temperatures and were difficult to isolate and purify. Yields of both alkyldichlorophosphines and bis[dichlorophosphino]alkanes generally decreased as the molecular mass of the alkene increased. Steric hindrance around the double bond also reduced the yield. Many minor dichlorophosphine products were observed in these reactions, more than in the syntheses from simple mono-alkenes. Thus it was difficult to obtain analytically pure samples, uncontaminated with other dichlorophosphines, because of the chemical similarity of all the products. No polyphosphine products were isolated.

The phosphines derived from all dienes are saturated systems, no alkene products are recovered from the autoclave after the high temperature and pressure reaction, as detected by ^{13}C NMR. Therefore addition of dichlorophosphine units or hydrogen atoms must have occurred across all the carbon-carbon double bonds. Decomposition of the diene may also occur, possibly generating the polymeric material. Three hydrogen atoms are added to the diene rings in synthesising the monophosphine, and two hydrogen atoms are added during the synthesis of the diphosphine. Therefore there must be a significant source of hydrogen atoms present at some stage in the reaction.

Higher molecular mass, and more unsaturated, alkenes generated much less polymer material than mono-alkenes under the reaction conditions. The polymer material was usually a black powder, coated around the walls of the autoclave. Therefore it is probably a form of alkene decomposition product, catalysed by the iron surface.

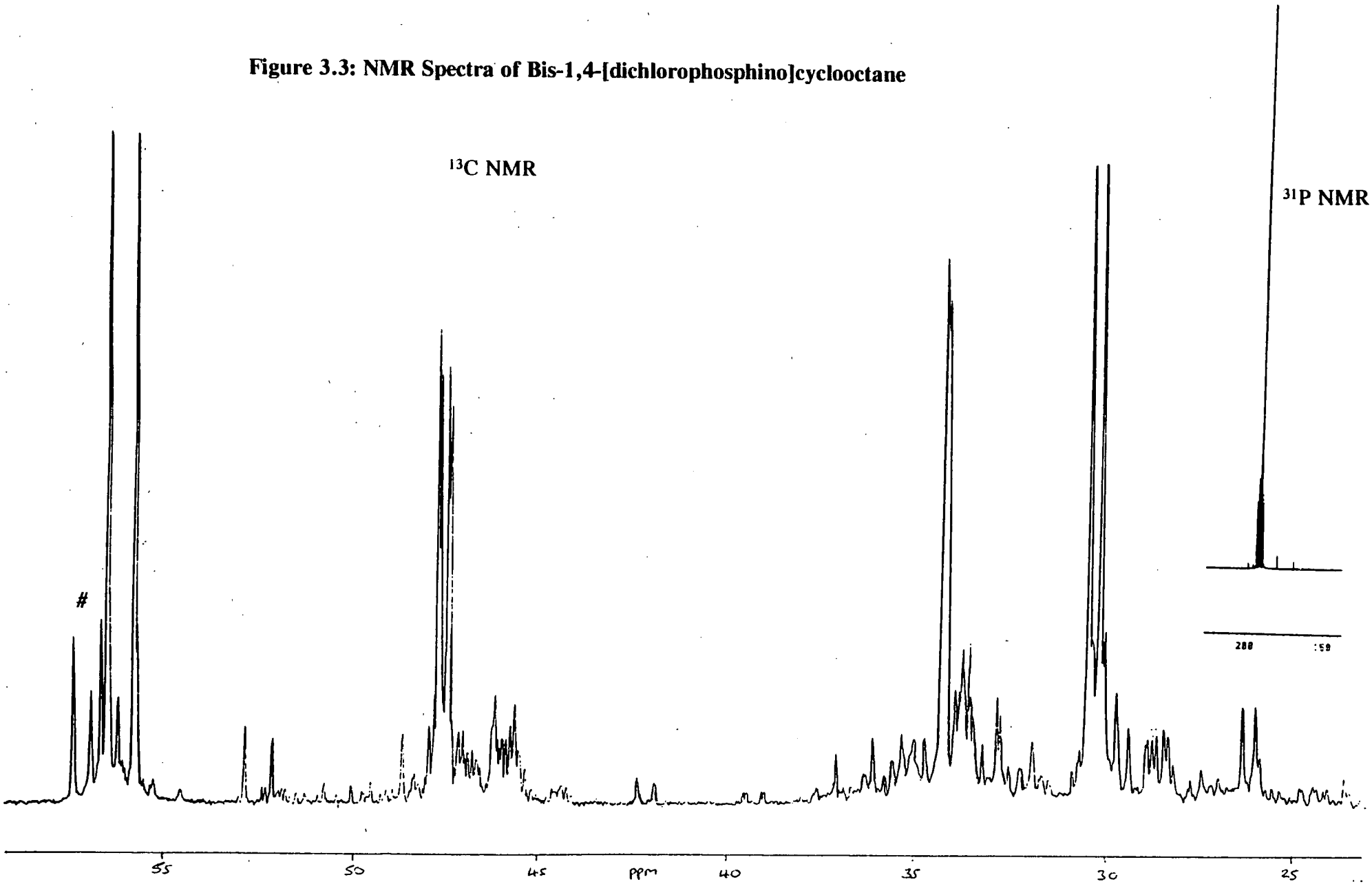
Acetonitrile did not react with phosphorus and phosphorus trichloride at high temperature under high pressure. Only the staring materials were isolated from the autoclave after 40 hours at 260°C. The carbon-nitrogen triple bond was not hydrogenated under the reaction conditions and no polymeric material was generated.

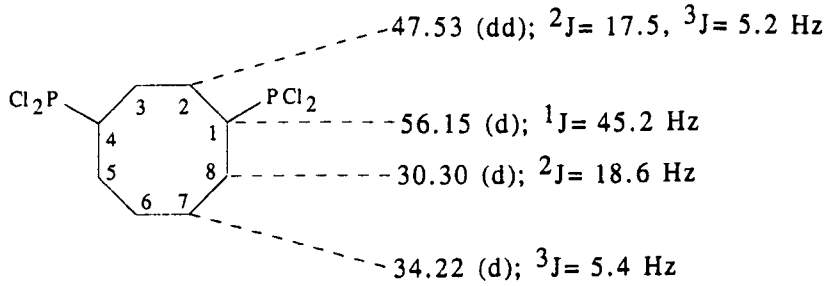
3.3.2. Reaction with 1,5-Cyclooctadiene

1,5-cyclooctadiene reacted with phosphorus and phosphorus trichloride at high temperature under high pressure producing cyclooctyldichlorophosphine [16] and bis-1,4-[dichlorophosphino]cyclooctane [17]. This was the only diphosphine isolated, no 1,2- or 1,5-isomers were detected in significant amounts, suggesting the double bonds isomerise forming the conjugated ring system under the reaction conditions. Michael-type addition (1,4-addition) of the dichlorophosphine units across the conjugated system would result in the observed diphosphine. The ^{13}C NMR spectrum for bis-1,4-[dichlorophosphino]cyclooctane is shown in Figure 3.3, and the assignments are outlined below.

Only four resonances were observed, so the cyclooctane derivative is symmetric. The doublet at 56.15 ppm (^1J = 45.2 Hz) is typical of the carbon atom directly bonded to the phosphorus atom (α-carbon). At 30.30 ppm the ^{31}P-^{13}C coupling constant of 18.6 Hz shows a methylene group adjacent to the α-carbon. Similarly there is a second β-carbon at 47.53 ppm (^2J = 17.5 Hz). This latter resonance, however, is split into a doublet-of-doublets, showing the carbon atom is interacting with two phosphorus atoms. The smaller of these coupling constants (5.2 Hz) is typical of a three-bond coupling. Therefore the carbon atom is two bonds from one of the phosphorus atoms and three bonds from the second phosphorus atom. The 1,4-diphosphine isomer is the only one to fulfil this criterion. The doublet at 34.22 ppm (J = 5.4 Hz) is also assigned as a methylene group three bonds from a phosphorus atom. This interpretation can be summarised as:

Figure 3.3: NMR Spectra of Bis-1,4-[dichlorophosphino]cyclooctane





The 1,2-diphosphine isomer would split the α-carbon resonance at 56 ppm into a doublet-of-doublets ($^1J \approx 45$, $^2J \approx 20$ Hz)[1,2] similar to those observed for other cyclic 1,2-diphosphines, such as those described in the previous chapter. This product may be detected at the impurity level in the ^{13}C NMR spectra, the α -carbon doublet-of-doublets (#) being centred at 56.81 ppm (^1J = 45.9, ^2J = 28.8 Hz). The high value of the two-bond coupling constant shows the phosphorus groups are sterically compressed, probably by each other and the ring conformation. Large ^2J coupling constants indicate a small dihedral angle, therefore the phosphorus lone-pair orbital is close to the β-carbon atom. Other resonances of the 1,2-diphosphine are not easily resolved. However some may be detected at the base of the major product peaks: 33.63 ppm (J = 11.4 Hz); 30.04 ppm (J = 3.5 Hz); 26.03 ppm (J = 21.9 Hz). The doublet at 30 ppm may be part of a doublet-of-doublets, suggesting this is $C_{3/8}$, the other part being covered by a more intense resonance from the major product. However it is impossible to confidently assign these peaks because they are not sufficiently resolved.

Cyclooctane rings usually adopt the chair-boat conformation, which is analogous to the chair form in cyclohexane. In both conformers the transannular (diaxial) interactions are minimised, although there is more ring strain (Baeyer and Pitzer strain) in the cyclooctane ring than the cyclohexane ring[3], especially in the 1,2-isomer as the phosphorus centres are closer. Thus, in both ring systems the substituents prefer to adopt the equatorial position, producing the lowest energy conformer. Similarly the diequatorial conformation is favoured in disubstituted systems, although rapid interconversion between the different conformers occurs. Since the phosphorus groups in 1,2-diphosphines are in relatively close proximity, at ambient temperature, cyclooctyldichlorophosphine, bis-1,2-[dichlorophosphino]cyclooctane or bis-1,4-[dichlorophosphino]-cyclooctane all exist as interconverting conformers, with the equatorial or diequatorial conformations being preferred.

Varying the ratio of 1,5-cyclooctadiene to phosphorus trichloride did not alter the nature of the products formed. One aim of these experiments was to attempt the synthesis of the dialkylchlorophosphine obtained from the high

pressure reaction with 1,3-butadiene (dichloro-2,2'-diphospholane or 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane, see below) because dimerisation of butadiene appears to be an integral step of the reaction. However, only the monophosphine and bis-1,4-[dichlorophosphino]cyclooctane were isolated from the reaction with 1,5-cyclooctadiene. As the concentration of diene increased, the yield of monophosphine product and polymer material increased, relative to the yield of diphosphine. Optimum yields of diphosphine were obtained when excess phosphorus trichloride was used, a molar ratio of 1,5-cyclooctadiene to phosphorus trichloride of approximately 1:2 being used to obtain the best overall yields. However the yield was not significantly affected by small changes in this ratio.

3.3.3. Reaction with Cyclopentadiene

Cyclopentadiene reacts identically to dicyclopentadiene under the reaction conditions, suggesting that the dimer is cracked in the autoclave prior to reaction with the phosphorus reagents. Both substrates react identically to cyclopentene forming cyclopentyldichlorophosphine [12] and bis-1,2-[dichlorophosphino]-cyclopentane [13] only. Bis-1,3-[dichlorophosphino]cyclopentane was not detected, even at very low levels. The yield of both products from cyclopentadienes was much lower than the yield from cyclopentene, for no apparent reason.

3.3.4. Reaction with 2,5-Norbornadiene

2,5-norbornadiene reacts similarly to 2-norbornene, producing endo- and exo-2-norbornyldichlorophosphine [14a/b] (endo:exo, 1:3) and trans,bis-2,3-[dichlorophosphino]norbornane [15] only. Other diphosphines, such as the 2,5-, 2,6- or 2,7- isomers were not detected. Figure 3.4 shows the NMR spectra of 2-norbornyldichlorophosphine synthesised from 2,5-norbornadiene. Comparing the NMR data of the monophosphine derived from the mono-alkene with that from the diene shows the ^{31}P NMR data is almost identical.

^{31}P	2-Norbornene	2,5-Norbornadiene
Exo	185.8	185.6
Endo	194.5	194.4

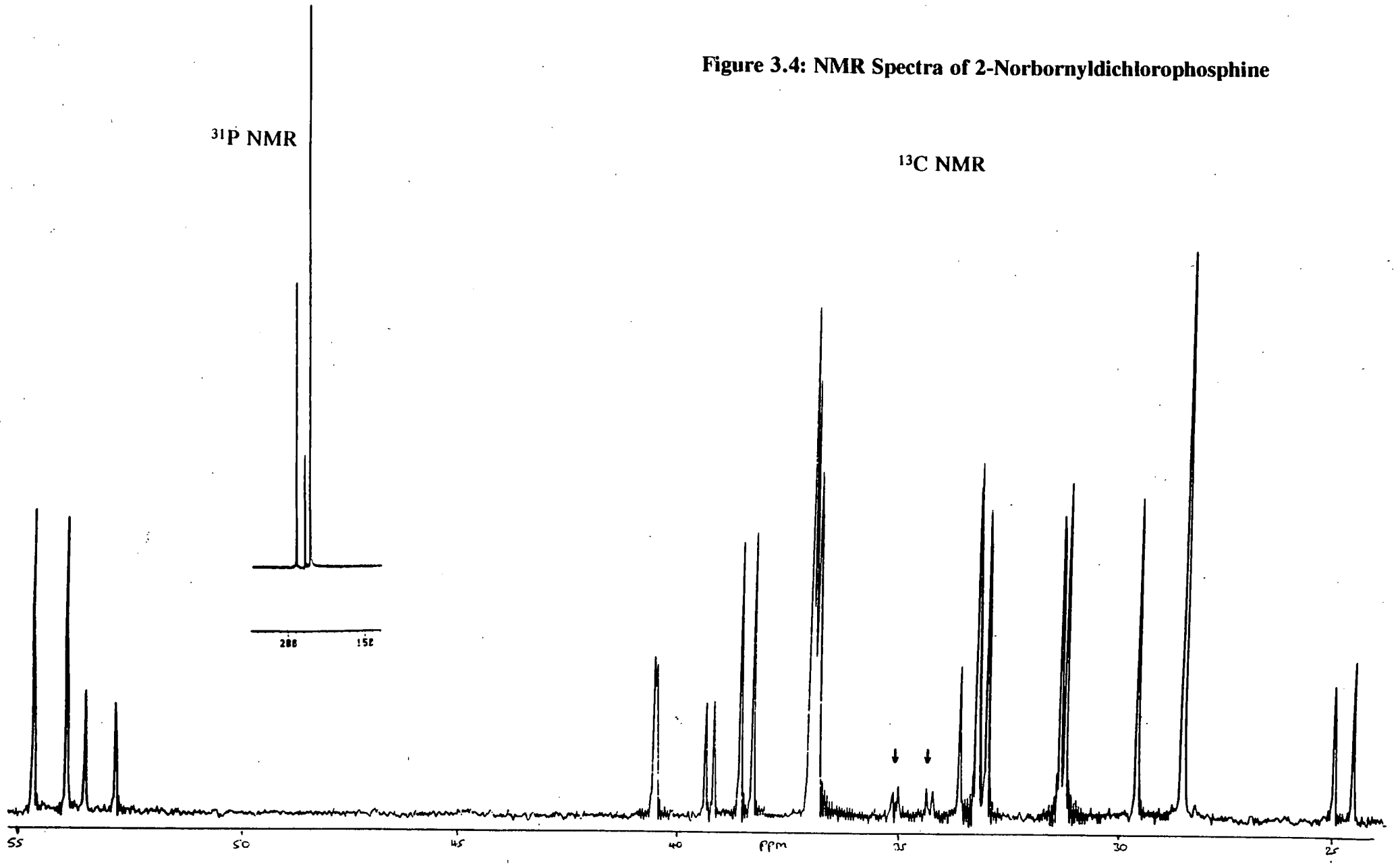
Table 3.1: ^{13}C NMR Data for Exo-2-Norbornyldichlorophosphine

alkene:	2-Norbornene		2,5-Norbornadiene	
^{13}C (neat)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	38.09	18.0	38.42	18.2
C_2	53.99	46.0	54.40	49.2
C_3	32.74	14.4	33.05	14.0
C_4	36.50	s	36.82	s
C_5	28.19	s	28.50	s
C_6	30.99	7.3	31.23	8.0
C_7	36.68	3.4	36.95	3.8

Table 3.2: ^{13}C NMR data for Endo-2-Norbornyldichlorophosphine

alkene:	2-Norbornene		2,5-Norbornadiene	
^{13}C (neat)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	38.92	11.5	39.24	11.7
C_2	52.89	43.8	53.25	43.1
C_3	34.64	8.8	---	---
C_4	33.23	s	33.54	s
C_5	29.24	s	29.54	s
C_6	24.50	27.3	24.75	27.2
C_7	40.13	3	40.47	2.7

Figure 3.4: NMR Spectra of 2-Norbornyldichlorophosphine



Both ^{13}C NMR spectra compare favourably with the literature compound[4], within experimental error, as described in the previous chapter. There are, however, some discrepancies between the two experimental ^{13}C NMR spectra, shown in Tables 3.1 and 3.2. The ^{13}C NMR spectra of the exo- derivative from both 2-norbornene and 2,5-norbornene are very similar, the chemical shifts and coupling constants of the phosphine derived from the diene being almost identical to those in the literature compound[4].

Two intense doublets observed in the products from 2-norbornene are not observed in the products from 2,5-norbornadiene. These are at 33.84 ppm (J= 8.8 Hz) and 34.64 ppm (J =8.8 Hz), this latter doublet being assigned as C_3 in the endo-derivative synthesised from 2-norbornene. Both doublets are detected at almost trace levels in the spectrum of the monophosphine obtained from 2,5-norbornadiene (↓, Figure 3.4). If these doublets are not from 2-norbornyldichlorophosphine another, unknown, alkyl phosphorus compound is present in the product from the mono-ene. Thus either C_3 in the endo- derivative has been incorrectly assigned in the mono-ene product, or it is not seen in the diene product, the former explanation being the more likely. Therefore the real C_3 resonance was probably not observed, possibly being covered by another resonance. Otherwise there is good agreement between both products and with the literature data.

The trans-conformation is adopted by the substituents in diphosphine ring systems. Thus the phosphorus groups attached to the cyclooctane and cyclopentane rings prefer the diequatorial conformation, but they adopt the P_{endo}, P_{exo} arrangement in the rigid norbornane ring. This is analogous to the diphosphines derived from the respective mono-alkenes. Only one diphosphine configurational isomer is synthesised in significant quantities from each diene, showing the reaction is very selective.

Although 1,5-cyclooctadiene reacts to produce bis-1,4-[dichlorophosphino]-cyclooctane, the diphosphines obtained from cyclopentadiene and 2,5-norbornadiene are the 1,2- and 2,3-derivatives respectively. Thus the dichlorophosphine unit only adds across one double bond of cyclopentadiene and 2,5-norbornadiene, the other double bond being completely hydrogenated. This is surprising because the phosphorus groups are on adjacent carbon atoms in the products and so are closer in the 1,2- or 2,3-isomer than in the other possible isomers. Therefore the predicted steric constraints are much greater in these isomers. The bis-2,5- or bis-2,6-[dichlorophosphino]norbornane isomers would be expected to adopt the sterically

favourable, lower energy, P_{exo},P_{exo} configuration, but surprisingly these isomers are not detected. This suggests both dichlorophosphine units add simultaneously, possibly in the form of diphosphorus tetrachloride. Conjugation of the double bonds in 1,5-cyclooctadiene followed by a Michael-type addition (1,4-addition) of the phosphorus groups would lead to formation of the observed 1,4-diphosphine product. There is however no evidence to support this theory, although P_2Cl_4 has been detected in the crude products[5]. The mechanism is discussed in more detail later.

3.3.5. Reaction with 1,3-Butadiene

Reaction of 1,3-butadiene with white phosphorus and phosphorus trichloride under high temperature and pressure conditions produces the expected 2-butyldichlorophosphine [2] and bis-1,2-[dichlorophosphino]butane [3]. Additionally small quantities of bis-1,4-[dichlorophosphino]butane [18] were also observed, but not isolated. Interestingly 1,4-diaryl-1,3-butadienes react with dichlorophosphines producing 2,5-phospholes[6], and a similar compound may have been detected under the experimental conditions. Because the double bonds are conjugated, Michael-type addition can occur producing the 1,4-disubstituted chain product, as also observed in the 1,5-cyclooctadiene ring system (see above). Additionally a reproducible singlet at 125.9 ppm in the decoupled spectrum and at 126.2 ppm in the proton coupled ^{31}P NMR was also observed, suggesting a dialkylchlorophosphine, with no phosphorus-hydrogen or unsymmetric phosphorus-phosphorus bonds had been prepared[1,2]. Surprisingly, a slightly different chemical shift for this compound was obtained in the proton coupled and decoupled modes. After three months under an inert atmosphere very little decomposition of the sample had occurred, although deliberate oxidative hydrolysis of the material generated a singlet in the proton coupled ^{31}P NMR at 43.7 ppm. Therefore the oxidised product, $R_2P(O)Cl$, rather than the hydrolysed and oxidised product, $R_2P(O)H$, was detected.

^{13}C NMR spectra of the R_2PCl fraction were recorded at both 62.896 MHz (Figure 3.1) and 125.759 MHz (Figure 3.2), and although samples were slightly contaminated with bis-1,2-[dichlorophosphino]butane (#), four multiplets were observed. DEPT135 (Figure 3.2 inset) showed no methyl groups were present, the alkyl group consisting of three methylene groups (CH_2) and one methyne group (CH) only. The alkyl group could not be the α,ω-disubstituted chain alkane (1,4-diphosphine) because this was observed, having two resonances. Therefore cycloalkyl based structures were proposed.

A phospholane ring structure, caused by 1,4-phosphorus bridging of butadiene, would produce a dialkylchlorophosphine. Being a symmetric compound, only 2 resonances would be observed in the ^{13}C NMR spectrum. However, unsymmetric substitution of the phospholane ring at either the 2- or 3-position would generate the observed 4 carbon resonances. A major feature of heterocyclic chemistry is the preference for ring substitution at the 2- rather than 3- position, therefore a 2-substituted phospholane compound was proposed. The nature of the substituent is important, and may be chlorine. However, MS determined the empirical formula of the compound as $C_8H_{14}PCl$, suggesting that a phospholane dimer, such as a 2,2'-diphospholane derivative, was the most likely product.

Butadiene is known to readily dimerise in the presence of a metal catalyst at high temperature under pressure forming 1,5-cyclooctadiene and other dimers[7]. The four multiplets observed in the NMR could thus be caused by a symmetric cyclooctane ring. ^{31}P NMR showed that a dialkylchlorophosphine was present, suggesting a 1,4- or 1,5-disubstituted bicyclic cyclooctane system had formed. The former ring system would generate four resonances in ^{13}C NMR, the 1,5-bicyclic system three resonances. Therefore a 1,4-phosphorus bridged cyclooctane structure such as 9-chloro-9-phosphabicyclo[4.2.1]nonane [21] or 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane [20] was proposed. The chlorine atoms in all these postulated products must adopt the same orientation because only one sharp resonance in the ^{31}P NMR spectrum is observed. In the bicyclic ring systems, the chlorine atoms will be fixed in either the syn- or anti-type configuration, as shown in Figure 3.5. Therefore two further possible cyclic dialkylchlorophosphine structures were proposed. The assignment of the ^{13}C NMR data is described below for all the postulated species.

The ^{13}C NMR spectrum recorded as a neat liquid at 62.896 MHz (Figure 3.1) showed that all four resonances were split into a doublet-of-doublets, suggesting all the carbon atoms are close to two phosphorus atoms. The carbon attached directly to a chlorophosphine group (α-carbon) is a CH group and gives a signal at 50.20 ppm (^1J = 49.1 Hz). A secondary coupling (J = 4.9 Hz) may be either a two-, three- or four bond coupling constant or caused by spatial interactions with phosphorus.

In the 2,2'-phospholane system, this α-carbon will be in the 2-position, also attached to the second phospholane ring, because it is a methyne group. The observed secondary coupling may result from two-bond coupling to the other phospholane ring, although the magnitude of this coupling constant is small (4.9

Hz). Interestingly, at 125 MHz this smaller coupling constant is not observed. Another α-carbon, in the 5-position, must also be present. This methylene group may be detected at 35.85 ppm (^1J = 33.9 Hz), having a low frequency chemical shift and small one-bond coupling constant for an α-carbon. Secondary coupling may be observed over four-bonds through the phosphorus centre, which is unusual. The β-Carbons are detected at 35.38 (C_3) and 28.45 (C_4) ppm. Higher frequency chemical shifts (and larger coupling constants) suggest a closer proximity to the phosphorus atoms, so the doublet-of-doublets at 35.38 ppm (^2J = 26.8 Hz) is assigned as C_3. The large two-bond coupling constant may result from steric interactions with the second phospholane ring.

Adjacent to the α-carbon, in the cyclooctane ring bicyclic ring system, are two different methylene groups, both in a similar environment, at 35.38 ppm ($C_{5/8}$; ^2J = 26.8 Hz) and 35.85 ppm ($C_{2/3}$; ^2J = 33.9 Hz). Both two-bond coupling constants are large suggesting these carbon atoms are in a sterically hindered position, close to the lone-pair orbital of the phosphorus atom(s) (as the dihedral angle is small), which is compatible with a bicyclic structure. The $C_{2/3}$ multiplet appears at lower frequency, with a larger two-bond coupling constant, because the carbon atoms suffer greater ring strain than those at $C_{5/8}$. Secondary couplings of J = 12.4 and 8.1 Hz respectively were also observed and are probably due to three-bond coupling. The nature of the coupling suggests that the diphosphabicyclo[4.2.2]decane structure is more likely than the phosphabicyclo[4.2.1]nonane structure. The low frequency resonance at 28.45 ppm must therefore be assigned as $C_{6/7}$ (^3J = 20.6 Hz), the secondary coupling (J = 4.6 Hz) possibly being caused by a four-bond or spatial interaction. The ^3J coupling at $C_{5/8}$ must therefore occur through C-P-P. Surprisingly a similar two-bond coupling of the α-carbon is not observed.

Proton coupled ^{13}C NMR showed that all the carbon-hydrogen coupling constants were similar. The multiplicites confirmed the information obtained from the DEPT135 data concerning the number of hydrogen atoms attached to each carbon atom. Phosphorus-carbon coupling did not aid interpretation of this spectrum, and proton coupled ^{13}C NMR spectra were very complex.

The ^{13}C NMR spectrum recorded in $CDCl_3$ at 125.759 MHz (Figure 3.2) resolved both multiplets at 35 ppm. However the resonances at 50 ppm and 28 ppm appeared as simple doublets, suggesting the secondary coupling observed in the neat liquid (at 62.896 MHz) may be caused by spatial interactions rather than those through bonds. Both doublet-of-doublets at 35 ppm are accurately resolved, permitting the coupling constants to be accurately calculated. Consequently, the

2,2'-diphospholane or diphosphabicyclo[4.2.2]decane system, rather than the phosphabicyclo[4.2.1]nonane system, appear to be present. ^{31}P-^{31}P coupling in the diphosphabicyclo[4.2.2]decane ring should affect the ^{13}C NMR spectrum, generating a complicated pattern of multiplets which includes triplets. The absence of this pattern suggests this bicyclic system may not be present.

Mass spectroscopy showed a peak in the CI spectrum at $^{M}/_{Z}$ 177 representing the parent ion of the phosphabicyclo[4.2.1]nonane system ($C_8H_{14}PCl$). However it may also represent a [MH-PCl] peak of the diphosphabicyclo[4.2.2]decane and 2,2'-diphospholane systems, which have an identical empirical formula, $C_8H_{14}P_2Cl_2$, the parent ion not being observed. All the peaks fit all proposed structures due to their similar chemical composition, and the structural similarity of the bicyclic derivatives. Within experimental error, elemental analysis (C,H,N,P,Cl) could not discriminate between any structure, the results being closer to the theoretical value of the 2,2'-diphospholane and diphosphabicyclo[4.2.2]decane ring systems.

Thus the data does not conclusively prove any of the postulated structures, although the NMR spectra strongly suggest the 2,2'-diphospholane system [19] rather than the diphosphabicyclo[4.2.2]decane ring system [20] is present. However, some of the observed multiplets and calculated coupling constants suggest some discrepancies exist between the postulated structure and isolated product. Conclusive proof, such as an X-ray structure of a metal complex containing the ligand, is necessary before the structure can be unambiguously assigned.

Diphosphabicyclo[4.2.2]decane chemistry is interesting, and therefore briefly reported below. The syn- and anti- configurational isomers of this diphosphabicyclo[4.2.2]decane system, shown in Figure 3.5, do not interconvert at ambient temperature according to the spectral data collected. However, at elevated temperature the anti- isomer of a similar molecule is converted into the syn- isomer[8,9]:

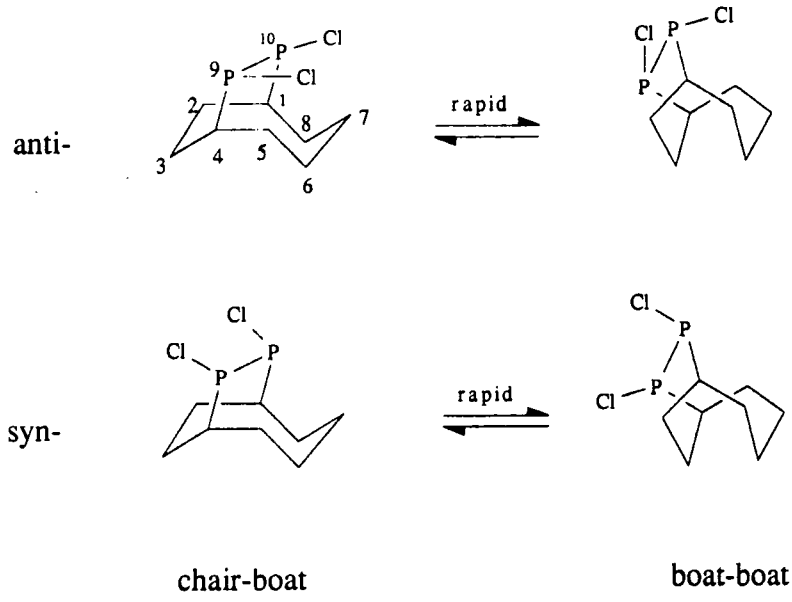


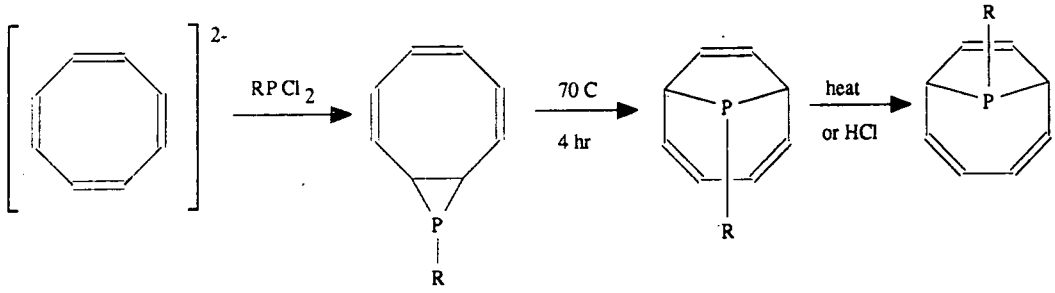
Figure 3.5: Configuration and Conformation in 9,10-Dichloro-9,10-diphosphabicyclo[4.2.2]decane

If the observed product is the diphosphabicyclo[4.2.2]decane, both configurational isomers may be present in the analysed sample, their respective spectra being superimposed, causing some of the multiplets to be misinterpreted as a doublet-of-doublets. However since the high temperature and pressure synthesis is achieved at over 200°C, probably the syn- isomer only is isolated from the autoclave. Thus the experimental spectra are probably not a mixture of both isomers superimposed upon each other and all the observed coupling constants are genuine, and arise from the syn-form. The chair-boat and boat-boat conformational isomers of cyclooctane rings rapidly interconvert at ambient temperatures and would not be separated on the NMR time-scale.

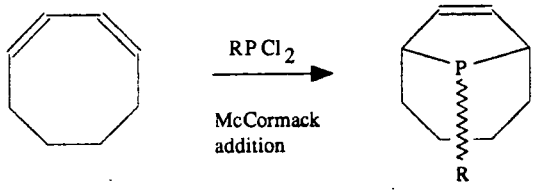
Both chlorine atoms must adopt the same orientation because only one sharp resonance appears in the ^{31}P NMR spectrum. The energy barrier for trialkylphosphine inversion is sufficiently high to allow resolution of enantiomers. However, more electronegative phosphorus substituents may reduce the energy barrier, increasing rate of inversion. There are significant steric interactions associated with all conformers. In the chair-boat conformation of the syn-isomer, chlorine atoms (which are in equivalent positions to the lone-pair orbitals of phosphorus in the anti-isomer) interact with the hydrogens of $C_{2/3}$, which themselves interact with the hydrogens of $C_{6/7}$. A similar interaction between the chlorine atoms or the lone-pair orbitals also occurs in the boat-boat isomer. This latter conformation also suffers transannular interactions as the axial hydrogens of C_2 and C_6 compete for the same space in all boat-boat forms of cyclooctane rings.

Previous syntheses of similar mono-bridged compounds have been reported. 9-Phenyl-9-phosphabicyclo[4.2.1]nonane and the bicyclo[3.3.1]nonane configurational isomer were first prepared[10,11] by reacting phenylphosphine, 1,5-cyclooctadiene and a radical initiator (such as di-t-butylperoxide) at elevated temperatures under high pressure. 1,4-Cyclooctadiene reacts with alkyldichlorophosphines producing a 9-alkyl-9-phosphabicyclo[4.2.1]nonene phosphonium salt[6], although this is not the only isomer. The stereochemistry and conformation[12] of the bicyclo[3.3.1]nonane analogue has also been investigated.

L.D. Quin has made many bridged ring systems containing phosphorus[13-7], including derivatives of 9-phosphabicyclo[4.2.1]nonene and nonatrienes[10,13,14]. Synthesis of this latter, fully unsaturated, bicyclic ring system is achieved by the reaction of alkyldichlorophosphines with cyclooctatetraene dianions (and the metal counter-ion):



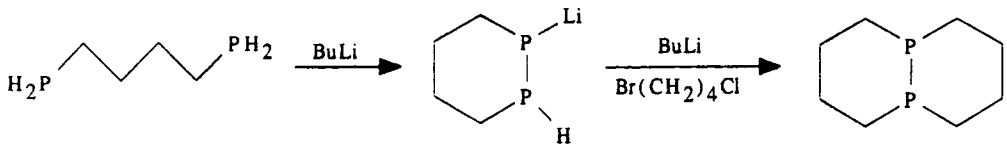
McCormack cycloaddition[8,18,19] (1,4-addition) of alkyldichlorophosphines with 1,3-cyclooctadiene generates the partially unsaturated 9-phosphabicyclo[4.2.1]non-2-ene system:



Stereochemical investigations of these unsaturated bicyclo[4.2.1]nonene systems confirms the existence of syn- and anti- substituents, the former isomer obtained in significantly higher yield (syn:anti, 4:1).

A versatile and elegant synthesis of phosphabicyclic ring systems, with a bridgehead phosphorus atom, was described by Issleib[20]. Free radical cyclisation of diallyl substituted monoalkylphosphines results in the formation of bicycloalkanes, as described in chapter 1. Other compounds containing

bridgehead phosphorus atoms have also been synthesised. 1,6-Diphosphabicyclo[4.4.0]decane derivatives, containing a phosphorus-phosphorus bond, have been prepared[21] from the reaction of 1,2-diphosphacyclohexane with 1,4-dihalobutane:



In the present study, varying the experimental ratio of 1,3-butadiene to phosphorus trichloride did not alter the nature of the products formed. As the diene concentration increased the yield of 2-butyldichlorophosphine also increased, relative to the yield of diphosphines. Optimum yields of bis-1,2-[dichlorophosphino]butane were obtained when excess phosphorus trichloride was used. The relative amount of dialkylchlorophosphine isolated did not change significantly as the mass of 1,3-butadiene was altered. Therefore a molar ratio of diene to phosphorus trichloride of approximately 1:1.8 was used to obtain the best overall yields.

The synthesis of this dialkylchlorophosphine, dichloro-2,2'-diphospholane [19] or 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane [20], was also attempted from 1,5-cyclooctadiene (as described above) because the dimerisation of butadiene is believed to be an important stage during the synthesis. No dialkylchlorophosphine was detected in the reaction with cyclooctadiene, suggesting butadiene dimerisation occurs as an integral part of the high pressure reaction rather than before the reaction began[7]. Therefore dimerisation of 1,3-butadiene under the reaction conditions may be mediated by the phosphorus atom or group.

3.3.6. Reaction with Aromatic Compounds

^{31}P NMR of the crude reaction products derived from styrene showed that many different types of phosphine had formed. No analysis of the purified products was possible because the distillation temperature of each component was very similar, preventing separation by fractional distillation. Resonances at 201.6, 194.0 and 185.9 ppm in the ^{31}P NMR spectrum of the crude mixture are in the normal alkyldichlorophosphine region[1,2]. These products may be formed by addition of the phosphorus group to the exocyclic double bond. Alternatively addition of the phosphorus group to the aromatic ring may be accompanied by reduction of the aromatic ring, producing a cyclohexyl derivative. The major

component was at 177.5 ppm which may be provisionally assigned as (methylbenzyl)dichlorophosphine [$C_6H_5CH(CH_3)PCl_2$]. The proximity of the aromatic ring would shield the phosphorus atom, moving the chemical shift to a relatively high frequency. An aryldichlorophosphine was detected at 162.1 ppm and there is evidence for a dialkylchlorophosphine at 114.0 ppm. The resonance at 162 ppm is close to the resonance for P_2Cl_4, which is a colourless, high boiling (180°C), unstable liquid which is normally detected at 155 ppm[1,22]. A similar resonance is also observed in the crude reaction products from natural products. However diphosphorus tetrachloride is a very unstable compound and readily decomposes above 0°C, so the samples are unlikely to contain this species. The precise identity of the 162.1 ppm compound remains unknown.

To test the reactivity of aromatic rings without exocyclic double bonds under the high temperature and pressure conditions, benzene and toluene were used as substrates. No reaction was observed, although red rather than white phosphorus was recovered from the autoclave after it had cooled to ambient temperature. No other phosphorus compounds, such as diphosphorus tetrachloride, were detected by ^{31}P NMR. Previous work[23] has shown that halobenzenes react with phosphorus, phosphorus trichloride and an iodine catalyst at 340°C producing the aryldichlorophosphine.

Thus the styrene ring reacts with phosphorus and phosphorus trichloride under high temperature and pressure conditions but benzene and toluene do not. The unexpected results from these aromatic substrates cannot easily be explained. A speculative reaction pathway involves decomposition of the exocyclic double bond of styrene, liberating hydrogen atoms and generating the polymer material. Subsequent reduction of at least one aromatic double bond with hydrogen generates an unsaturated cyclohexene ring which reacts with the phosphorus and phosphorus trichloride in the normal manner (see chapter 2). However this proposed reaction route involves destroying the aromaticity of the substrate ring, which is not usually a thermodynamically favoured reaction. Therefore more analysis of this system is needed before the postulated mechanism can be proven. Polymeric material is recovered from the reaction with styrene but not from the reaction with benzene or toluene. Interestingly, niobium compounds[24] are known to catalyse the reduction of phenylphosphines to cyclohexylphosphines at 100°C under hydrogen (80 atm). Iron in the autoclave walls may be involved in a similar reaction of alkenes, hydrogenating the carbon-carbon double bonds under the experimental high temperature and pressure conditions (260°C, >100 atm).

3.3.7. Reaction with Natural Products

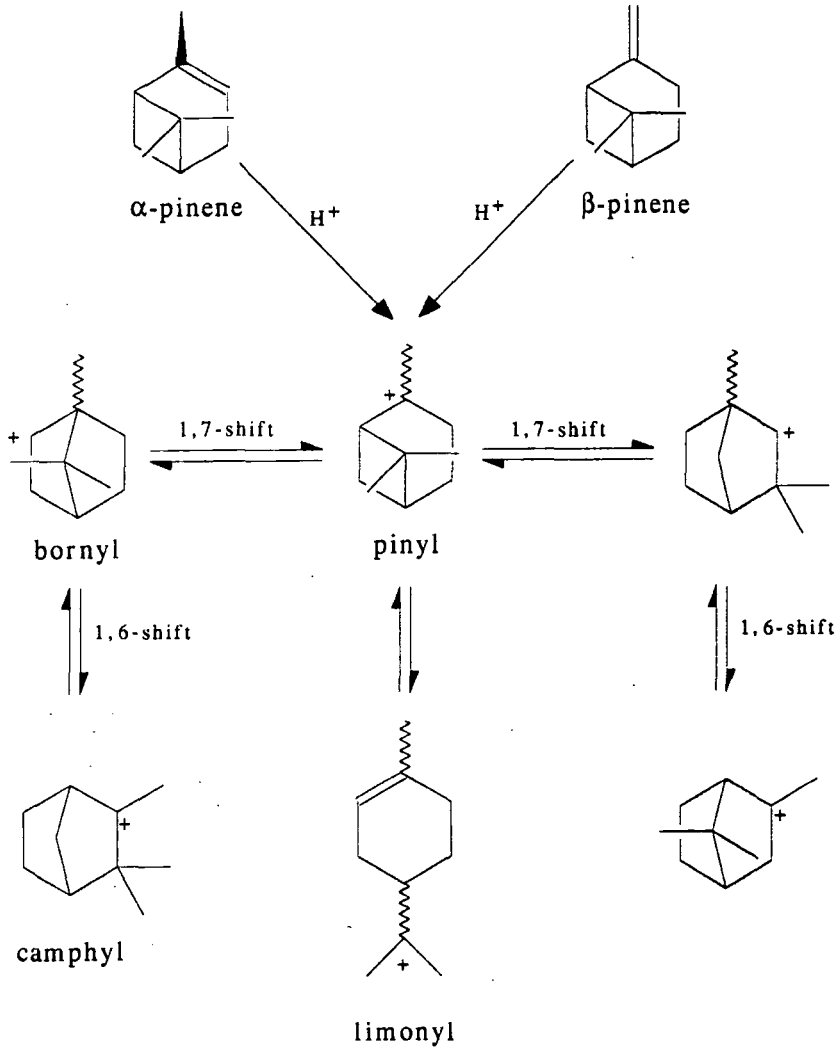
The products from the reaction with the terpenes could not be purified, even using a high resolution distillation system. ^{31}P NMR identified up to 15 components in the crude product mixture. Initial distillation yielded five major fractions, none containing a pure material. Repeated distillations concentrated the major fraction but could not isolate samples sufficiently pure for analysis. Attempts to obtain analytically pure samples using a high resolution, low volume, spinning column (approximately 30 theoretical plates) also failed. Therefore no structural information concerning the substitution and conformation of the terpene rings could be obtained. Mass spectroscopy of these fractions also gave no structural information.

The products from both α- and β-pinene were almost identical, as determined by ^{31}P NMR. In both crude mixtures major resonances at 196.0, 194.6 and 189.7 ppm were observed, suggesting the two pinenes interconvert by double bond isomerism under the reaction conditions.

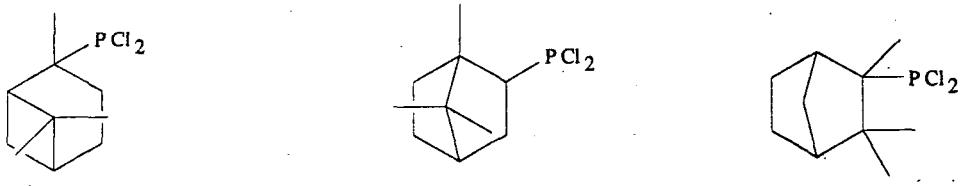
Camphene reacted, generating a major singlet at 161.5 ppm in the ^{31}P NMR spectrum. A similar resonance, although less intense, was also observed in the reaction products from pinenes. Analogously, a singlet at 196.0 was observed from both the limonene and pinene reactions, suggesting all the terpenes interconvert under the reaction conditions. However a singlet at 162 ppm was also observed in the reaction with styrene, which was provisionally assigned as an aryldichlorophosphine (see above). If all the singlets at 162 ppm represent the same compound, the phosphorus substituents are less electron withdrawing, so exerting a greater shielding effect, than in other dichlorophosphines analysed. This singlet could be caused by diphosphorus tetrachloride which boils at 180°C, but this is not possible since the molecule is very unstable. Several months after isolation of the reaction products the singlet was still observed suggesting it was not caused by diphosphorus tetrachloride. The origin of this resonance remains unknown.

The interconversion of terpenes by rearrangement, in the presence of a proton source, is called the Wagner-Meerwein Rearrangement, and is shown overleaf:

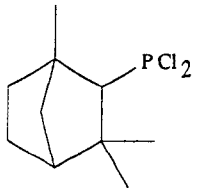
Figure 3.6: The Wagner-Meerwein Rearrangement of Terpenes



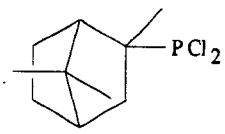
If an analogous reaction occurred in the autoclave, under the reaction conditions, the carbocations (or radical centres) in the rings could react with phosphorus and phosphorus trichloride. The expected major products would then be:



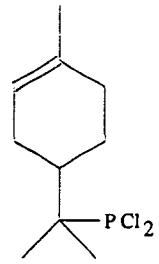
pinyl bornyl camphyl



fenchyl



isobornyl



limonyl

The chemical similarity of these phosphines would make separation very difficult. It is therefore not surprising that the reaction products were not isolated by fractional distillation. Preparative HPLC may provide an improved method of separation, each configurational isomer being resolved on the column prior to characterisation by NMR and MS. However a suitable solvent system would have to be developed, and the dichlorophosphine would have to be derivatised to prevent its decomposition and reaction with the mobile or stationary phases in the chromatograph. Unfortunately, during these operations the phosphine would be oxidised to the phosphine oxide, and would have to be subsequently reduced with trichlorosilane. Thus careful preparation of each sample would be necessary and significant quantities of the crude mixture injected to obtain enough pure material for analysis. This would be a very time consuming procedure and the quantities of pure phosphines isolated would be low.

The stereochemistry of the terpene substrate will be retained in the reaction products because the stereocentre is not at the reaction centre. Additionally a chiral centre, at the carbon atom attached to phosphorus (α-carbon), is normally generated in the reaction. Thus the terpenoid phosphine contains several chiral centres which would need resolving, but would probably be highly selective in asymmetric synthesis, as are chiral phosphines derived from menthol[25] and chiral organoboranes based on α-pinene[26].

The forcing experimental conditions and the possibility of natural product isomerism results in very little reaction selectivity. Combined with the chemical similarity of the reaction products, the difficulty of their separation and the moderate yields normally obtained, the high temperature and pressure synthesis of these natural product derivatives was inefficient. Other synthetic methods, such as Grignard and related techniques, would appear to be more appropriate in producing specific terpenoid phosphines. However these reactions are also sometimes complex. For example[27], α-terpinene reacts with methyldichlorophosphine, forming the hexahydrophosphindole oxide as the major product rather

than the expected natural product phosphine because the double bond in the starting material isomerises during the reaction.

3.3.8 Chirality

New stereocentres are generated at the α-carbon by the addition of the phosphorus group to the pro-chiral centre of an unsymmetric alkene, so many of the phosphines synthesised contain new chiral centres. 2-Substituted norbornane rings consist of a pair of diastereoisomers (endo- and exo- forms), due to their rigid structure. The 2,3-disubstituted norbornane ring exists in the trans-(P_{endo},P_{exo}) form due to the steric compression at these positions. Non-rigid rings, such as cyclooctane, rapidly interconvert into an equilibrium mixture of axial and equatorial conformers. 9,10-Dichloro-9,10-diphosphabicyclo[4.2.2]decane interconverts between the chair-boat and the less favoured boat-boat ring conformations, although the interconversion may be partially restricted. Because this is a rigid bicyclic ring, syn- and anti- diastereoisomers are also possible, although these may interconvert at elevated temperatures and under strong acid conditions. The inherent chiral properties of terpenes are complemented by the introduction of a stereocentre at the α-carbon. However, these isomers could not be separated or resolved, so their advantageous chiral properties could not be fully realised.

3.4. Mechanism

Previous theories concerning the reaction route were described in chapter 1. However, no theory explained the synthesis of 2-alkyldichlorophosphines. This study shows the mechanisms of mono- and diphosphine synthesis are probably different. Formation of the polymeric material and the associated source of hydrogen atoms is also discussed. Additionally several aspects of the reaction mechanism, other than 1,2-diphosphine synthesis and the formation of Markownikoff-type (2-alkyl) phosphines as the exclusive monophosphine product, are described.

3.4.1. Source of Polymeric Material

Analysis of the polymer material shows the presence of iron (3-6%), phosphorus (9-33%), chlorine (12-32%), carbon (39-41%) and hydrogen (2-6%), and is reported to be a mixture of iron phosphide and phosphorus halides[5], although some carbon-containing material must also be present. However the

physical appearance of the polymer varied from a brown viscous liquid to a black powder, usually coated around the inner surface of the autoclave. It is insoluble in water and organic solvents, so purification by solvent extraction, recrystalisation etc. were not possible. Consequently analyses were not reproducible. More polymer material is generated from the high pressure and temperature reaction with ethene than the other reactions, the mass produced decreasing as the molecular mass of the alkene increased. No polymer is observed in the blank experiment (with no alkene present) or from substrates that did not react under the reaction conditions, such as acetonitrile, benzene and toluene, although polymer material remained in the autoclave after the abortive reactions with perhaloalkenes.

Production of the polymer and the source of the hydrogen atoms seem to be related, both apparently are produced by the decomposition of the alkene under the high pressure and temperature conditions. However the amount of additional hydrogen in the product molecules generated in the diene reactions seems in excess of the amount of polymer produced, since in all these reactions sufficient hydrogen atoms were transferred to saturate all the alkene double bonds of the liquid products, as determined by ^{13}C NMR. To form monophosphine products from dienes requires a molar ratio of hydrogen atoms to dichlorophosphine units ($H:PCl_2$) of 3:1. Interestingly the only aromatic substrate (styrene) to react in the autoclave contains exocyclic carbon-carbon double bonds and generated polymeric material during the high pressure reaction. The autoclave temperature, reaction time or ratio of phosphorus trichloride to alkene do not significantly affect the mass of polymeric material formed.

Other possible sources of the hydrogen atoms may be hydrolysis products derived from phosphorus trichloride, such as hydrogen chloride, phosphorous and phosphoric acids. Although these impurities may be present, they occur only at impurity level. Reagents were distilled under nitrogen immediately before use and the autoclave contents were degassed before reaction commenced to ensure air was removed from the reactants.

Iron Catalysis

Iron, in some form, may act as a catalyst for the reaction forming diphosphines and polymeric material, since previous work suggests[28] that in the absence of an iron source no reaction occurs. Different forms of iron, such as iron powder, anhydrous iron (II) chloride or iron oxide, were mixed with the reagents prior to sealing the autoclave. However, in the present study, the nature

and amount of products formed was unaffected by the addition of iron in any form. Since the autoclave is made of iron, the inner walls probably provide a suitable surface to catalyse the reaction. Previous work[29] suggests the active form is iron (III) trichloride, although a more likely species would be an iron chloride (phosphorus trichloride) complex. Iron may be involved, as a heterogeneous catalyst, in the reduction of the alkene to form alkyl derivatives such as alkyldichlorophosphines. Copper, from the gasket, may also catalyse the reaction. After the reaction the gasket is always slightly corroded, as it is attacked by phosphorus trichloride.

3.4.2. Mechanism of Monophosphine Formation

The monophosphine derivatives formed were exclusively Markownikoff addition-type products, 2-alkyldichlorophosphines. This strongly suggests that the hydrogen atom adds across the double bond before the phosphorus group, generating the more stable secondary intermediate. If the phosphorus group adds before the hydrogen atom, 1-alkyl derivatives would be the predicted products. Thus the alkene is partially reduced by the hydrogen atoms before reaction with the phosphorus reagents occurs. This intermediate is likely to be a radical, because the reactants would not stabilise an ionic intermediate. Phosphorus trichloride readily undergoes homolytic fission in UV[30] generating dichlorophosphine radicals and chlorine radicals. A similar reaction under the reaction conditions used in this work, followed by reaction with an alkyl radical would generate the observed products. Phosphorus may be involved in this process, for example by abstracting the chlorine radical from phosphorus halide or by scavenging chlorine radicals. Alkyl radical attack of phosphorus trichloride producing an alkyldichlorophosphine and chlorine radical is also a valid reaction. Reaction of white phosphorus with phosphorus trichloride generating a radical intermediate of the type $\cdot P_4\text{-}PCl_2$ is thought unlikely, as no species of this type are known. Thus the processes involved are envisaged to be:

1. $C(R)H{=}CH_2 + H\cdot \rightarrow \cdot C(R)H\text{-}CH_3$
2. $PCl_3 \rightarrow \cdot PCl_2 + Cl\cdot$
3. $\cdot C(R)H\text{-}CH_3 + \cdot PCl_2 \rightarrow CH_3\text{-}CH(R)\text{-}PCl_2$

or $\cdot C(R)H\text{-}CH_3 + PCl_3 \rightarrow CH_3\text{-}CH(R)\text{-}PCl_2 + Cl\cdot$

This mechanism depends on the source of hydrogen atoms, without which the reaction would apparently not proceed. It also predicts the partial reduction of styrene to a cyclohexene system, possibly involving iron as the hydrogenation catalyst, coordinating the alkene and even the hydrogen radicals. The alkene may

also be coordinated to the iron centre during its subsequent reaction with the dichlorophosphine radical generated from phosphorus trichloride.

Stereoselectivity of 2-norbornyldichlorophosphine synthesis from the two norbornenes was observed in the ratio exo:endo of 3:1, suggesting the exo-diastereoisomer is the kinetically and thermodynamically favoured product. A polar mechanism would involve addition of a proton to the exo-face of the double bond, generating a transient π-complex as an intermediate, which could not be stabilised in the reaction matrix. Subsequent approach of the phosphorus would be expected from the endo-side, generating the endo-diastereoisomer. Addition of a hydrogen atom generates a secondary radical centre at the 2-position, which surprisingly does not migrate to the 1- or 7-positions. The dichlorophosphine unit may then approach the ring from either side, favouring the exo-face on steric grounds. Iron may mediate the reaction by coordinating the alkene and/or hydrogen atoms, although a higher diastereoselectivity would be expected if the metal centre was involved.

The mechanism of monophosphine synthesis thus involves addition of a hydrogen radical to the alkene, followed by reaction of this alkyl radical with a dichlorophosphine radical or phosphorus trichloride.

3.4.3. Mechanism of Diphosphine Formation

Diphosphine synthesis probably involves insertion of phosphorus trichloride into the double bond generating the chloroalkyldichlorophosphine. This reaction is known to occur in the presence of a free radical initiator[31]. Trace amounts of this compound were formed when ethene and phosphorus trichloride reacted at 250°C under pressure[32]. In the current study, the reaction of phosphorus trichloride and 1,5-cyclooctadiene at high temperature and pressure generated black polymeric material and produced several alkyldichlorophosphines, detected by ^{31}P NMR. Elemental analysis and ^{13}C NMR showed some of these products were probably chloroalkyldichlorophosphines. Reaction of chloroalkyldichlorophosphines with phosphorus trichloride and phosphorus at high temperature and pressure, possibly accompanied by hydrogen chloride elimination, has been reported[33] to produce diphosphines. Chloroalkanes are known[34] to react at high temperature with white phosphorus producing alkyldichlorophosphines (and some dialkylchloro-phosphines) via a radical mechanism. With red phosphorus in the presence of copper at 450°C, chloroalkanes react[34] in the vapour phase forming the analogous chlorophosphines, presumably via an insertion mechanism. In this study, further

reaction of the chloroalkyldichlorophosphines with white phosphorus and phosphorus trichloride under the high temperature and pressure conditions produced the bis[dichlorophosphino]alkane, although in very low yield (3% from 1,5-cyclooctadiene). Alkyldichlorophosphine products were also synthesised. Therefore synthesis of the chloroalkyldichlorophosphine may be catalysed or mediated by phosphorus. An equilibrium between the starting materials, chloroalkyldichlorophosphine and products may also operate. This mechanism would account for only one double bond of dienes reacting with the phosphorus reagents, generating the 1,2-diphosphine or 1,4-addition products. The proposed mechanism is shown below:

$$6\ CH_2{=}CH_2 + 6\ PCl_3 \rightarrow 6\ ClCH_2\text{-}CH_2PCl_2$$
$$6\ ClCH_2\text{-}CH_2PCl_2 + P_4 + 2\ PCl_3 \rightarrow 6\ Cl_2PCH_2\text{-}CH_2PCl_2$$

A second insertion mechanism[5] involves the addition of diphosphorus tetrachloride across the double bond. Both dichlorophosphine units are presumed to add simultaneously, accounting for both the 1,2- and 1,4-addition products. No traces of diphosphorus tetrachloride were detected in this work through reaction with phosphorus and phosphorus trichloride. However this diphosphorus species was observed[5] and may have been detected in the reaction products from terpenes.

Conjugated dienes, such as 1,3-butadiene, undergo Michael-type addition producing bis-1,4-[dichlorophosphino]alkanes. 1,5-cyclooctadiene isomerises under the reaction conditions, allowing a Michael-type addition to generate the 1,4-diphosphine. However, no 1,4-phosphorus bridged species were observed. Other dienes studied could not isomerise to a conjugated system, so only the 1,2-diphosphines were observed. The mechanism of 1,4-addition will be analogous to 1,2-addition.

The anomalous reaction of 1,3-butadiene to produce a dialkylchlorophosphine, probably either dichloro-2,2'-diphospholane or 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane, in addition to the chain products, suggests dimerisation under the reaction conditions may be mediated by phosphorus. Alternatively dimerisation may proceed via the reaction of 2-alkyldichlorophosphine with a second butadiene molecule. Of the postulated bicyclic derivatives, only the bicyclo[4.2.2]alkane ring system is detected, no bicyclo[3.3.2]alkane derivatives are observed.

More evidence is required before either mechanism for 1,2-diphosphine synthesis is conclusively proved, although the data collected in this work suggests the former insertion mechanism is favoured. The high temperatures and pressures involved in the reaction prevents complex or subtle mechanistic studies by spectroscopic methods.

3.5. Conclusion

All dienes reacted with phosphorus and phosphorus trichloride at high temperature and pressure producing alkyldichlorophosphines and bis-[dichlorophosphino]alkanes. No alkene resonances were detected at the end of the reactions by ^{13}C NMR, the double bonds having been saturated by either phosphorus groups or hydrogen atoms. Varying the ratio of alkene to phosphorus trichloride did not significantly alter the nature or yields of the products. Isolation of the products by fractional distillation was complicated by their high distillation temperature. However ^{31}P and ^{13}C NMR analysis provided sufficiently detailed information to characterise the products.

Cyclopentadiene dimer was cracked in the autoclave and reacted identically to cyclopentene, although with lower yields, forming the monophosphine and 1,2-diphosphine products. Similarly, 2,5-norbornadiene reacted analogously to 2-norbornene. However, the ^{13}C NMR spectra of the monophosphines produced were slightly different, possibly caused by impurities in the sample derived from the mono-ene. 1,5-Cyclooctadiene reacted generating the monophosphine and the Michael addition product, bis-1,4-[dichlorophosphino]cyclooctane, suggesting conjugation of the double bonds occurred prior to reaction with the phosphorus reagents. A small amount of the 1,2-diphosphine, but no bridged phosphine, was also detected.

Monophosphine, 1,2- and 1,4-diphosphine products were isolated from the reaction with butadiene. Additionally either a 2,2'-diphospholane or a 1,4-phosphorus bridged ring system was thought to be formed. The data, especially high resolution NMR spectra and elemental analysis, suggested the 2,2'-diphospholane compound was isolated. A second, alternative, interpretation of the data suggested a 9,10-diphosphabicyclo[4.2.2]decane rather than a 9-phosphabicyclo[4.2.1]nonane system had formed. Detailed analysis failed to fully characterise this product, although the 2,2'-diphospholane structure is favoured.

Natural product alkenes were also substituted with phosphorus groups under the reaction conditions. However, the terpene double bond readily isomerised under the reaction conditions. This rearrangement generated chemically similar products that could not be separated by fractional distillation. Aromatic rings and nitriles did not react under the reaction conditions, the only compounds isolated from the autoclave being red phosphorus and phosphorus trichloride.

Monophosphines are apparently formed by a simple radical mechanism, the hydrogen atom adding before the phosphine dichloride unit, generating a secondary radical intermediate and hence the 2-alkyldichlorophosphine. Hydrogen atoms arise during alkene decomposition, forming the polymeric material. Iron probably catalyses the reaction although the nature of the active species is not known.

A different, insertion, mechanism operates in the formation of diphosphines products. Evidence for the insertion of phosphorus trichloride into the alkene double bond, to generate a chloroalkyldichlorophosphine, was collected. Haloalkanes are known to react with phosphorus, producing alkyldihalo-phosphines. Phosphorus and phosphorus trichloride reacted with the chloroalkyl-dichlorophosphine intermediate under the normal reaction conditions forming the bis[dichlorophosphino]alkane. A second proposed mechanism, preforming diphosphorus tetrachloride, is thought not to occur because this highly reactive species was not detected in any product mixture. However, this mechanism cannot be disproved.

Before the chlorophosphines synthesised are used as transition metal ligands they are normally derivatised to increase the air-stability and reduce the reactivity of the phosphine. The following chapter describes this process.

3.6. References

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CHAPTER 4:

THE SYNTHESIS OF PHOSPHINE LIGANDS FROM DICHLOROPHOSPHINES

4.1. Introduction

Alkyldichlorophosphines are not widely used as ligands, the air-sensitive nature and high reactivity of the phosphorus-halogen bond restricting their wider application. However the reactivity of this bond means chlorophosphines are versatile precursors, and are readily converted into a variety of phosphines, phosphites and aminophosphines etc. suitable for transition metal chelation. Phosphorus-carbon bonds may be formed by coupling chlorophosphines with an organometallic reagent, such as alkyl lithium. Phosphorus-chalcogen or phosphorus-group V element bonds may be formed by reaction of chlorophosphines with compounds containing a suitably active hydrogen atom, for example alcohols. A base is usually required to neutralise the hydrogen halide side-product formed during the reaction, preventing oxidation of the phosphine.

4.2. Experimental

4.2.1. Synthesis of Bis-1,4-[dimethylphosphino]cyclooctane [22]

Dry magnesium turnings (13.3g, 0.55 mol) were weighed into a dry 500 ml round bottom flask fitted with a reflux condenser and a 100 ml pressure equalising dropping funnel. After being evacuated, the apparatus was filled with nitrogen and this inert atmosphere was maintained for the entire experiment. The pressure equalising dropping funnel was charged with methyl iodide (33 ml, 0.53 mol) in dry, degassed diethyl ether (20 ml). Approximately 10 ml of this solution was added to the magnesium turnings, and the remaining solution diluted to 100 ml with dry, degassed diethyl ether. Gently warming the reactants in the flask initiated reaction, then the remaining methyl iodide solution was added dropwise to the magnesium turnings over 90 minutes with rapid stirring. To maintain gentle reflux of the reactants during addition, the flask was occasionally cooled in an ice-bath. After complete addition, the Grignard solution was refluxed for three hours until all the magnesium turnings had reacted, cooled to ambient temperature and diluted with dry, degassed diethyl ether (200 ml) to aid rapid stirring.

The pressure equalising dropping funnel was recharged with bis-1,4-[dichlorophosphino]cyclooctane (40g, 0.13 mol) in dry, degassed diethyl ether (60 ml). With vigorous stirring, this dichlorophosphine solution was added dropwise to the cooled Grignard solution over 90 minutes forming a large amount

of white solid magnesium dihalide. After complete addition the solution was stirred at ambient temperature for three hours.

This solution was decanted and the residual solid washed with dry, degassed petroleum ether (40-60°C; 3 x 100 ml). These ether fractions were combined and the volatile components removed under reduced pressure at ambient temperature. The residual liquid was distilled under reduced pressure to yield pure bis-1,4-[dimethylphosphino]cyclooctane at 72±1°C (0.01 mmHg); yield 15.4g (52% from bis-1,4-[dichlorophosphino]cyclooctane).

A similar method was used to prepare bis-1,2-[dimethylphosphino]ethane (DMPE), bis-1,2-[dimethylphosphino]butane, 2-hexyldimethylphosphine, cyclohexyldimethylphosphine, 2-norbornyldimethylphosphine and dimethyl-2,2'-diphospholane or 9,10-dimethyl-9,10-diphosphabicyclo[4.2.2]decane from the related chlorophosphine.

Data

i. Bis-1,4-[dimethylphosphino]cyclooctane

distillation temperature: 72±1°C (0.01 mmHg).

yield: 15.4g (52% from dichlorophosphine).

NMR (neat); ^{31}P (ppm): -42.5 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	48.99	d	$^{1}J = 10.2$
$C_{2/3}$	35.00	d	$^{2}J = 6.7$
$C_{5/8}$	32.45	d	$^{2}J = 16.3$
$C_{6/7}$	30.70	s	---
Me_a	13.69	d	$^{1}J = 6.3$
Me_b	13.43	d	$^{1}J = 8.0$

MS; EI: 169 $[M\text{-}H_2PMe_2]^+$.

CI: 233 $[MH]^+$.

ii. Bis-1,2-[dimethylphosphino]ethane (DMPE)

distillation temperature: 54±1°C (0.7 mmHg).

yield: 7g (58% from bis-1,2-[dichlorophosphino]ethane).

NMR (neat); ^{31}P (ppm): -48.2 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/2}$	32.10	d	^{1}J = 15.8
$Me_{a/b}$	18.63	d	^{1}J = 7.7

MS; EI: 135 $[M\text{-}Me]^+$; 122 $[P_2Me_4]^+$; 107 $[P_2Me_3]^+$.
CI: 151 $[MH]^+$.

iii. Bis-1,2-[dimethylphosphino]butane

distillation temperature: 67±1°C (0.9 mmHg).

yield: 3g (52% from bis-1,2-[dichlorophosphino]butane).

^{31}P NMR (ppm in diethyl ether): -44.9 singlet.
-39.3 singlet.

iv. 2-Hexyldimethylphosphine

distillation temperature: 86±1°C (0.05 mmHg).

yield: 13g (40% from 2-hexyldichlorophosphine).

NMR (neat); ^{31}P (ppm): -41.6 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	15.08	d	^{2}J = 12.6
C_2	34.42	d	^{1}J = 15.2
C_3	30.18	d	^{2}J = 10.8
C_4	32.09	s	---
C_5	22.86	s	---
C_6	14.13	s	---
Me_a	12.24	d	^{1}J = 17.6
Me_b	11.34	d	^{1}J = 17.5

v. Cyclohexyldimethylphosphine

distillation temperature: 49±1°C (0.4 mmHg).

yield: 2g (43% from cyclohexyldichlorophosphine).

NMR (neat); ^{31}P (ppm): -41.7 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	43.34	d	$^1J = 9.5$
$C_{2/6}$	30.47	d	$^2J = 4.4$
$C_{3/5}$	24.53	s	---
C_4	17.85	s	---
Me_a	13.62	d	$^1J = 5.8$
Me_b	12.99	d	$^1J = 6.0$

vi. Dimethyl-2,2'-phospholane or 9,10-Dimethyl-9,10-diphosphabicyclo-[4.4.2]decane

The product oxidised before being analysed:

NMR (neat):

^{31}P (decoupled)(ppm):58.6 singlet.

^{31}P (^1H coupled)(ppm): 59.1 singlet.

vii. 2-Norbornyldimethylphosphine

distillation temperature: 28±1°C (0.2 mmHg).

yield: 7g (47% from 2-norbornyldichlorophosphine).

MS; EI: 156 $[M]^+$; 95 $[M\text{-}PMe_2]^+$;
CI: 157 $[MH]^+$; 96 $[MH\text{-}PMe_2]^+$; 62 $[HPMe_2]^+$.

NMR (neat):

Exo-Phosphorus

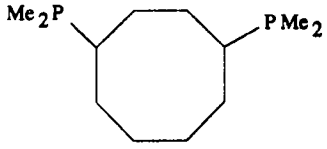
^{31}P (ppm): -40.1 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	39.29	d	$^2J = 14.8$
C_2	45.63	d	$^1J = 10.3$
C_3	34.73	d	$^2J = 11.9$
C_4	36.62	d	$^3J = 4.4$
C_5	29.33	s	---
C_6	31.69	d	$^3J = 6.8$
C_7	37.07	s	---
Me_a	14.65	d	$^1J = 16.5$
Me_b	11.91	d	$^1J = 16.7$

Endo-Phosphorus

^{31}P (ppm): -47.2 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	38.95	d	$^2J = 11.4$
C_2	44.64	d	$^1J = 8.6$
C_3	34.90	d	$^2J = 20.2$
C_4	40.51	d	$^3J = 2.9$
C_5	29.89	s	---
C_6	24.84	d	$^3J = 23.9$
C_7	36.93	s	---
Me_a	14.06	d	$^1J = 15.8$
Me_b	13.29	d	$^1J = 15.5$



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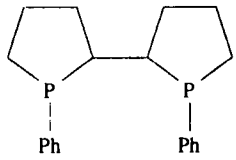

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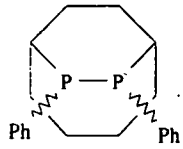


[24]

4.2.2. Synthesis of Diphenyl-2,2'-diphospholane [23] or 9,10-Diphenyl-9,10-diphosphabicyclo[4.2.2]decane [24]

Dry degassed diethyl ether (40ml) under nitrogen in a 250 ml round bottom flask fitted with a serum cap was cooled in an ice-bath. This inert atmosphere was maintained while the dialkylchlorophosphine (5g, 28 mmol) dissolved in the ether, and throughout the experiment. With vigorous stirring, phenyl lithium solution (1.8M in cyclohexane-ether; 18 ml, 32 mmol) was added dropwise to the chlorophosphine solution using standard syringe techniques. A white suspension of lithium chloride formed during the addition, this was removed by filtration after the mixture had been stirred at ambient temperature for three hours. Under reduced pressure the volatile components were removed from the filtrate leaving the dialkylphenylphosphine as an oily liquid; yield 1.3g, 23% from dialkylchlorophosphine.

NMR (neat); ^{31}P (ppm): -9.7 singlet.

^{13}C (ppm): 128.60, 128.21, 127.02, 126.72.

No alkyl resonances were observed.

4.2.3. Synthesis of Cyclohexyl diethylphosphite [25]

A 500 ml round bottom flask fitted with a 100 ml pressure equalising dropping funnel was evacuated and filled with nitrogen, this inert atmosphere was maintained for the entire experiment. The apparatus was cooled in an ice-bath and the flask filled with dry, degassed ethanol (20 ml, 0.34 mol), dry degassed triethylamine (40 ml, 0.29 mol) and dry, degassed diethyl ether (200 ml). Simultaneously the pressure equalising dropping funnel was charged with cyclohexyldichlorophosphine (10g, 0.54 mol) and dry degassed diethyl ether (80 ml). This solution was slowly added to the rapidly stirred, cool ethanol solution forming a bulky white precipitate of triethylamine hydrochloride. After being stirred for two hours at ambient temperature the solution was filtered and the solid residue washed with dry, degassed diethyl ether (2 x 50 ml). Under reduced pressure the volatile components of the combined ether fractions were removed leaving a pale yellow oil. Distillation of this oil under reduced pressure gave pure cyclohexyl diethylphosphite at 71±2°C (0.05 mmHg); yield 7.5g, 68% (from cyclohexyldichlorophosphine).

Using a similar method cyclooctyl diethylphosphite, bis-1,4-[diethoxyphosphino]cyclooctane and either diethoxy-2,2'-diphospholane or 9,10-diethoxy-9,10-diphosphabicyclo[4.2.2]decane were prepared from the corresponding chlorophosphine.

Data

i. Cyclohexyl diethylphosphite

distillation temperature: 71±2°C (0.05 mmHg).

yield: 7.5g (68% from cyclohexyldichlorophosphine).

NMR (neat); ^{31}P (ppm): 176.1 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	39.20	d	$^1J = 18.0$
$C_{2/6}$	33.35	d	$^2J = 9.6$
$C_{3/5}$	25.24	s	---
C_4	18.61	s	---
CH_2	16.41	s	---
Me	11.14	s	---

ii. Cyclooctyl diethylphosphite

distillation temperature: 86±2°C (0.07 mmHg).

yield: 6g (69% from cyclooctyldichlorophosphine).

NMR (neat) ^{31}P (ppm): 184.9 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
C_1	48.24	d	^1J = 19.3
$C_{2/8}$	37.52	d	^2J = 11.8
$C_{3/7}$	33.69	s	---
$C_{4/6}$	32.11	s	---
C_5	25.67	s	---
CH_2	17.68	s	---
Me	13.39	s	---

iii. Bis-1,4-[diethoxyphosphino]cyclooctane

distillation temperature: 140±2°C (1.0 mmHg).

yield: 8g (76% from 1,4-[dichlorophosphino]cyclooctane).

NMR (neat) ^{31}P (ppm): 184.0 singlet.

^{13}C (neat)	δ (ppm)	multiplicity	J [^{31}P-^{13}C] (Hz)
$C_{1/4}$	45.57	d	^1J =21.4
$C_{2/3}$	49.50	dd	^2J =13.6
			^3J = unres
$C_{5/8}$	28.33	d	^2J = 10.8
$C_{6/7}$	33.95	s	---
CH_2	12.62	d	^1J = unres
Me	17.32	s	---

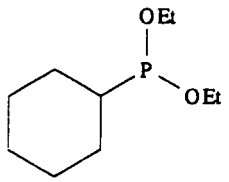
iv. Diethoxy-2,2'-diphospholane or 9,10-Diethoxy-9,10-diphospha-bicyclo[4.2.2]decane

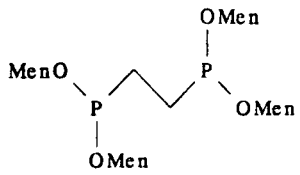
The product oxidised before being analysed:

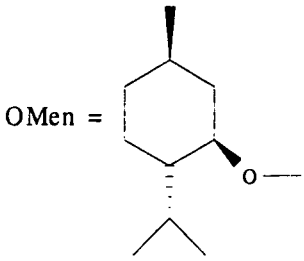
NMR (neat):

^{31}P (decoupled, ppm): 65.2 singlet

^{31}P (^1H coupled, ppm): 64.8 singlet







[25] [26]

4.2.4. Synthesis of Bis-1,2-[dimenthoxyphosphino]ethane [26]

(1R,2S,5R)-(-)-Menthol (29.6g, 0.19 mol) was dissolved in dry triethylamine (40 ml, 0.29 mol) and dry diethyl ether (250 ml) in a 500 ml round bottom flask fitted with a 100 ml pressure equalising dropping funnel. The apparatus was cooled in an ice-bath then evacuated and filled with nitrogen, this inert atmosphere was maintained throughout the reaction. The pressure equalising dropping funnel was charged with bis-1,2-[dichlorophosphino]ethane (10g, 43 mmol) and dry degassed diethyl ether (80 ml). With rapid stirring, this dichlorophosphine solution was slowly added to the cold menthol solution forming a bulky white precipitate of triethylamine hydrochloride. After complete addition, the solution was stirred at ambient temperature for three hours before the solid was removed by filtration and washed with dry degassed diethyl ether (2 x 50 ml). Under reduced pressure the volatile components from the combined ether fractions were removed leaving a pale yellow waxy solid. ^{31}P NMR showed this was bis-1,2-[dimenthoxyphosphino]ethane; yield 19g (62% from bis-1,2-[dichlorophosphino]ethane).

A similar method was used to prepare 2-hexyl dimenthylphosphite, cyclopentyl dimenthylphosphite, cyclohexyl dimenthylphosphite, 2-norbornyl dimenthylphosphite, cyclooctyl dimenthylphosphite and bis-1,4-[dimenthoxy-phosphino]cyclooctane from the corresponding dichlorophosphine.

An analogous method replacing menthol with catechol (10.1g, 92 mmol) was used to prepare bis-1,2-[bis,catechylphosphino]ethane [27] or the dicatechyl derivative [28], and bis-1,4-[bis,catechylphosphino]cyclooctane or the dicatechyl analogue.

The products were not purified by fractional distillation due to their high distillation temperature. Consequently they were not fully characterised. However the ^{31}P NMR data (below) shows only dialkylphosphites are present. The ^{13}C

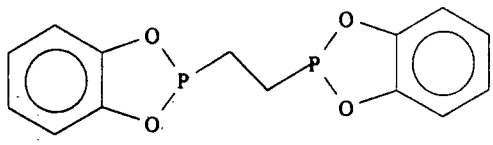
NMR data could not be fully interpreted, but suggested the only notable impurity was menthol (or catechol).

^{31}P NMR Data ($CHCl_3$):

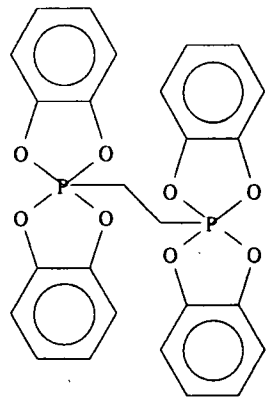
Alkyl dimenthylphosphite	δ (ppm)
Bis-1,2-[dimenthoxyphosphino]ethane	183.3
2-Hexyl dimenthylphosphite	180.7
Cyclopentyl dimenthylphosphite	182.4
Cyclohexyl dimenthylphosphite	179.6
2-Norbornyl dimenthylphosphite	178.9, 184.7
Cyclooctyl dimenthylphosphite	181.9, 180.5
Bis-1,4-[dimenthoxyphosphino]cyclooctane	183.8, 182.6

Alkyl dicatechylphosphite*	δ (ppm)
Bis-1,2-[bis,catechylphosphino]ethane	0.3
Bis-1,4-[bis,catechylphosphino]cyclooctane	2.6

* The values tabulated suggest a P^v species is present, such as a dicatechyl derivative or a phosphine oxide.



[27]



[28]

4.2.5. Synthesis of 2-Norbornyl-1,3,2-dioxaphosphepane [29]

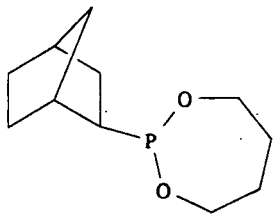
1,4-Butanediol (2.6g, 29 mmol) was dissolved in dry degassed triethylamine (40 ml, 0.29 mol) and dry degassed diethyl ether (250 ml) in a 500 ml round bottom flask fitted with a 100 ml pressure equalising dropping funnel. After cooling in an ice-bath the flask was evacuated and filled with nitrogen, this inert atmosphere was maintained during the experiment. The pressure equalising dropping funnel was charged with 2-norbornyldichlorophosphine (10g, 51 mmol)

and dry degassed diethyl ether (80 ml). This solution was slowly added to the vigorously stirred alcohol solution forming a white precipitate of triethylamine hydrochloride, which was removed by filtration after the solution had stirred at ambient temperature for three hours. The solid was washed with dry degassed diethyl ether (2 x 50 ml), and the volatile components from the combined ether fractions removed under reduced pressure leaving a pale yellow solid. ^{31}P NMR showed this contained dialkylphosphite compounds. However the products were not further purified.

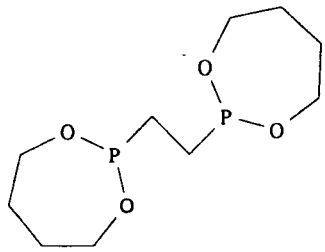
A similar method was used to prepare bis-1,2-[1,3,2-dioxaphosphepano]ethane [30]; 2-hexyl-1,3,2-dioxaphosphepane; cyclohexyl-1,3,2-dioxaphosphepane; bis-1,2-[1,3,2-dioxaphosphepano]cyclohexane; cyclo-octyl-1,3,2-dioxaphosphepane and bis-1,4-[1,3,2-dioxaphosphepano]cyclooctane.

^{31}P NMR Data ($CHCl_3$):

Alkyl-1,3,2-dioxaphosphepane	δ (ppm)
2-Norbornyl-1,3,2-dioxaphosphepane	186.5, 179.5
Bis-1,2-[-1,3,2-dioxaphosphepano]ethane	180.7
2-Hexyl-1,3,2-dioxaphosphepane	187.3, 186.9, 182.5
Cyclohexyl-1,3,2-dioxaphosphepane	183.8, 183.3
Bis-1,2-[-1,3,2-dioxaphosphepano]cyclohexane	185.5, 185.0, 181.0
Cyclooctyl-1,3,2-dioxaphosphepane	183.2, 174.2
Bis-1,4-[-1,3,2-dioxaphosphepano]cyclooctane	180.5



[29]



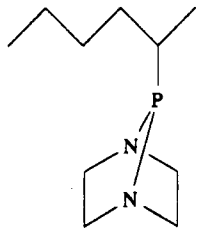
[30]

4.2.6. Synthesis of 7-(2-Hexyl)-7-phospha-1,4-diazanorbornane [31]

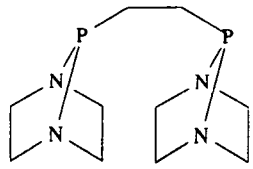
Piperazine (2.5g, 29 mmol) was dissolved in dry triethylamine (40 ml, 0.29 mol) and dry diethyl ether (250 ml) in a 500 ml two neck round bottom flask fitted with a reflux condenser and 100 ml pressure equalising dropping funnel. The apparatus was cooled in an ice-bath then evacuated and filled with nitrogen. This inert atmosphere was maintained during the experiment. The pressure

equalising dropping funnel was charged with 2-hexyldichlorophosphine (10g, 53 mmol) and dry degassed diethyl ether (80 ml). This dichlorophosphine solution was slowly added to the rapidly stirred, cold piperazine solution forming a white precipitate of triethylamine hydrochloride. After complete addition the solution was refluxed for three hours to ensure complete reaction, then cooled to ambient temperature. The solid was removed by filtration and washed with dry degassed diethyl ether (2 x 50 ml). Under reduced pressure, at ambient temperature, the volatile components from the combined ether fractions were removed leaving a pale yellow waxy solid. ^{31}P NMR showed the presence of diaminophosphines. However the products were not further purified.

A similar method was used to prepare bis-1,2-[7-phospha-1,4-diazanorbornyl]ethane [32]; 7-(-2-norbornyl)-7-phospha-1,4-diazanorbornane; 7-(cyclooctyl)-7-phospha-1,4-diazanorbornane and bis-1,4-[-7-phospha-1,4-diaza-norbornyl]cyclooctane.



[31]



[32]

^{31}P NMR Data ($CHCl_3$):

7-Alkyl-7-phospha-1,4-diazanorbornane	δ (ppm)
7-(-2-Hexyl)-7-phospha-1,4-diazanorbornane	100.5, 100.2
Bis-1,2-[7-phospha-1,4-diazanorbornyl]ethane	141.6, 91.8
7-(-2-Norbornyl)-7-phospha-1,4-diazanorbornane	95.9, 94.2
7-Cyclooctyl-7-phospha-1,4-diazanorbornane	134.3, 95.7
Bis-1,2-[7-phospha-1,4-diazanorbornyl]cyclooctane	116.3, 99.2

4.3. Discussion

Isolation of the products was attempted by fractional distillation under reduced pressure. As the molecular mass of the products increased the distillation temperature also rose preventing purification of some products, such as dimenthylphosphites. Dioxaphosphepane products could not be separated due to their similar chemical properties; the exact product nature is discussed later.

Similarly, products from the reaction with piperazine were not separated. These impure products could not be fully characterised. However the corresponding dichlorophosphine had previously been unambiguously characterised. The alkyl group does not participate in these derivatisation reactions, only the nature of the phosphorus centre is altered. Therefore ^{31}P NMR was sufficient to determine the nature of the products, the instrumental parameters are shown in appendix 1.

High yields of all derivatives were obtained from dichlorophosphines. Most product losses were caused either by oxidation of the dichlorophosphine, the derivative or by adhesion of the derivative to the solid side-products, such as triethylamine hydrochloride.

^{13}C NMR chemical shifts of the products were generally similar to those of the analogous dichlorophosphine, the inductive effect of the chlorine atoms attached to the phosphorus apparently having very little effect on the chemical shift of the alkyl group. ^{31}P-^{13}C Coupling constants were smaller in dimethylphosphines and diethylphosphites than in the corresponding dichlorophosphines because alkyl and alkoxy groups are much less electron withdrawing than chlorine[1]. No three-bond coupling constants in these derivatives were observed, for a similar reason. ^{2}J [^{31}P-^{13}C] coupling constants in ^{13}C NMR provide detailed stereochemical information concerning the phosphorus lone-pair orbital orientation, and its influence on the alkyl substituent (as described in chapter 2). Large dihedral angles result in small ^{2}J coupling constants because the phosphorus lone-pair orbital projects away from the alkyl group, minimising any phosphorus-β-carbon interactions.

4.3.1. Reactions with Organometallic Reagents

Dimethylphosphines were readily isolated by fractional distillation in approximately 50% yield from the dichlorophosphine. Their distillation temperature was significantly lower than that of the dichlorophosphine; for example 2-norbornyldimethylphosphine distilled at ambient temperatures under reduced pressure. Most Grignard methods advise quenching the activated metal with saturated aqueous ammonium chloride before isolating the products. However this procedure invariably oxidised the phosphine and produced more magnesium dihalide as a fine precipitate, which was difficult to filter efficiently. Therefore isolation of the phosphine was complicated, and this step consequently omitted in this work. A slight molar excess of magnesium was used in producing the Grignard reagent, preventing any unreacted methyl iodide oxidising the phosphine to the phosphonium salt. Bis-1,2-[di-n-butylphosphino]ethane (DBPE)

was made and characterised using NMR by Lord Lewis[2] using similar Grignard methods. L.D. Quin suggested[3,4] that reverse Grignard methods, adding the Grignard reagent to the dichlorophosphine solution, may generate higher yields although this was not attempted in this work.

In many dimethylphosphines, the methyl groups were non-equivalent, being in a different chemical environment and therefore prochiral. These groups were detected at slightly different frequencies in the ^{13}C NMR; for example the methyl groups in 2-hexyldimethylphosphine were observed at 12.24 and 11.34 ppm. There is very little steric strain in all these phosphines, the ^{1}J coupling constants of both methyl groups being very similar (17.6 and 17.5 Hz respectively) and of the expected magnitude for a phosphorus-methyl coupling constant (approximately 15 Hz)[5]. The observed phosphorus-methyl coupling constants in bis-1,4-[dimethylphosphino]cyclooctane were low (6.3 and 8.0 Hz) suggesting the groups were not interacting with the ring, minimising the transannular interactions by preferentially adopting the diequatorial conformation.

Comparison of ^{2}J [^{31}P-^{13}C] coupling constants in dimethylphosphines shows a range of values from 4 to 20 Hz, with a typical constant of 11 Hz. Large dihedral angles, when the lone-pair orbital on phosphorus is aligned away from the β-carbon of the alkyl group, generate low two-bond coupling constants. For example the low value observed from cyclohexyldimethylphosphine (^{2}J = 4.4 Hz) shows the lone-pair orbital extends away from the ring framework. However the lone-pair orbital is apparently closer to $C_{5/8}$ than $C_{2/3}$ in bis-1,4-[dimethylphosphino]cyclooctane because the former two-bond coupling constant is 10 Hz larger (16.3 and 6.7 Hz). Higher values of the ^{2}J coupling constants for exo-C_1 and endo-C_3 in 2-norbornyldimethylphosphine (14.8 and 20.2 Hz) suggest the lone-pair orbital is closer to these β-carbons than those at exo-C_3 and endo-C_1, as predicted by molecular models.

The experimental NMR data for exo- and endo-2-norbornyl-dimethylphosphine (Figure 4.1) is compared with published data[6] in Tables 4.1, 4.2 and 4.3.

Table 4.1: ^{31}P NMR Data for 2-Norbornyldimethylphosphine Isomers

^{31}P	Experimental (ppm)	Literature[6] (ppm)
Exo	-40.1	-43.2
Endo	-47.2	-47.4

Figure 4.1: NMR Spectra of 2-Norbornyldimethylphosphine

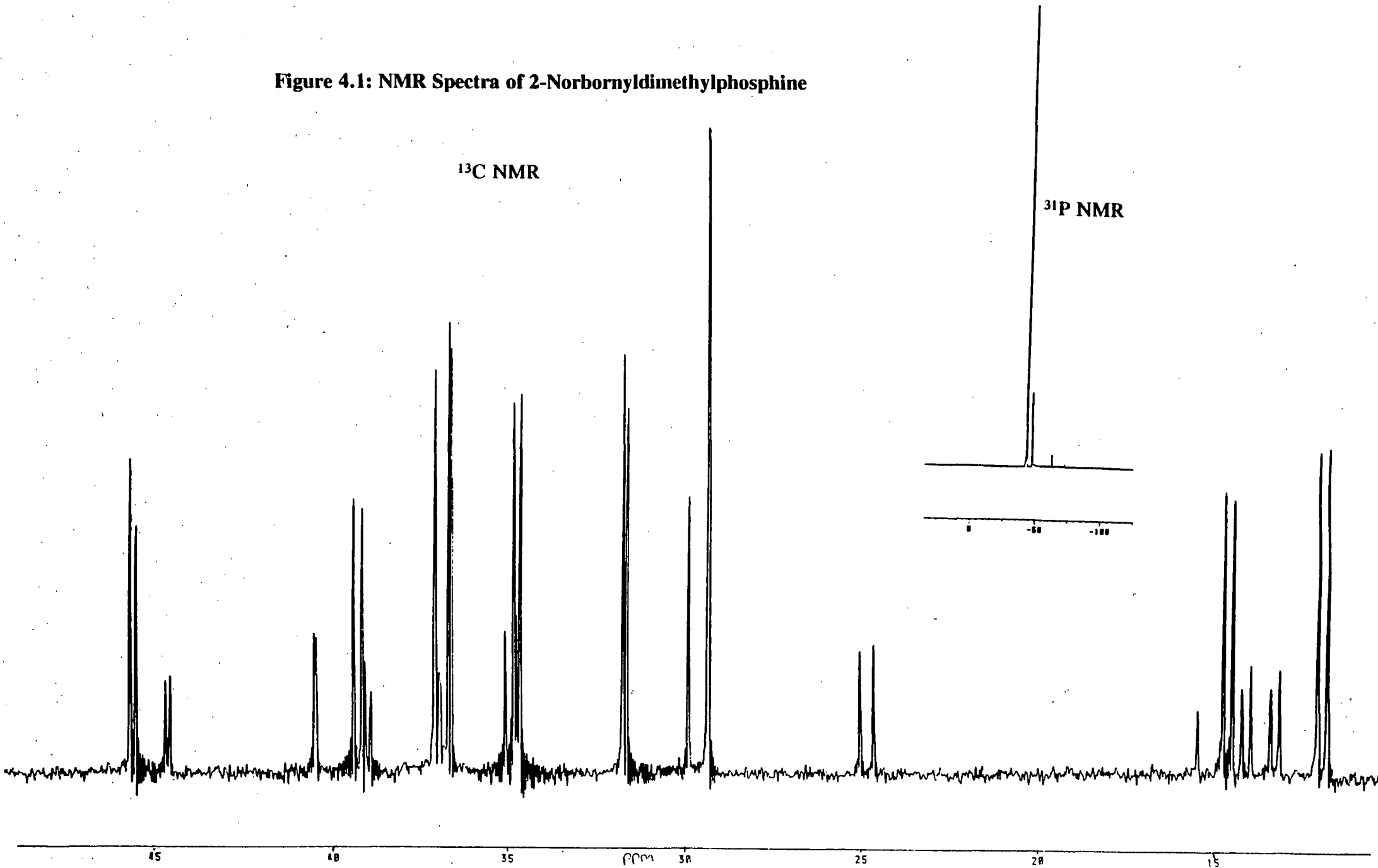


Table 4.2: ^{13}C NMR Data for Exo-2-Norbornyldimethylphosphine

^{13}C	Experimental		Literature[6]	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	39.29	14.8	38.2	14.8
C_2	45.63	10.3	44.2	8.5
C_3	34.73	11.9	33.7	11.0
C_4	36.62	4.4	35.7	3.5
C_5	29.33	s	28.2	s
C_6	31.69	6.8	30.7	6.3
C_7	37.07	s	36.0	2.3
Me_a	14.65	16.5	13.7	13.3
Me_b	11.91	16.7	10.7	14.8

Table 4.3: ^{13}C NMR Data for Endo-2-Norbornyldichlorophosphine

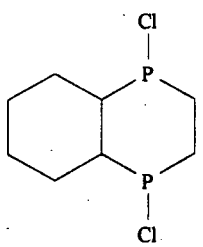
^{13}C	Experimental		Literature[6]	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
C_1	38.95	11.4	38.0	8.5
C_2	44.64	8.6	43.3	6.3
C_3	34.90	20.2	33.8	18.3
C_4	40.51	2.9	---	---
C_5	29.89	s	28.9	s
C_6	24.84	23.9	23.9	22.8
C_7	36.93	s	39.5	3.5
Me_a	14.06	15.8	12.8	11.6
Me_b	13.29	15.5	11.9	11.6

The literature compound was synthesised from phosphorus trichloride and 2-chloronorbornane, followed by reaction with methyl iodide, using Grignard methods. In both syntheses the diastereoisomers could not be separated and so mixtures were used in determining the structures[6]. Because of the greater intensity of the exo- signal, the structures are easily resolved. For both

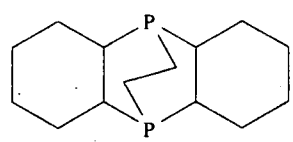
diastereoisomers there is good agreement between the experimental and literature data, the slight differences being similar to those described for the experimental and literature dichlorophosphines in chapter 2.

Both the experimental and literature data are similar. However, all the experimental ^{13}C NMR resonances appear at about 1 ppm lower than the literature values, probably caused by either a systematic error in the spectrometer resolution (as in chapter 2; the experimental data was acquired at 62.896 MHz, the literature data at 15 MHz) or by a slight shift in the reference value. The experimental phosphorus-methyl coupling constants are higher than the literature values, and if genuine suggest the methyl groups in the experimental compound are more sterically compressed than those in the literature compound, this is unlikely for the same compound. Similarly, the coupling constants in the endo-isomer are higher in the experimental data than the literature data. This may be due to steric differences between the two compounds, which is unlikely, or differences in the spectrometers used. At C_7 in both diastereoisomers, a singlet was observed in the experimental spectrum, although a doublet was reported in the literature.

Syntheses of 1,4-diphosphadecalin derivatives such as [33] and [34] were attempted using Grignard methods. 1,2-cyclohexyldi[magnesium bromide] was prepared by mixing cyclohexene with a dilute bromine solution producing 1,2-dibromocyclohexane, which reacted with magnesium at low temperature. Subsequent reaction of this Grignard reagent with bis-1,2-[dichlorophosphino]ethane or the cyclohexane analogue produced a large amount of white solid. However ^{31}P NMR of this crude reaction solution showed the phosphorus-chlorine bonds had not reacted. After removing the solid and reducing the volume of liquid under reduced pressure at ambient temperature, the ^{31}P NMR showed only the dichlorophosphine starting material was present. Elemental analysis of the solid showed the presence of magnesium and halogens. Very little carbon, hydrogen and phosphorus was detected.



[33]



[34]

Residual chlorophosphines were quenched with methylmagnesium iodide, generating methylphosphines. ^{31}P and ^{13}C NMR suggested these reaction products were dimethyl derivatives, proving the 1,2-diGrignard reagent had decomposed. Reactions with 1,2-diiodocyclohexane produced similar results. The Grignard reagent probably decomposed during the reaction producing magnesium dibromide. Similar reactions are known to occur in other 1,2-diGrignard reagents. Therefore this work was discontinued. A more elegant synthesis of these ring systems may involve coupling vinyl phosphines with phosphorus-hydrogen bonds. Both starting materials are readily prepared from dichlorophosphines, either by Grignard methods or lithium aluminium hydride reduction. However these reactions were not attempted.

Only one reaction with phenyl lithium was performed, attempting to synthesise dialkylphenylphosphine from the chlorophosphine, and hence prove its structure. ^{13}C NMR of the product only showed an aromatic multiplet, so no structural information was obtained. Oxidation of this product generated a singlet at 26.9 ppm in the proton coupled ^{31}P NMR. Diphenyl derivatives may be routinely prepared by the reaction of triphenylphosphine with lithium. Subsequent metal coupling of this phosphide with a haloalkane generates the alkyldiphenylphosphine.

4.3.2. Reaction with Alcohols

Dichlorophosphines reacted readily with alcohols producing the corresponding dialkylphosphite. All phosphites readily undergo the Arbusov reaction[7,8] in the presence of haloalkanes or hydrogen halides, nucleophilic displacement of the halogen atoms accompanying oxidation of the phosphite.

$$RP(OR)_2 + 2\ R'Cl \rightarrow RP(O)(R')OR$$
$$RP(OR)_2 + 2\ HCl \rightarrow RP(O)(H)OR \rightarrow RP(O)(H)OH$$

Therefore dialkylphosphites were prepared in the presence of a tertiary amine base to neutralise the hydrogen chloride produced during the reaction, and were stored under an inert atmosphere to prevent their decomposition.

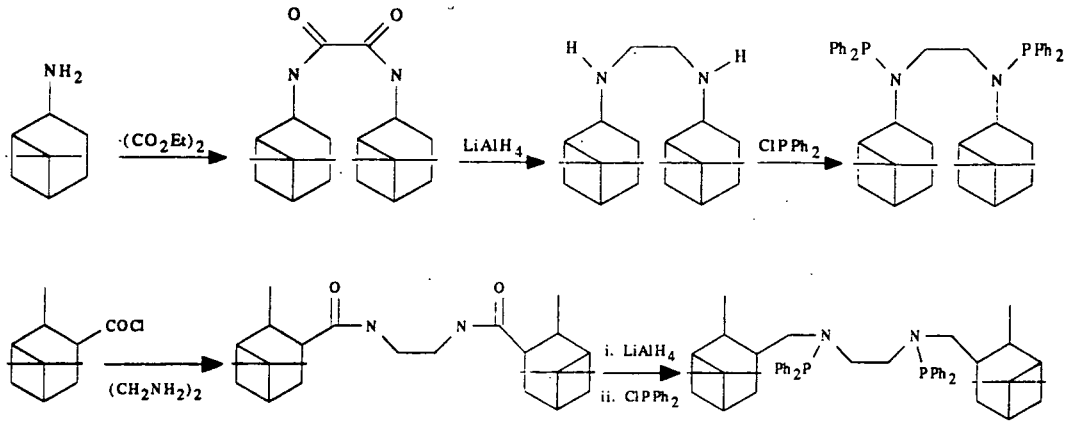
Although there is a significant difference in phosphorus-methyl coupling constants of dimethylphosphines, no similar coupling constants are observed for diethylphosphites. The position of the oxygen atom in phosphites prevents ^{13}C-^{31}P coupling and generally reduces steric compression around phosphorus, resulting in a smaller cone angle[9]. Therefore, the lone-pair phosphorus orbital in

diethylphosphites will be further away from the parent alkyl group than in the analogous diethylphosphines and so will interact with the β-carbons less. The smaller steric size of dimethylphosphines reduces the phosphine cone angle, and thus the β-carbon interactions.

A very high chemical shift (49.50 ppm) for $C_{2/3}$ in bis-1,4-[diethoxyphosphino]cyclooctane is observed, suggesting the carbon atoms are sterically compressed. However the coupling constants (^2J = 13.6 Hz, ^3J = unres.) do not confirm this hypothesis.

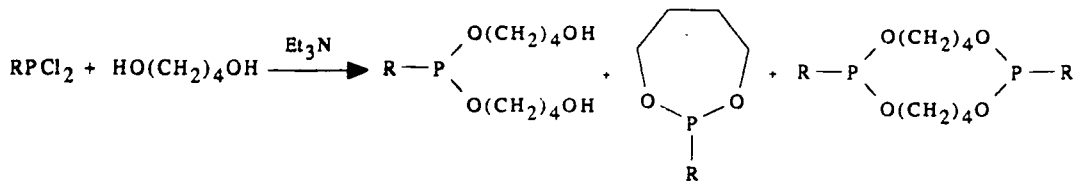
Menthol rings probably retained their chirality during the reaction, generating dimenthylphosphites containing substituent chirality. However the isomers were not resolved because the products could not be purified. Two resonances were observed in the ^{31}P NMR spectra of the cyclooctyl and 2-norbornyl dimenthylphosphites, caused by the bulky menthyl rings being in different orientations and environments. Endo- and exo- forms of the norbornyl derivative will generate separate resonances (as observed in the dichloro- and dimethyl- derivatives). Cyclooctyl dimenthylphosphite and the corresponding diphosphine generate two different resonances. Slow interconversion between the axial and equatorial forms in the monophosphine may cause these two resonances to be observed. While slow interconversion may be expected, a significant population of the equatorial conformation would also be predicted. Unfortunately only measurements of this system at ambient temperatures were possible. A similar explanation may account for the resonances observed in the diphosphine. Alternatively, both phosphorus atoms may adopt a different orientation with respect to their substituents and the cyclooctyl ring, thus producing two resonances.

Menthyl substituted phosphorus compounds, containing phosphorus-ring bonds, may be synthesised by Grignard methods[10,11]. However these reactions were not attempted, although similar preparations have been undertaken previously using the following approaches. Methyldichlorophosphine reacts with α-terpinene[12] forming a hexahydrophosphoindole derivative rather than the expected McCormack cycloaddition product, 7-phosphanorbornene. Camphor dimethylhydrazone reacts with butyl lithium and diphenylchlorophosphine forming exo-diphenylphosphine camphor derivatives stereospecifically[13]. Beck[14] obtained optically active bidentate phosphines derived from (+)-camphoric acid, (-)-norpinylamine or (-)-pinane-3-carboxylic acid via amide formation and reaction with chlorophosphines, for example:



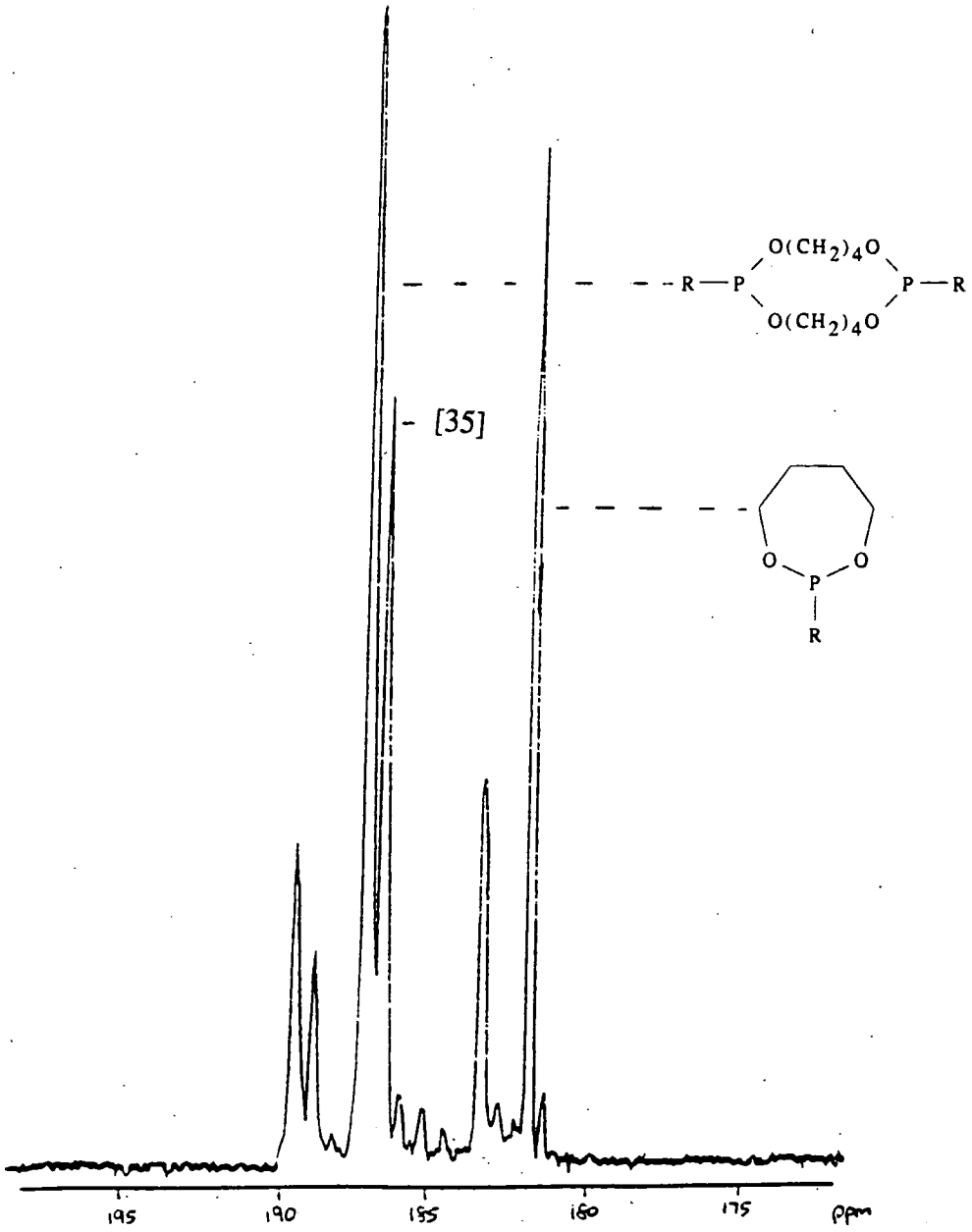
The observed chemical shift in the ^{31}P NMR spectra of the catechyl derivatives suggest a phosphorus (V) species is present. Either the product oxidised prior to analysis, generating a phosphine oxide, or two molecules of catechol reacted with each phosphorus dichloride unit generating a 5-coordinate phosphorus centre, such as [28]. Analogous reactions of catechol with some phosphorus compounds are known.

In the present work, 1,4-butanediol reacts with dichlorophosphines forming three major products; a dialkylphosphite (4,4'-dihydroxydibutylphosphite) [35], a phosphepane ring [36] and a macrocyclic phosphite [37], all previously characterised by J-P. Dutasta[15-18]. Assignment of the spectra from the reaction of 2-hexyldichlorophosphine with 1,4-butanediol is shown below in Figure 4.2. The relative amounts of each compound depend on the concentration of reactants and maximum temperature generated during the reactions. At elevated temperature the monomer [36] readily opens and dimerises[16] forming [37]. All the phosphites synthesised from 1,4-butanediol contained an inseparable mixture of these three types of compounds. Ring phosphites, such as phosphepanes, exist as an equilibrium of conformers, the phosphorus substituent preferring the pseudo-equatorial to the pseudo-axial position[19]. Other studies[20] report molybdenum complexes prepared with these unusual ligands.



[35] [36] [37]

Figure 4.2: ^{31}P NMR after the Reaction of 2-Hexyldichlorophosphine with 1,4-Butanediol



R= 2-hexyl	[35]	[36]	[37]
^{31}P (ppm)	186.8	182.5	187.3
ratio	1	1.8	2

4.3.3. Reaction with Amines

Amines, such as piperazine, reacted analogously to alcohols, forming both 7-phospha-1,4-diazanorbornane (7-phospha-1,4-diazabicyclo[2.2.1]heptane) ring systems [31], 1,1'-dipiperazinoalkylphosphines and their bridged analogues. All these compounds contain phosphorus-nitrogen bonds. For these compounds a diverse range of chemical shifts was observed, probably caused by conformational and configurational effects. Alternatively, steric crowding around the phosphorus centre caused by the reaction of one phosphorus-chlorine bond prevented reaction of the second bond. The product would thus contain a chlorine atom, which would cause a significant downfield shift in the ^{31}P NMR. More ring strain in 7-Phospha-1,4-diazanorbornanes than norbornane rings is expected, but a similar stereochemistry to that reported by L.D. Quin for 7-phosphanorbornanes[21-6] will be adopted. Severe bond angle contraction at phosphorus forces the non-bonding orbitals into close proximity[22-4]. Similar effects are less apparent in the nitrogen bridgehead atoms. Because amines are pyramidal and little geometric distortion occurs in the bridgehead atoms, normal base and nucleophilic behaviour is expected. Three electron σ-bonding between phosphorus and nitrogen is believed to occur in some heteroatom interbridgehead chemistry[27].

The reaction mixture of piperazine and dichlorophosphine was refluxed to increase the solubility of piperazine in diethyl ether. Piperazine will also act as the base during the reaction, to neutralise the hydrogen chloride formed. However, since tertiary amines are more basic than secondary amines, addition of triethylamine was undertaken to minimise piperazine salt formation.

4.4. Conclusion

Chlorophosphines are versatile precursors, and were readily converted into phosphines, phosphites and aminophosphines in high yields. Chiral phosphine derivatives can be prepared by using chiral reagents, generating substituent chirality.

Some reactions produced products which could not be separated from the reaction mixture because distillation temperatures were too high, or too similar, or the general properties were too similar. Such products could not be fractional distilled, purified or characterised, only ^{31}P NMR providing any identification or structural information. However the structure of the alkyldichlorophosphine

starting material, in particular the nature of the alkyl group, was previously unambiguously characterised. Since only the phosphorus-halogen bond participates in the derivatisation reaction, and the nature of the alkyl group is unchanged, determining the substitution pattern around phosphorus in the products was vital, and this was achieved by ^{31}P NMR.

Dimethylphosphines were synthesised using Grignard techniques, although the activated metal intermediate was not quenched before the products were isolated to avoid phosphine oxidation. Large amounts of magnesium dihalide were produced during these reactions, complicating isolation of the phosphine and lowering the overall yield. For many dimethylphosphines the methyl groups were in different chemical environments, as detected by ^{13}C NMR. Other reactions, with the aim of producing 1,4-diphosphadecalin systems were attempted, however the dichlorophosphine apparently did not react with the Grignard reagent. Phenyl lithium reacts with chlorophosphines producing phenylphosphines, but these are more easily prepared by metal diphenylphosphide coupling with dihaloalkanes.

Alcohols readily react with dichlorophosphines at ambient temperature in the presence of a base. Isolation and purification of phosphites was often complicated by their high distillation temperature. Therefore the products were not isolated as pure materials or fully characterised, although the nature of the phosphorus substituents was determined by ^{31}P NMR. Oxidation of phosphites occurred both during the reaction and work-up, but was minimised by handling the materials in the presence of base under an inert atmosphere. Diols reacted forming several similar products which could not be separated by conventional methods and characterised. However, the different structures could be assigned by reference to previous work. Piperazine reacted analogously to diols, forming a 7-phospha-1,4-diazanorbornane ring structure in addition to 1,1'-dipiperazinophosphines, although the results were sometimes unclear.

The novel phosphorus ligands synthesised in this chapter are suitable for transition metal chelation. The following chapters describe the synthesis and study of some metal phosphine complexes.

4.5. References

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CHAPTER 5:

FT-IR STUDIES OF THE REACTIONS OF PHOSPHINES WITH GROUP VIIa METAL CARBONYL BROMIDES

5.1. Introduction

Carbonyl stretching frequencies in transition metal complexes provide a powerful and elegant method for analysing the electronic properties of phosphines[1-5]. Using nickel tetracarbonyl complexes, an electronic parameter (χ) for the bonding properties of many phosphines has been derived[1-4]. The value of χ (in cm^{-1}) is a measure of the π-acidity of the phosphine. Initial work in the present study concentrated on the reaction of manganese pentacarbonyl bromide with cyclohexyldichlorophosphine, to optimise the reaction conditions. Then a systematic study of manganese-carbonyl-bromide-phosphine complex formation with a variety of phosphines, including those synthesised in the preceding chapter, was undertaken to determine the electronic parameter of each phosphine. Hence the effects of the phosphorus substituent on the strength of the metal-phosphine bond could be measured. Manganese carbonyl halides were used in this study because they are readily prepared and much less toxic than nickel carbonyls. Previous studies of the reaction rate and mechanism of manganese-carbonyl-phosphine complex formation permitted facile identification of the products. ^{31}P NMR was used to monitor the reaction of rhenium pentacarbonyl bromide with some phosphines, although no systematic study was undertaken.

5.2. Theory

5.2.1. Bonding

Bonding in transition metal-carbonyl complexes is very similar in principle to metal-phosphine bonding[6]; in an octahedral complex, a σ-bond is formed by donation of electrons from an sp hybrid orbital on carbon to an empty d^2sp^3 metal hybrid orbital and a π-bond is formed by backdonation of electron density from a filled metal d-orbital to the π^*-anti-bonding orbital of the carbonyl group. Both phosphine and carbonyl ligands form σ-bonds and π-bonds with metal orbitals of the same symmetry, and therefore will compete for the metal's electron density. Thus the electronic properties of a phosphine will have profound effects on the metal-carbonyl bond in a complex, which can be measured by the C-O infra-red stretching frequency (υ_{CO}). Generally substitution of carbonyl groups by phosphines results in a lower υ_{CO} of the complex because carbonyl ligands are weaker σ-donors but stronger π-acceptors than phosphines. Therefore, in phosphine complexes, metal-carbonyl backbonding is enhanced compared with the starting complex, and the increased π-bonding results in lower stretching frequencies. Generally metal-ligand σ-bond formation increases the

carbonyl stretching frequency and π-bond formation lowers the stretching frequency.

Force constants provide detailed data concerning the nature of the metal-carbonyl bond, and are controlled by the extent of backdonation to the carbonyl group. Although force constants for symmetric complexes can be accurately calculated, for less symmetric complexes approximate methods must be used. Cotton and Kraihanzel[5] related the force constants to the observed stretching frequencies of metal-carbonyl complexes. Other methods are also widely employed[6], but are not used in this study.

Literature studies[1-4] showed the electronic properties of phosphines could be quantitatively related to the A_1 carbonyl stretching frequency (ν_{CO}) in nickel-carbonyl-phosphine complexes. An electronic parameter (χ) could be assigned to each phosphine ligand relative to tri-t-butylphosphine (ν_{CO} = 2056.1 cm^{-1}) using the equation below, where χ_i is the electronic parameter associated with each substituent on the phosphorus:

$$\nu_{CO}\,[A_1] = 2056.1 + \Sigma\chi_i$$

5.2.2. Phosphine Complexes of Manganese Pentacarbonyl Bromide

Angelici[7-12] and Zingales [13-15] studied the reaction kinetics of manganese and rhenium-carbonyl-bromide-phosphine complex formation by monitoring the carbonyl stretching frequencies in chlorinated solvents. Manganese pentacarbonyl bromide was also used in this study because of the relative ease of preparation, air-stability, solubility and low toxicity compared with nickel tetracarbonyl derivatives. Manganese pentacarbonyl bromide derivatives react with monodentate phosphines following a dissociative mechanism to form a cis-monophosphine derivative. The rate limiting step is loss of carbon monoxide to produce a 16-electon five coordinate intermediate, which is stabilised by the halogen substituent[16] and the remaining carbonyl groups.

Generally ligand displacement is facilitated by the trans-effect of coordinated ligands, weak metal-ligand bonds and a low activation energy of the transition state. Therefore a phosphine displaces carbonyl ligands in manganese pentacarbonyl bromide because one carbonyl group labilises the carbonyl group trans to itself, weakening the metal-carbonyl bond, by competition for the same metal d-orbital electron density. Because phosphines are weaker π-acids than carbonyl groups, a carbonyl group trans- to a phosphine will accept more electron

density from the metal, and be more strongly bonded, than a carbonyl group trans- to a second carbonyl group.

Similarly carbonyl groups cis- to bromine are more labile than that trans- because[17,18] halogens are not good π-acceptors. Therefore halogens do not exert a significant trans-effect and stabilise the carbonyl group in the trans-position. Rapid attack at the activated manganese centre by the incoming phosphine thus displaces one of the equatorial (trans-paired) carbonyl groups, and generates the cis-monophosphine complex, $Mn(CO)_4BrL$ (L = phosphorus ligand). The rate is found to be first order in metal carbonyl concentration and independent of entering ligand concentration[9]. Subsequent reaction of the mono-phosphine complex with excess free phosphine produces the fac-diphosphine complex as the kinetic product, which isomerises at elevated temperatures to the trans,mer-isomer (thermodynamic product). Initial substitution of the monophosphine complex generates the fac-isomer because groups trans- to CO are labilised by the trans-effect (described in chapter 1). Isomerism of the fac-isomer to the trans,mer-isomer also occurs by a dissociative mechanism[10] and is favoured by bulky phosphine ligands[19]. Further reaction to the trisubstituted product is prevented by steric rather than electronic factors[20-22]. The reaction scheme is shown below:

$$Mn(CO)_5Br + L \rightarrow Mn(CO)_4BrL + L \rightarrow \text{fac-}Mn(CO)_3BrL_2 \rightarrow \text{mer-}Mn(CO)_3BrL_2$$

L = phosphorus ligand

Interestingly, amines replace the bromine atom of manganese pentacarbonyl bromide, forming a carbonyl cation[23-5].

5.2.3. FT-IR Spectral Assignment

Cis-monophosphine complexes of manganese tetracarbonyl halides show a characteristic sharp peak at around 2100 cm^{-1}, as shown in Figure 5.2. This peak is easily identifiable and remote from other carbonyl stretches, so may be used to derive a similar equation to that used by Tolman[1]. If triphenylphosphine is used as a standard:

$$\nu_{CO}\,[A_1] = \nu_{CO}[M\text{-}PPh_3] + {}^{Mn}\chi$$

Carbonyl stretching modes in transition metal complexes depend upon the symmetry of the molecule. Manganese pentacarbonyl bromide (C_{4v} point group) possesses 3 ($2A_1$+E) infra-red active stretching modes[5,26]: a radial A_1 mode at

high frequency (2138 cm^{-1}) caused by the symmetric stretch for the four equatorial carbonyl groups; an intense E (doubly degenerate, radial) band at 2053 cm^{-1} and the second (axial) A_1 mode, caused by the trans-interactions between CO groups, at 2009 cm^{-1}. The spectrum is shown in Figure 5.1. Monosubstituted manganese tetracarbonyl phosphine bromide complexes belong to the C_S point group[27] and so have a maximum of 4 (3A' and A") IR active stretching modes, although not all the bands are observed. The spectrum, shown in Figure 5.2, shows the A"+2A' observed modes, both axial and radial A_1 modes (CO cis- to Br and P[28]) are seen as medium intensity due to their dipole changes. The intense A" mode corresponds to the E mode in the parent complex.

Fac-diphosphine complexes derivatives also possess C_S symmetry and the 2A'+A" bands are again observed[9]. All bands are strong because all modes possess significant dipole moment changes, the highest two bands (A' and A") being caused by the symmetric and asymmetric stretching vibrations of two cis-carbonyl groups and the lowest frequency band due to the radial carbonyl bond stretch. Figures 5.3. and 5.4. show the fac- and trans,mer-diphosphine derivatives. Trans,mer-diphosphine complexes show C_{2V} symmetry and hence 3 ($2A_1+B_1$) IR active modes[9]. A very weak A_1 mode (symmetric stretch) may be observed at high frequency as only a weak dipole change occurs. The second A_1 band appears at low frequency because the carbonyl trans- to Br has the strongest metal-carbonyl π-bond[10]. An intense B_1 band is observed at a similar frequency and intensity to the A" band of the fac-isomer.

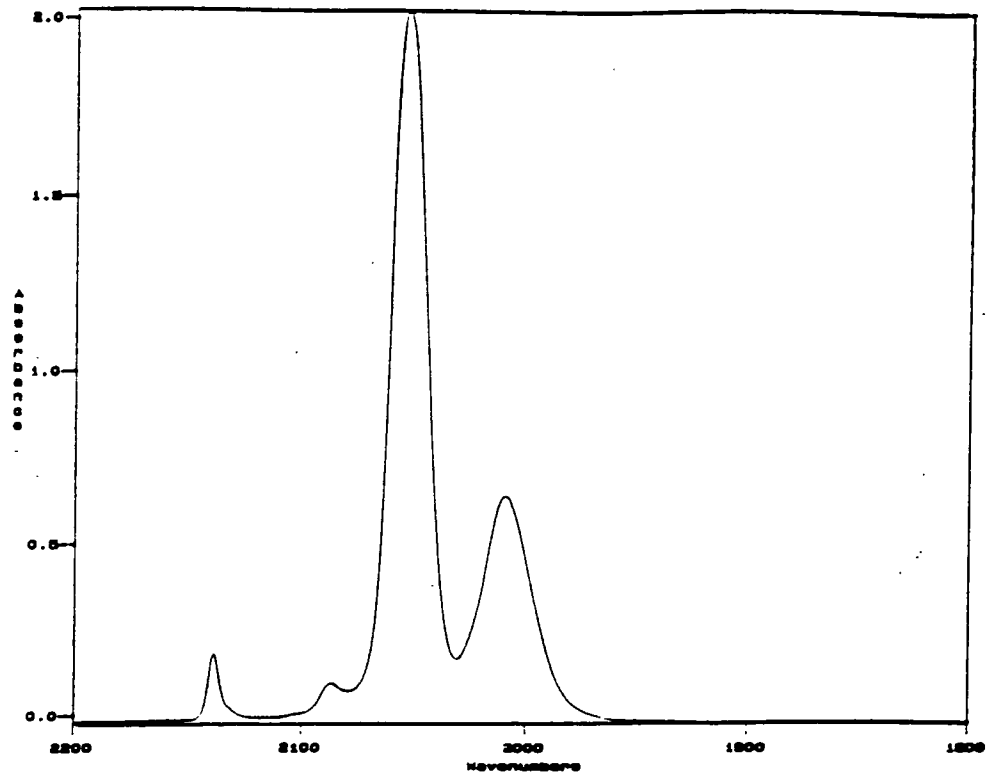


Figure 5.1: FT-IR Spectrum of Manganese Pentacarbonyl Bromide; $Mn(CO)_5Br$

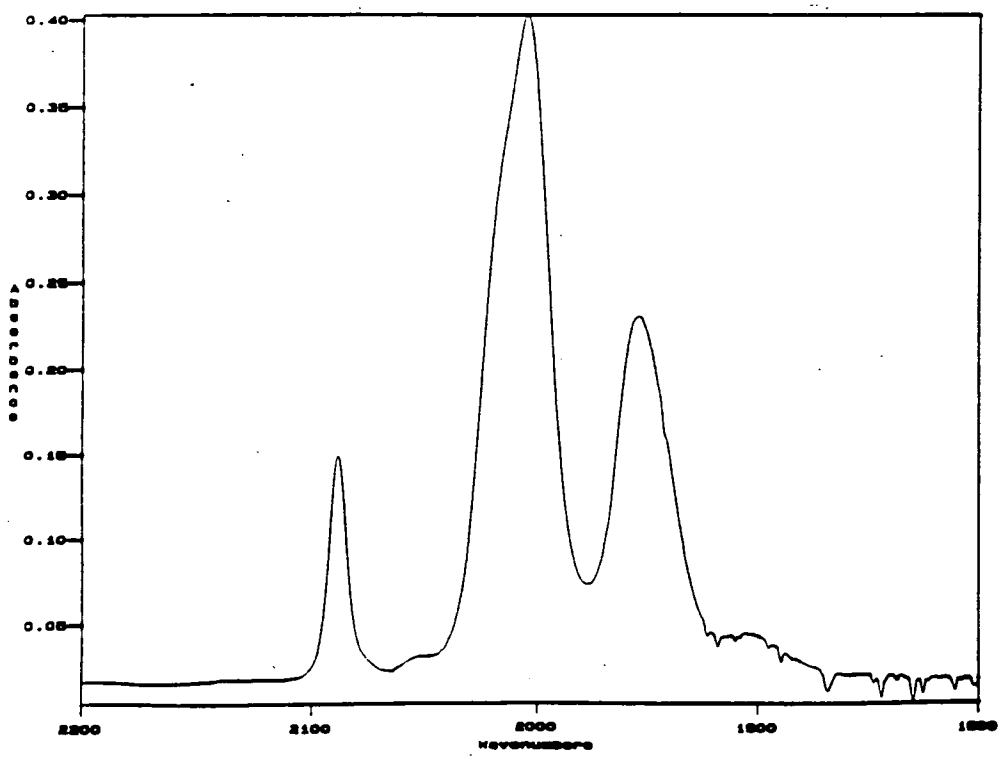


Figure 5.2: FT-IR Spectrum of a Cis-monosubstituted Manganese Tetracarbonyl Bromide; $Mn(CO)_4Br(C_6H_{13}PMe_2)$

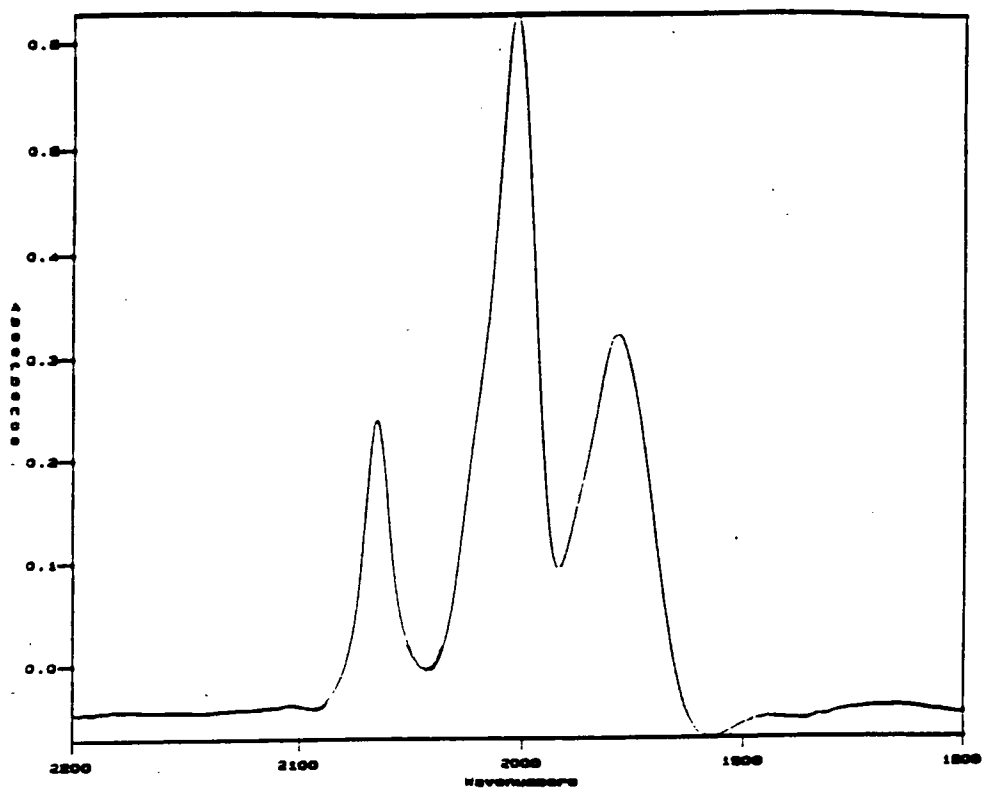


Figure 5.3: FT-IR Spectrum of a Fac-disubstituted Manganese Tricarbonyl Bromide; $Mn(CO)_3Br(C_6H_{13}PMe_2)_2$

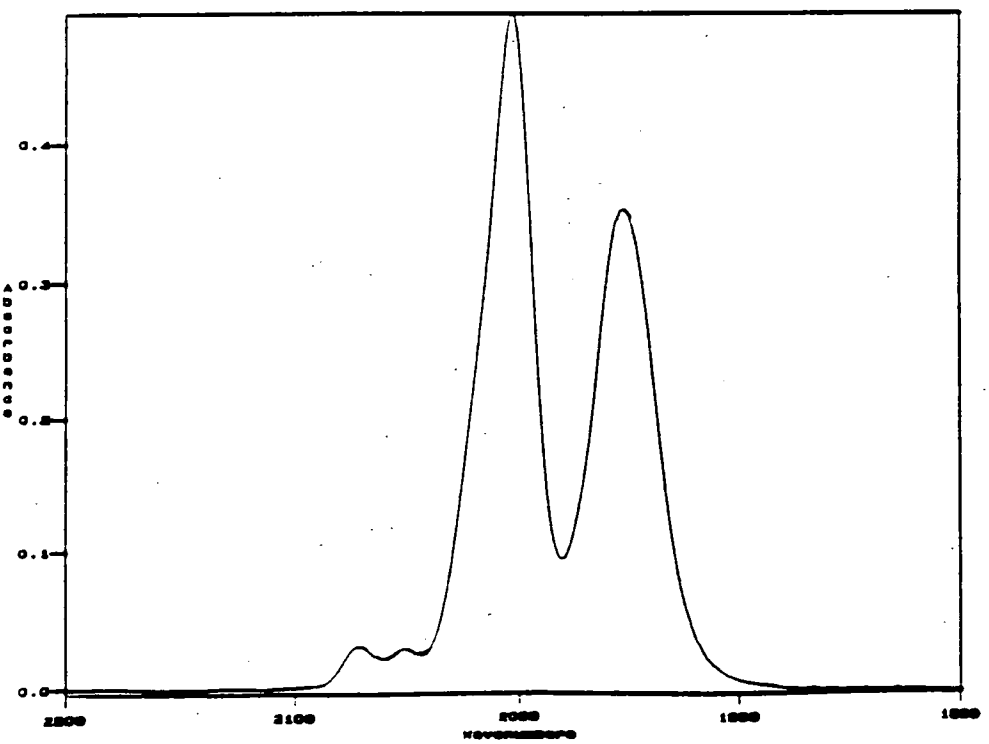


Figure 5.4: FT-IR Spectrum of a Trans,mer-disubstituted Manganese Tricarbonyl Bromide; $Mn(CO)_3Br(C_6H_{13}PMe_2)_2$

5.3. Experimental

5.3.1 Synthesis of Manganese Pentacarbonyl Bromide, $Mn(CO)_5Br$

Using the literature method[29,30], dimanganese decacarbonyl ($Mn_2(CO)_{10}$; 6.80g, 17.4 mmol) was dissolved in dry degassed chloroform (70 ml) under nitrogen in a 250 ml round bottom flask fitted with a 100ml pressure equalising dropping funnel. The dropping funnel was charged with chloroform (50 ml) and bromine (2.82g, 17.6 mmol). With rapid stirring, the bromine solution was added dropwise to the manganese decacarbonyl solution. After complete addition the resulting orange solution was stirred at ambient temperature for four hours and the excess bromine and solvent removed under reduced pressure. Manganese (II) bromide was washed from the orange residue with water (3 x 20 ml) and methanol (20 ml). Recrystalisation of this orange solid from chloroform:hexane (1:1) yielded manganese pentacarbonyl bromide as a bright orange powder, 6.9g (72% from dimanganese decacarbonyl). The FT-IR spectrum (Figure 5.1) showed peaks (cm^{-1}) at 2138.5 vw, 2053.7 vs and 2008.9 m, and compares favourably with the literature values[29].

EA; found (required): %Br 30.64 (29.07); %C 21.18 (21.85);
%H 0.28 (0.00); %N 0.45 (0.00).

5.3.2. Reaction of Manganese Pentacarbonyl Bromide with Cyclohexyldichlorophosphine

A solution of manganese pentacarbonyl bromide (0.05g, 0.18 mmol) in dry, degassed 1,1,2,2-tetrachloroethane (TCE; 40ml) was stirred under nitrogen in a 100 ml round bottom flask. The temperature of the solution was slowly raised to 60±0.5°C in an oil-thermostat and maintained at this temperature during the reaction. Cyclohexyldichlorophosphine (2g, 10.8 mmol) was dissolved in dry degassed TCE (50 ml) under nitrogen producing a 0.216M dichlorophosphine volumetric standard solution. This solution (1ml, 0.22 mmol) was added to the hot manganese solution against a gentle counter-current of nitrogen, to maintain the inert atmosphere, and the IR spectrum of the solution recorded between 1800 and 2200 cm^{-1} (16 scans at 2 cm^{-1}, the instrumental parameters are shown in appendix 1). The reaction was monitored by IR, recording a spectrum every five minutes until no spectral changes were observed. A second mole equivalent of cyclohexyldichlorophosphine solution (1 ml, 0.22 mmol) was then added to the reaction mixture, and the spectra recorded until no further changes were observed. After 24 hours reaction, an 'infinity' spectrum was recorded. The

experiment was repeated with dimanganese decacarbonyl, producing similar spectra to those observed with manganese pentacarbonyl bromide.

To determine the effects on the reaction rate, the experiment was repeated at 45, 70 and 100°C, the optimum temperature was found to be 70°C. At this temperature the reaction proceeded smoothly, the monophosphine complex being readily observed and the trans,mer-diphosphine complex forming after approximately two hours reaction time.

A control experiment, replacing cyclohexyldichlorophosphine with triphenylphosphine, was also performed. Triphenylphosphine could be used as a known standard by which the relative electronic properties of other phosphines could be measured. Thus a systematic study of various dichlorophosphines and their derivatives was undertaken to determine the electronic parameter of each phosphine, and the relative effect of the substituents. 2-hexyldichlorophosphine and bis-1,2-[dichlorophosphino]ethane, and their derivatives, were used to compare the effects of mono- and diphosphines with small steric requirements. 2-Norbornylphosphines would be expected to have significant steric requirements, consequently altering the electronic properties of the complex. Cyclooctyl-phosphines and bis-1,4-[phosphino]cyclooctanes provided a good model system to compare the effects of mono and 1,4-disubstituted phosphines based on the same parent ring. The derivatives of these alkylphosphines used were: dichlorophosphines, dimenthylphosphites, 1,4-butylphosphites and piperazino-phosphines. The preparation of these ligands was described in the preceding chapter. Thus comparisons of both the parent alkylphosphines and the substituent effects could be determined. Both ^{31}P NMR and FT-IR were used to monitor the reaction between manganese pentacarbonyl bromide and bis-1,2-[dichlorophosphino]cyclopentane, although the poor signal-to-noise ratio and broad peaks in the NMR spectra complicated their interpretation.

IR Data

i. Cyclohexyldichlorophosphine Complexes, L = $C_6H_{11}PCl_2$

Complex	(T = 70°C)	ν (cm^{-1})	
$Mn(CO)_4BrL$	2104.1 m	2038.4 s	2008.6 s
fac-$Mn(CO)_3BrL_2$	2046.7 s	2016.3 s	1985.9 m
mer-$Mn(CO)_3BrL_2$		2011.9 vs	1956.1 m
$Mn_2(CO)_9L$	2096.4 m	2027.4 s	2001.9 s
cis-$Mn_2(CO)_8L_2$	2049.1 s	1986.9 vs	1942.1 m
trans-$Mn_2(CO)_8L_2$	2042.8 w	1980.7 s	1942.6 m

ii. Triphenylphosphine Complexes, L = PPh_3

Complex	ν (cm^{-1})		
$Mn(CO)_4BrL$	2091.1 m	2008.2 s	1962.3 m
fac-$Mn(CO)_3BrL_2$	2020.2 s	1957.7 s	1914.6 m
mer-$Mn(CO)_3BrL_2$		1951.7 vs	1914.6 m

iii. Complexes of Bis-1,2-[dichlorophosphino]ethane Derivatives, L = $C_2H_4(PX_2)_2$

X	Complex	ν (cm^{-1})		
OMen	$Mn(CO)_4BrL$	2097.3 m	2015.4 vs	1974.4 s
	fac-$Mn(CO)_3BrL$	2038.0 vs	1971.1 vs	1937.7 s
Cl	$Mn(CO)_4BrL$	2106.5 w		
	fac-$Mn(CO)_3BrL_2$	2065.0 vs	2022.6 s	1973.9 m
	mer-$Mn(CO)_3BrL_2$		2019.7 s	1947.4 s
1,4-but-anediol	$Mn(CO)_4BrL$	2095.9 w	2014.4 s	
	facMn$(CO)_3BrL_2$	2033.7 w	1967.2 s	1926.1 m
	mer-$Mn(CO)_3BrL_2$		1967.2 vs	1928.4 m
piperazine	$Mn(CO)_4BrL$	2095.4 w	2011.5 s	1954.6 m
	fac-$Mn(CO)_3BrL$	2028.9 vs	1947.4 s	1911.7 s

iv. Complexes of 2-Hexyldichlorophosphine Derivatives, L = $C_6H_{13}PX_2$

X	Complex	ν (cm^{-1})		
OMen	$Mn(CO)_4BrL$	2091.6 m	2008.7 vs	1956.1 s
	fac-$Mn(CO)_3BrL_2$	2021.6 vs	1956.6 s	1908.8 m
	mer-$Mn(CO)_3BrL_2$	2034.2 w	1959.4 s	1916.5 m
Cl	$Mn(CO)_4BrL$	2104.9 m	2049.1 s	1983.1 m
	isomerises to[(a)]	2095.9 m	2025.0 vs	1980.6 s
	fac-$Mn(CO)_3BrL_2$	2044.3 m	2002.4 vs	1959.4 s
	mer-$Mn(CO)_3BrL_2$		1994.2 vs	1955.6 s
1,4-butane-diol	$Mn(CO)_4BrL$	2091.6 w	2009.6 s	1962.3 vs
	fac-$Mn(CO)_3BrL_2$	2033.2 m	1962.3 vs	1919.9 s
	mer-$Mn(CO)_3BrL_2$		1963.3 vs	1919.9 m
	reacts to[(b)]	2015.4 s	1965.2 vs	1920.4 m
piperazine	$Mn(CO)_4BrL$	2090.1 m	2009.6 vs	1955.6 s
	fac-$Mn(CO)_3BrL_2$	2017.3 m	1963.8 s	1915.6 m
	mer-$Mn(CO)_3BrL_2$	2036.1 w	1972.5 vs	1918.9 m
Me	$Mn(CO)_4BrL$	2088.7 m	2004.7 s	1954.2 m
	fac-$Mn(CO)_3BrL_2$	2018.3 vs	1948.8 s	1902.1 m
	mer-$Mn(CO)_3BrL_2$		1942.6 s	1899.2 m

(a) The monophosphine complex reacts further before the second mole-equivalent of phosphine solution is added, generating a different monophosphine complex.

(b) The 'infinity' spectrum of the diphosphine complex shows a different complex is present.

v. Complexes of 2-Norbornyldichlorophosphine Derivatives,
$L = C_7H_{11}PX_2$

X	Complex	ν (cm^{-1})		
OMen	$Mn(CO)_4BrL$	2099.3 w	2015.8 vs	
	fac-$Mn(CO)_3BrL_2$	2038.0 m	1977.7 s	1933.8 m
	mer-$Mn(CO)_3BrL_2$	not	observed	
Cl	$Mn(CO)_4BrL$	2103.6 m	2022.6 vs	1971.0 s
	fac-$Mn(CO)_3BrL_2$	2065.0 s	2002.3 vs	1942.2 m
	mer-$Mn(CO)_3BrL_2$		2002.4 vs	1952.7 s
1,4-butane-diol	$Mn(CO)_4BrL$	2097.8 m	2018.7 vs	1975.4 s
	fac-$Mn(CO)_3BrL_2$	2040.4 m	1978.7 vs	1932.0 m
	mer-$Mn(CO)_3BrL_2$		1978.7 vs	1932.0 s
piperazine	$Mn(CO)_4BrL$	2087.2 m	2004.7 s	1948.8 s
	fac-$Mn(CO)_3BrL_2$	2021.7 s	1954.1 s	1919.9 m
	mer-$Mn(CO)_3BrL_2$		1947.4 s	1908.8 m

vi. Complexes of Cyclooctyldichlorophosphine Derivatives,
$L = C_8H_{15}PX_2$

X	Complex	ν (cm^{-1})		
OMen	$Mn(CO)_4BrL$	2097.3 m	2012.9 vs	1962.3 s
	fac-$Mn(CO)_3BrL_2$	2029.4 m	1970.5 s	1922.3 m
	mer-$Mn(CO)_3BrL_2$		1970.5 vs	1917.0 m
Cl	$Mn(CO)_4BrL$	2097.3 m	2012.9 vs	1969.5 s
	fac-$Mn(CO)_3BrL_2$	2031.8 s	1988.4 vs	1939.7 s
	mer-$Mn(CO)_3BrL_2$	2065.2 vw	1988.8 vs	1937.7 s
1,4-butane-diol	$Mn(CO)_4BrL$	2090.1 m	2008.6 vs	1960.4 s
	fac-$Mn(CO)_3BrL_2$	2029.8 m	1958.5 s	1913.6 m
	mer-$Mn(CO)_3BrL_2$	2032.2 vw	1951.0 vs	1917.0 m
	at t = infinity	2029.3 s	1960.4 vs	1918.9 s
piperazine	$Mn(CO)_4BrL$	2097.8 w	2013.9 vs	1960.4 s
	fac-$Mn(CO)_3BrL_2$	2033.7 s	1969.6 vs	1918.5 s
	mer-$Mn(CO)_3BrL_2$		1973.9 vs	1922.3 m

vii. Complexes of Bis-1,4-[dichlorophosphino]cyclooctane Derivatives, $L = C_8H_{14}(PX_2)_2$

X	Complex	ν (cm^{-1})		
OMen	$Mn(CO)_4BrL$ (i)[c]	2092.5 m	2009.1 s	1955.1 s
	isomerises to (ii)	2095.3 m	2025.6 s	1958.0 s
	isomerises to (iii)	2099.3 m	2015.9 vs	1967.6 s
	fac-$Mn(CO)_3BrL_2$	2031.1 s	1971.5 s	1924.7 m
	mer-$Mn(CO)_3BrL_2$	2031.3 vw	1964.7 s	1923.7 s
Cl	$Mn(CO)_4BrL$	2100.7 w	2011.5 vs	1967.2 s
	fac-$Mn(CO)_3BrL_2$	2059.7 m	1995.1 vs	1946.4 s
	mer-$Mn(CO)_3BrL_2$	2049.1 w	1997.0 s	1924.7 s
1,4-but-anediol	$Mn(CO)_4BrL$	2094.4 w	2013.0 vs	1921.3 s
	fac-$Mn(CO)_3BrL_2$	2027.9 m	1959.9 vs	1918.6 s
	mer-$Mn(CO)_3BrL_2$		1960.9 vs	1915.0 s
piperazine	$Mn(CO)_4BrL$	2090.3 w	2007.7 vs	1951.7 vs
	fac-$Mn(CO)_3BrL$	2033.7 s	1936.3 vs	1847.5

(c) The monophosphine complex undergoes further reaction before the second mole-equivalent of phosphine solution is added, three different monophosphine complexes were observed spectroscopically.

viii. Bis-1,2-[dichlorophosphino]cyclopentane Complexes, $L = C_5H_8(PCl_2)_2$

Complex	ν (cm^{-1})			^{31}P NMR δ (ppm)
$Mn(CO)_4BrL$	2100.7 w	2011.5 vs	1967.3 s	227.6
fac-$Mn(CO)_3BrL_2$	2059.7 m	1955.1 vs	1946.4 s	242.6
mer-$Mn(CO)_3BrL_2$	2049.1 vw	1997.0 s	1924.7 s	239.5

5.3.3. Reaction of Rhenium Pentacarbonyl Bromide with Cyclohexyldichlorophosphine

Using the above method, rhenium pentacarbonyl bromide (0.25g, 0.610 mmol) in dry degassed TCE (40 ml) and one mole-equivalent of cyclohexyldichlorophosphine solution (3 ml, 0.66 mmol) reacted at 100°C. The reaction was monitored simultaneously by ^{31}P NMR and FT-IR, identical samples being used for both analyses. When no further spectral changes were observed a second mole-equivalent of cyclohexyldichlorophosphine solution (3

ml, 0.66 mmol) was added to the reaction mixture, and the spectra recorded until no further changes were observed. After 24 hours reaction, an 'infinity' spectrum was recorded. The experiment was repeated replacing cyclohexyldichlorophosphine with bis-1,2-[dichlorophosphino]ethane and bis-1,2-[dichlorophosphino]-cyclohexane.

IR and ^{31}P NMR Data

i. Bis-1,2-[dichlorophosphino]ethane Complexes, L = $C_2H_4(PCl_2)_2$

Complex	FT-IR ν (cm^{-1})			^{31}P NMR δ (ppm)
$Re(CO)_4BrL$	2114.2 w	2029.3 s	1968.7 m	125.9 183.8
fac-$Re(CO)_3BrL_2$	2072.0 vs	2019.4 s	1955.8 s	120.0
mer-$Re(CO)_3BrL_2$	2061.9 w	2027.6 s	1978.9 m	145.9

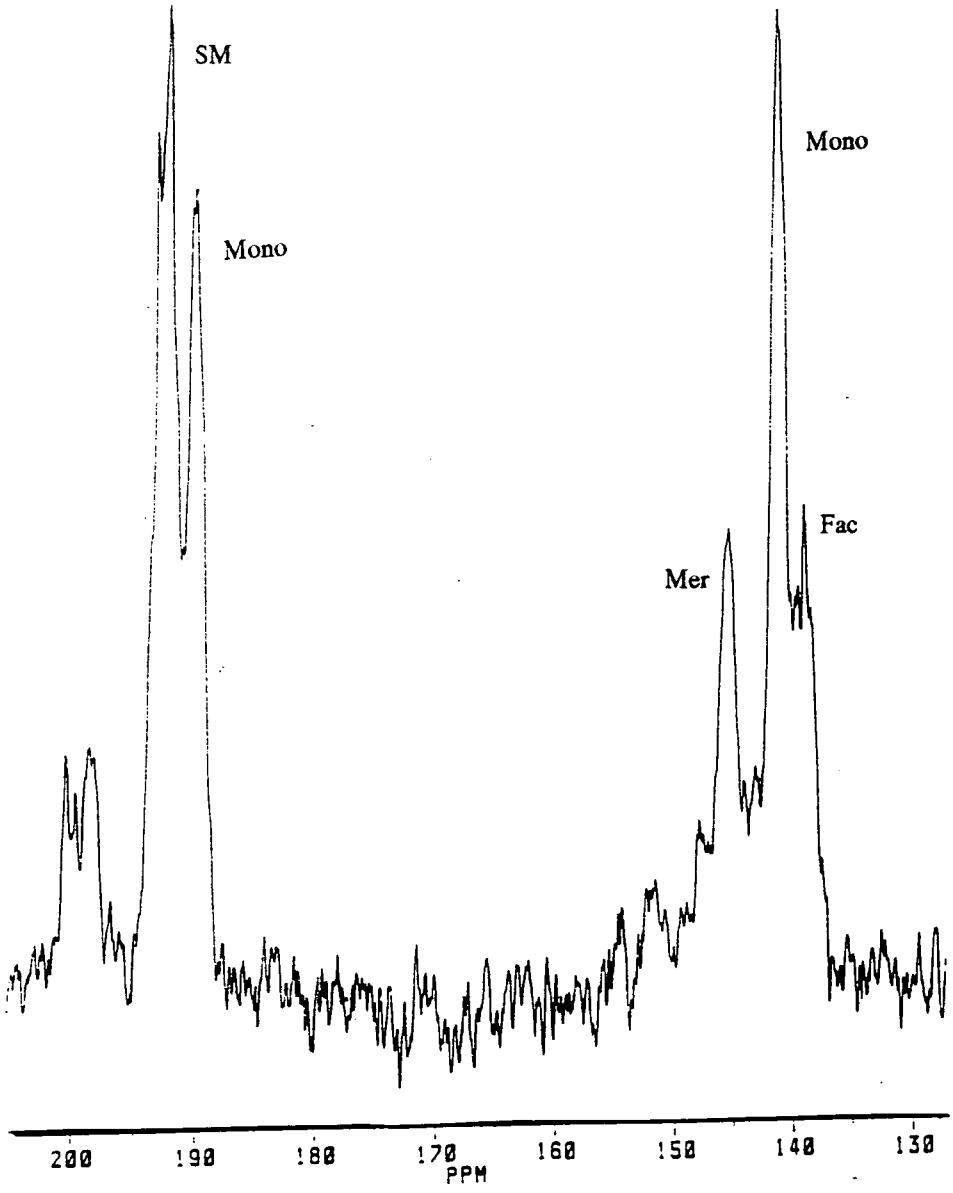
ii. Cyclohexyldichlorophosphine Complexes, L = $C_6H_{11}PCl_2$

Complex	FT-IR ν (cm^{-1})			^{31}P NMR δ (ppm)
$Re(CO)_4BrL$	2118.6 w	2023.6 s	1967.6 m	143.9
fac-$Re(CO)_3BrL_2$	2052.5 m	1999.5 s	1942.6 s	147.0
mer-$Re(CO)_3BrL_2$		1999.5 vs	1942.7 m	148.3

iii. Bis-1,2-[dichlorophosphino]cyclohexane Complexes, L = $C_6H_{10}(PCl_2)_2$

Complex	FT-IR ν (cm^{-1})			^{31}P NMR δ (ppm)
$Re(CO)_4BrL$	2117.1 w	2024.1 s	1968.3 m	141.3 189.4
fac-$Re(CO)_3BrL_2$	2070.7 vs	2016.9 s	1957.5 s	139.0
mer-$Re(CO)_3BrL_2$	2058.8 w	2029.3 s	1982.2 m	145.6

Figure 5.5: ^{31}P NMR Spectrum of the Reaction between Rhenium Penta-carbonyl Bromide and Trans,bis-1,2-[dichlorophosphino]-cyclohexane



key:		
	SM	Starting material (free phosphine)
	Mono	Monophosphine complex
	Fac	Fac-diphosphine complex
	Mer	Mer-diphosphine complex

5.4. Discussion

Manganese pentacarbonyl bromide was readily synthesised from dimanganese decacarbonyl. However the elemental analysis shows there is some impurity present in the product. This is probably a mixture of manganese tetracarbonyl bromide dimer and manganese dibromide, and could be removed from the sample by subliming the product from the crude material. Generally all the complex forming reactions proceeded smoothly and could be easily monitored by FT-IR. Most spectra contained a mixture of mono and disubstituted complexes because it was impossible to react an exact 1:1 mole ratio of manganese complex and phosphine. Usually a slight excess of manganese complex was preferred, although this was not always possible in practice. However one species was always predominant, having more intense peaks, so the spectra could be readily assigned. Several control experiments were performed with various standards, including triethylamine, piperazine, menthol and 1,4-butanediol. Alcohols did not react with manganese pentacarbonyl bromide, even after 24 hours at 100°C. Amines reacted forming carbonyl cations. Peaks of manganese pentacarbonyl bromide with triethylamine were observed at: 2098.3(w), 2022.4(s) 1976.9(m) and 1937.9(s) cm^{-1}.

Kinetics of the reaction were not studied quantitatively, although added phosphines rapidly replaced the carbonyl groups. At 70°C the monophosphine complex was usually observed after five minutes reaction time, similarly fac-diphosphines were readily detected within ten minutes of the second mole equivalent of phosphine being added to the reaction mixture. However isomerism of the fac-isomer was much slower, the rate depending on the steric bulk of the phosphine[19].

Previous kinetic studies[7-15] show the rate of substitution of manganese carbonyls[9] and nickel complexes[31] depends on steric factors. As the bulk of the phosphine decreases the rate of the limiting step of carbonyl dissociation from the complex also decreases; the rate of phosphine substitution decreases in the order[9]:

$$PAr_3 > PR_3 > P(OAr)_3 > PArCl_2 \approx P(OR)_3$$

Reactions of diphosphines with manganese pentacarbonyl bromide were also followed using FT-IR. However the spectra were occasionally complex and difficult to interpret. Initial formation of the monophosphine complex could be readily observed spectroscopically. Subsequent loss of carbon monoxide from the

reaction probably results in the thermodynamically favoured product, containing a five-membered chelate ring. Formation of diphosphine bridges between two metal centres is unlikely because dimer formation is not favoured in the dilute reaction medium. The possible reaction schemes are shown in Figure 5.6, although the chelated complex is the more probable product.

Addition of a second mole equivalent of phosphine did not always affect the chelate ring complex. However the added phosphine sometimes resulted in isomerisation of the initial product to a mer-isomer. The structure of this complex is not known, but opening of the chelate ring is an important, though unusual, first step. The steric properties of the ligands prevent trans-bridging, therefore formation of the mer-isomer with mutually trans-phosphorus atoms is very unlikely. However, a possible product of the isomerisation reaction may be the mer-isomer with one phosphorus atom trans- to bromine atom. However bromine does not π-bond to the metal, therefore π-backdonation from the metal to the carbonyl trans- to bromine is greater than the backdonation to carbonyl groups trans- to other carbonyl groups (the trans-effect, see earlier). Therefore displacement of the carbonyl group trans- to bromine is not kinetically favoured. A second possible isomer results from the formation of a diphosphine bridge between metal centres forming dimeric metal complexes. More evidence is necessary to prove these dimeric or trimeric structures, because dimerisation is not favoured in dilute reaction conditions.

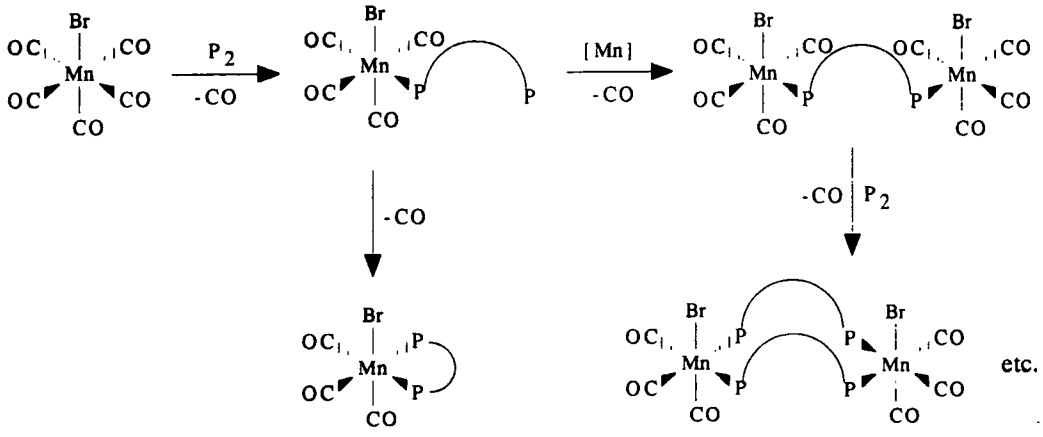


Figure 5.6: Reaction of Manganese Pentacarbonyl Bromide with Diphosphines

To facilitate assignment of the peaks, the ratio of manganese complex to diphosphine was varied. Initial reactions employed a ratio of 2:1 (manganese complex:diphosphine; equivalent to a ratio of Mn:L of 1:1). However, optimum resolution of the spectra was achieved using a ratio of 6:1 (manganese

complex:diphosphine). Progressively one sixth of a mole-equivalent of diphosphine was added to the reaction mixture and the spectra recorded until no further changes were observed, the next aliquot then being added and monitoring of the reaction continued.

The A_1 (radial) mode of the monophosphine complex was readily observed in every reaction as a sharp peak around 2100 cm^{-1}. Therefore the electronic parameters ($^{Mn}\chi$), relative to triphenylphosphine, of various mono- and diphosphines could be calculated from the observed stretching frequency (υ_{CO}) using an equation developed from Tolman's method[1]. The results are shown below in Tables 5.1 and 5.2.

All the values were calculated to one decimal place because the precision was limited by the spectral resolution (2 cm^{-1}). Higher stretching frequencies generate higher χ values and are associated with stronger π-acidic character of the phosphine (weaker σ-bases). Those phosphines with large χ values would be expected to have shorter and stronger metal-phosphine π-bonds, and hence more labile trans-carbonyl groups as they exert a stronger trans-effect (and influence), compared with phosphines with lower χ values. Therefore, not surprisingly, the tables clearly show a effect related to substituent electronegativity, as with the nickel complexes previously studied[1-5], and the order of $^{Mn}\chi$ decreases in the order:

$$Cl > OMen \approx C_4H_8O_2 > C_4H_8N_2 > Me$$

Although the calculated values of $^{Mn}\chi$ for 1,4-butyl- and dimenthylphosphites are similar for most alkyl groups (in the range 0 and 8 cm^{-1}), they are very different in cyclooctyl derivatives because $^{Mn}\chi$ for the 1,4-butylphosphite is much lower than for other phosphites. Generally, as the steric size of the alkyl group increases the difference in $^{Mn}\chi$ between the two phosphite derivatives also increases. $^{Mn}\chi$ values of piperazine derivatives also have a large range, and are sometimes negative. Interestingly neither piperazino- diphosphine derivative underwent isomerism, possibly due to the conformational requirements of the rings or other steric reasons. For alkyldichlorophosphines the effect of the alkyl group decreases in the order:

$$\text{1,2-ethyl} > \text{2-hexyl} \approx \text{cyclohexyl} \approx \text{2-norbornyl} > \text{cyclooctyl} > \text{1,2-cyclopentyl} \approx \text{1,4-cycloctyl}$$

Using the equation: $^{Mn}\chi = \nu_{CO} - \nu_{CO}[M\text{-}PPh_3]$ (cm^{-1})

Table 5.1: Electronic Parameters ($^{Mn}\chi$) for Monophosphines; RPX_2

R	X	ν_{CO} (cm^{-1})	$^{Mn}\chi$ (cm^{-1})
Ph	Ph	2091.1	0.0
2-hexyl	OMen	2091.6	0.5
	Cl	2104.9	13.8
	1,4-butanedioxy	2091.6	0.5
	piperazino	2090.6	-0.5
	Me	2088.7	-2.4
cyclohexyl	Cl	2104.1	13.0
2-norbornyl	OMen	2099.3	8.2
	Cl	2103.6	12.5
	1,4-butanedioxy	2097.8	6.7
	piperazino	2087.2	-3.9
cyclooctyl	OMen	2097.3	6.2
	Cl	2097.3	6.2
	1,4-butanedoxy	2090.1	-1.0
	piperazino	2097.8	6.7

Table 5.2: Electronic Parameters ($^{Mn}\chi$) for Diphosphines; X_2PRPX_2

R	X	ν_{CO} (cm^{-1})	$^{Mn}\chi$ (cm^{-1})
Ph	Ph	2091.1	0.0
1,2-ethane	OMen	2097.3	6.2
	Cl	2106.5	15.4
	1,4-butanedioxy	2095.9	4.8
	piperazino	2095.4	4.3
1,2-cyclopentane	Cl	2100.7	9.6
1,4-cyclo-octane	OMen	2092.5	1.4
	reacts to	2095.3	4.2
	reacts to	2099.3	8.2
	Cl	2100.7	9.6
	1,4-butanedioxy	2094.4	3.3
	piperazino	2090.3	-0.8

Thus as the molecular mass and steric size of the alkyl group increases the value of $^{Mn}\chi$ decreases. However the electronic parameter measures the electronic effect of phosphines exclusively, especially π-acidity, therefore the results show the close relationship of steric and electronic factors in metal-phosphine bonds in the complexes.

Surprisingly the $^{Mn}\chi$ values for the monophosphine complex derived from cyclooctylphosphines and bis-1,4-[phosphino]cyclooctanes were very different, strongly suggesting π-acidity of phosphines is significantly affected by their steric requirements. Bis-1,4-[phosphino]cyclooctane complexes show some additional interesting features. The piperazino derivative apparently forms a chelate ring with manganese pentacarbonyl bromide, and does not undergo isomerisation, even though molecular models of this diphosphine suggest the cyclooctane ring must adopt an energetically unfavourable boat-boat conformation, bringing both phosphorus atoms and their substituents into close proximity. The monophosphine complex of the dimenthoxy derivative apparently isomerises under the reaction conditions producing three different, detectable, monophosphine complexes. However these products could not be isolated and identified. One complex is probably the monochelated diphosphine. The stretching frequencies of this monophosphine complex are different to the analogous cyclooctyl dimenthylphosphite complex for both steric and the associated electronic reasons. Another product may contain a single diphosphine bridge between two metal centres, but the nature of the third complex is unknown.

Most of the phosphines investigated had higher $^{Mn}\chi$ values than triphenyl-phosphine, showing they are stronger π-acids and weaker σ-donors. This correlates well with literature values[3,5,32] as described in chapter 1, because most of the substituents are more electronegative than phenyl groups. Piperazine derivatives are less electronegative than phenyl groups and so would be expected to be weaker π-acids and have negative $^{Mn}\chi$ values, as observed in most complexes studied here.

^{31}P NMR studies of both manganese and rhenium complexes were complicated by poor spectral resolution. Broad peaks, a poor signal-to-noise ratio and sample impurities prevented accurate and detailed analysis of the spectra. The nuclear spin (I) of both metals[33] is $^{5}/_{2}$, and both nuclei are in 100% abundance (^{55}Mn = 100%, ^{185}Re = 37.1%, ^{187}Re = 62.9%), however the electric quadruple moment (Q) of manganese is approximately one fifth that of rhenium (0.5×10^{-24} and 2.65×10^{-24} cm^2 respectively). Therefore rhenium samples

produced better spectra than manganese samples, although no spectra were significantly well resolved to observe or calculate any coupling effects. Single peaks of Manganese-phosphine complexes were very broad, frequently covering 30 ppm, and were of very low intensity, possibly caused by exchange phenomena. Rhenium-phosphine complexes produced sharper, more highly resolved spectra, although a poor signal-to-noise ratio masked any coupling. Because concentrated samples and long scan-times were necessary to obtain suitable spectra, only selected samples were analysed by ^{31}P NMR.

Interestingly the chemical shift of manganese phosphine complexes moved to higher frequencies relative to the free phosphine, although rhenium phosphine complexes were observed at a lower δ-value. Since the chemical shift is determined by the electron density at phosphorus, the manganese complexes, having the larger electric quadruple moment, must remove electron density from the phosphorus centre to produce the signals observed. Similarly rhenium complexes must be donating electron density to the phosphorus centre, or reducing the electronegativity effects of other phosphorus substituents. Other effects, such as bond anisotropy and steric factors will also affect experimental δ-values.

5.5. Conclusion

Many novel phosphines and diphosphines have been synthesised, as described in the preceding chapters. By analysing the FT-IR spectra of the manganese and rhenium carbonyl complexes of these phosphines a value of the electronic parameter ($^{Mn}\chi$), reflecting the π-acidity of the phosphine, has been obtained.

Although most reaction solutions contained a mixture of complexes, spectral assignments could be routinely made because usually only one major product was present. Spectra of diphosphine complexes were more complicated to assign because diphosphine chelation and bridging reactions occurred. However the spectral pattern, arising from the molecular symmetry, showed the nature of the complexes present.

Experimental $^{Mn}\chi$ values were calculated from the radial A_1 stretching frequency of the monophosphine complex and were in good agreement with the expected (literature) trends obtained for nickel complexes. Generally the electronic parameter of phosphines vary with the electronegativity of the

individual substituents. More electronegative phosphorus substituents increase the π-acidity of the phosphine, producing a larger electronic parameter. These phosphines also exert a stronger trans-effect. However, steric factors will also affect the calculated values. Thus the range of $^{Mn}\chi$ values for individual substituents (χ_i) was large, and could not be calculated with precision.

^{31}P NMR spectroscopy was also used to monitor the experiments. However, the necessary sample concentration and volume, together with the number of sample-scans required and poor spectral resolution obtained, precluded a systematic and detailed study of the reaction.

5.6. References

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CHAPTER 6:

EXPLORATORY STUDIES OF SOME TRANSITION METAL PHOSPHINE COMPLEXES

6.1. Introduction

Phosphines frequently displace labile ligands attached to transition metal centres, forming metal-phosphine complexes. These reactions can be monitored by ^{31}P NMR, a powerful analytical tool for determining the structure and stereochemistry of metal-phosphine complexes. Dichloropalladium (II) phosphine complexes, formed from the 1,5-cyclooctadiene complex, were examined using ^{31}P NMR. Although some palladium phosphine crystals were obtained they were unsuitable for X-ray crystal-structure determinations.

Reactions of dichlorophosphines with sodium naphthalide and cyclopenta-dienyl sodium were studied, as a foundation for the synthesis of some unusual metal-chlorophosphine complexes, such as those formed from iron and tungsten hydrides[1-5] or metal arene carbonyl cations[6]. Trans-hydrido-2-naphthyl,bis[bis-1,2-(dimethylphosphino)ethane]iron(II) can be conveniently prepared from iron (II) chloride, and its reaction with dichlorophosphines monitored by ^{31}P NMR. Similarly hydridotricarbonylcyclopentadienylmolybdenum was synthesised from the sodium salt, and the reaction of both complexes with dichlorophosphines studied. The aim of these experiments was to investigate the interaction of metal hydrides with dichlorophosphines. The IR and NMR instrumental parameters for each series of experiments are shown in appendix 1.

The work outlined in this chapter provides a background for future work. A detailed and rigorous investigation of each system was attempted. However, some of the work produced inconclusive results allowing only a provisional assignment of the products.

6.2. Palladium Dichloride Complexes

6.2.1. Synthesis of Dichloro(η^4-1,5-Cyclooctadiene)Palladium (II)

Using the standard method[7], palladium dichloride (1.9g, 10.7 mmol) was dissolved in warm concentrated hydrochloric acid (9 ml) forming tetrachloropalladic acid (H_2PdCl_4) as a red solution. This solution was diluted with ethanol (90 ml) and stirred at ambient temperature for 24 hours before being filtered and cooled in an ice-bath. 1,5-cyclooctadiene (COD; 2 ml, 16.3 mmol) was added dropwise to the stirred cool solution, immediately precipitating dichloro(η^4-1,5-cyclooctadiene)palladium (II) ($PdCl_2$[COD]) as a bright yellow

powder. The product was collected by filtration, washed with warm ethanol (3 x 10 ml) and diethyl ether (1 x 20 ml) then recrystallised from warm chloroform. Yield 3.0g (96%from palladium dichloride).

EA; Found (required): %C 33.9 (33.66); %H 4.6 (4.24).

6.2.2. Synthesis of Dichlorodi(2-norbornyldimethylphosphine)-palladium(II)

Dichloro(η^4-1,5-Cyclooctadiene)Palladium (II) (0.2g, 0.7 mmol) was dissolved in dry degassed chloroform (20 ml) contained in a 50 ml round bottom flask fitted with a reflux condenser. 2-Norbornyldimethylphosphine (0.4g, 2.5 mmol) was added to the yellow solution against a gentle counter-current of nitrogen and the solution heated under reflux in a nitrogen atmosphere for two hours. After recording the ^{31}P NMR spectrum of the reaction solution, the volatile components (including excess phosphine) were removed under reduced pressure at ambient temperature. The resulting yellow residue was dissolved in dry degassed chloroform (6 ml), dry degassed hexane (4 ml) added, and the mixture stored at 0°C overnight. Yellow needles of dichlorodi(2-norbornyldimethylphosphine)-palladium(II) were removed by filtration. Yield 0.32g (93% from $PdCl_2$[COD]). A similar experiment was performed with bis-1,4-[diethoxyphosphino]cyclooctane.

Data

i. Dichlorodi(2-norbornyldimethylphosphine)palladium(II)

EA; found (required): %C 44.9 (44.15); %H 7.13 (7.00);
%P 11.79 (12.65); %Cl 15.02 (14.48).

ii. Dichlorodi(bis-1,4-[diethoxyphosphino]cyclooctane)palladium(II)

EA; found (required): %C 41.63 (41.07); %H 7.11 (6.89); %P 16.79 (17.65)
%Cl 10.85 (10.10); %O 9.84 (9.12).

A systematic study, similar to that reported in the previous chapter, was attempted. Approximate 0.5M standard solutions of each phosphine were accurately prepared by dissolving the phosphine (1g, 5 mmol) in TCE (20ml). Each metal phosphine synthesis was performed in a 5mm NMR tube, using dichloro(η^4-1,5-cyclooctadiene)palladium (II) (0.02g, 0.07 mmol), TCE (2 ml) and an excess of the relevant phosphine solution (1 ml, 0.25mmol). The NMR tube was closed under nitrogen in a Schlenk tube, and heated for several hours in a metal block at 80°C, the reaction being regularly monitored using ^{31}P NMR.

^{31}P NMR Data of Chloropalladium Complexes

i. Complexes of Bis-1,2-[-1,3,2-dioxaphosphepano]ethane, $C_2H_4(P[O_2C_4H_8])_2$

Time = 1 hour			Change after
δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)	12 hours*
175.5	s	---	decrease
165.5	t	21.9	decrease
164.7	t	25.2	large decrease
145.7	d	77.2	decrease
137.9	d	58.9	increase

* A new singlet at 148.2 ppm was also observed

ii. Complexes of 2-Hexyldichlorophosphine Derivatives, $C_6H_{13}PX_2$

X		δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
Cl		155.2	s	---
		153.1	t	7.9
		152.3	unres.	---
		151.7	d	3.8
Me	1 hr	104.8	t	14.9
	12 hr	108.0	s	---
		104.4	d	15.1
OMen		145.9	s	---
		134.1	q	77.4
1,4-butanediol		156.5	d	74.0
		151.1	d	60.6
		148.2	d	43.1
		140.6	d	79.9
		132.5	d	16.3
		126.5	d	61.0
		122.3	t	67.1

iii. Complexes of Cyclopentyldichlorophosphine, $C_5H_9PCl_2$

δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
151.5	d	18.4
149.5	d	18.2
149.1	d	25.3
143.6	d	60.7
142.1	d	21.6

iv. Complexes of Bis-1,2-[dichlorophosphino]cyclopentane, $C_5H_8(PCl_2)_2$

δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
185.1	s	---
162.5	s	---
144.4	d	17.2

v. Complexes of Cyclohexyldichlorophosphine Derivatives, $C_6H_{11}PX_2$

X	δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
Cl	167.8	s	---
	154.3	d	30.8
	144.1	d	27.3
	143.6	t	18.8
1,4-butanediol	119.1	d	173.6
	113.4	t	37.5

vi. Complexes of Bis-1,2-[dichlorophosphino]cyclohexane, $C_6H_{10}(PCl_2)_2$

δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
192.9	s	---
135.9	s	---
129.5	d	22.1
123.9	s	---
114.9	d	126.8

Figure 6.1: ^{31}P NMR Spectrum of $PdCl_2$(Bis-1,4-[1,4-butoxyphosphino]ethane)

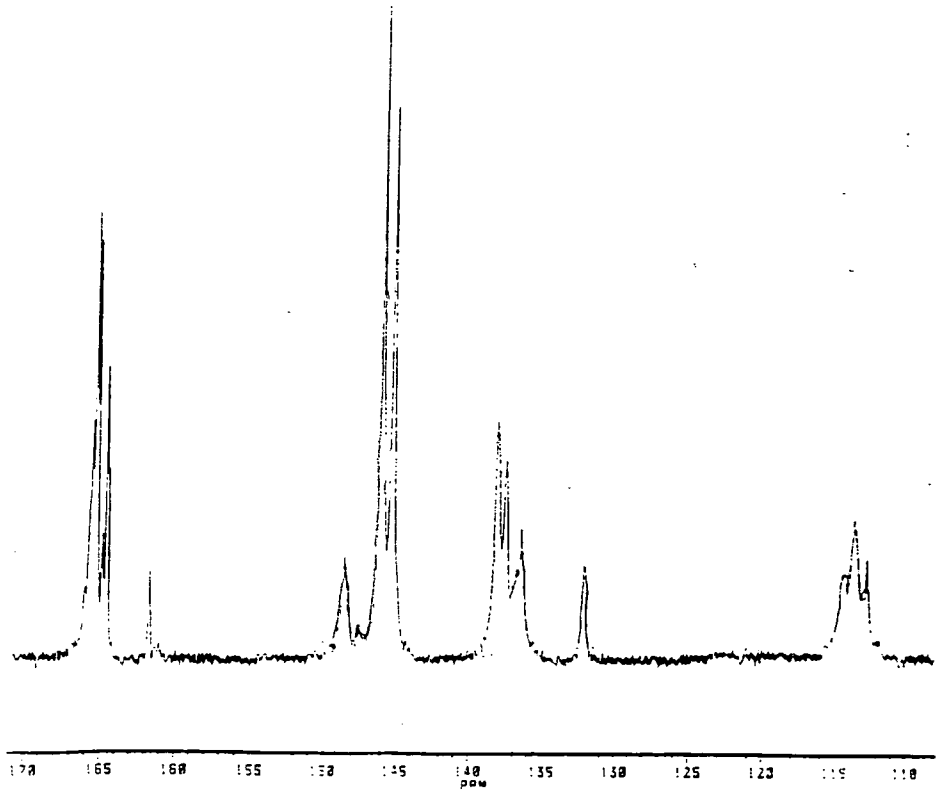
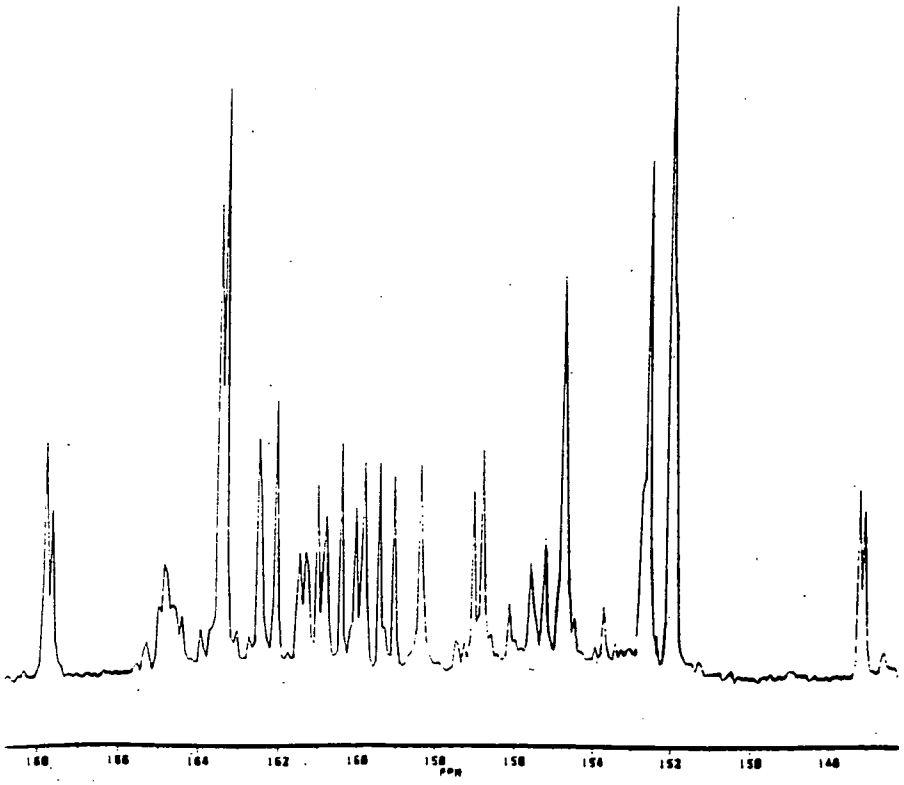


Figure 6.2: ^{31}P NMR Spectrum of $PdCl_2(NbP[OMen]_2)_2$



vii. Complexes of 2-Norbornyldichlorophosphine Derivatives, $C_7H_{11}PX_2$

X	δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
Cl	166.1	d	22.9
	161.8	d	30.2
	164.9	s	---
OMen	many unresolved resonances		
1,4-butanediol	132.9	d	15.2

viii. Complexes of Cyclooctyldichlorophosphine Derivatives, $C_8H_{15}PX_2$

X	δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
Cl	190.5	t	91.8
	149.5	d	37.2
	146.4	t	27.3
	141.8	d	38.1
	137.9	t	22.5
OMen	many unresolved resonances		
1,4-butanediol	151.8	t	22.3
	143.8	unres.	---

ix. Complexes of Bis-1,4-[dichlorophosphino]cyclooctane Derivatives, $C_8H_{14}(PX_2)_2$

X	δ (ppm)	multiplicity	J [^{31}P-^{31}P] (Hz)
Cl	152.9	d	14.8
	151.0	t	24.8
	149.5	d	22.6
	139.8	s	---
OMen	181.3	s	---
	131.6	unres.	---

The large number of peaks complicated spectral interpretation. Thus, although multiplets and coupling constants are quoted in the above tables, some of the data may be incorrect. For example, an assigned doublet may consist of two singlets.

6.3. Iron Phosphine Complexes

Chlorophosphines are known to react with iron and tungsten hydride compounds forming novel metal-phosphine complexes[1-6]. Dichloroiron (II) bisphosphines can be easily transformed into an iron hydride using sodium naphthalide[8]. Thus trans-dichloro,bis[bis-1,2-(dimethylphosphino)ethane]iron(II) and the analogous naphthyl iron hydride were synthesised and the reaction with 2-norbornyldichlorophosphine examined. The reaction of sodium naphthalide with a chlorophosphine was also investigated.

6.3.1. Reaction of Bis-1,2-[dichlorophosphino]ethane with Sodium Naphthalide

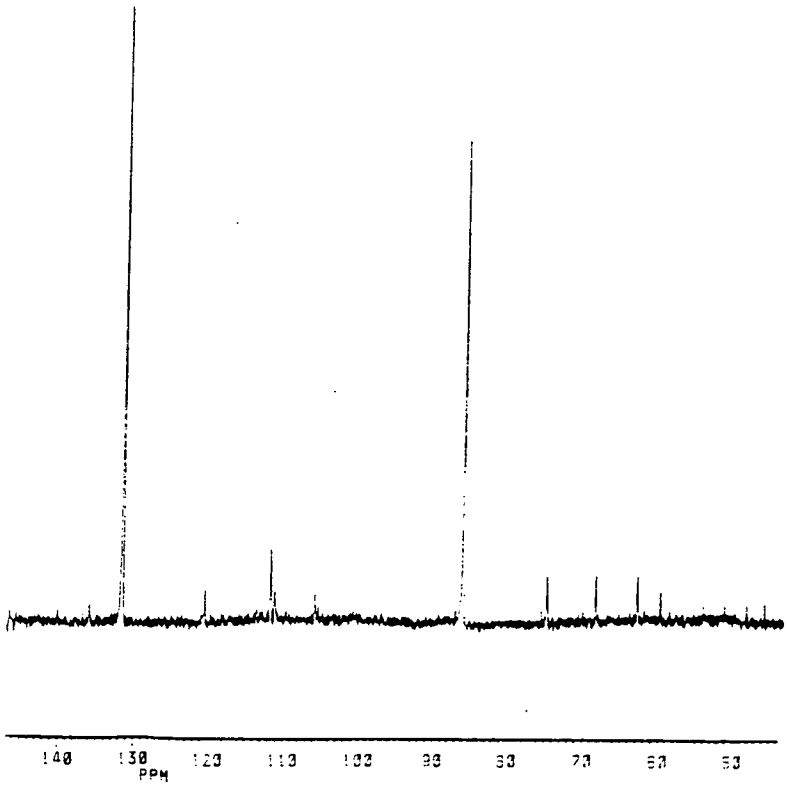
Naphthalene (10g, 78 mmol) was dissolved in dry degassed tetrahydrofuran (THF; 100 ml) in a 250 ml two neck round bottom flask. The apparatus was evacuated and filled with nitrogen. Small pieces of sodium (1.8g, 78 mmol) were slowly added to the rapidly stirred naphthalene solution against a gentle counter-current of nitrogen. The resulting solution was stirred for 24 hours at ambient temperature. Excess sodium was removed by filtration to give a dark green sodium naphthalide solution (approximately 0.7M).

Bis-1,2-[dichlorophosphino]ethane (10g, 43 mmol) was dissolved in dry degassed THF (100 ml) under nitrogen in a 2 neck round bottom flask fitted with a a serum cap. The apparatus was cooled in an ice-bath and stirred while sodium naphthalide solution (65 ml, 46 mmol) was slowly added using standard syringe techniques. The green colour was discharged and a yellow precipitate formed. After complete addition the mixture was stirred at ambient temperature overnight. The solid was removed by filtration and washed with dry degassed THF (3 x 40 ml) to give a bright yellow powder (4.1g). This was insoluble in water, alcohol, toluene, chlorinated and alkane solvents. Therefore the product could not be analysed or characterised using solution techniques.

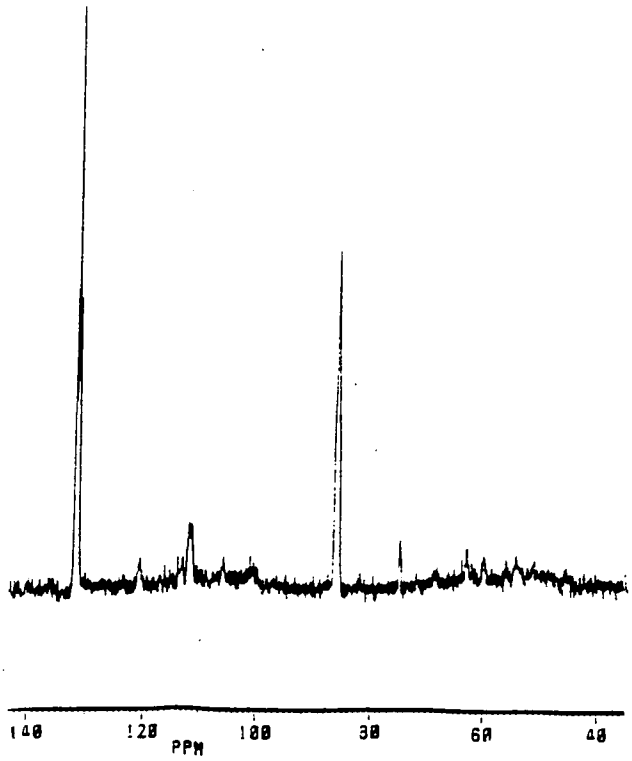
EA: %C 40.25; %H 3.97; %P 9.64.
ratio C:H:P, 10.78:12.76:1

MS; EI: 149 $[C_4H_8P_3]^+$; 128 $[C_{10}H_8]^+$
CI: 280 $[C_{14}H_{15}P_2Cl]^+$; 128 $[C_{10}H_8]^+$; 62 $[280\text{-}C_{12}H_{12}P_2]^+$

Figure 6.3: ^{31}P NMR Spectrum of the Reaction between Cyclooctyldichlorophosphine and Sodium Naphthalide



a. ^{1}H decoupled



b. ^{1}H coupled

Cyclooctyldichlorophosphine was also treated with sodium naphthalide to produce an orange solution.

^{31}P NMR (ppm in THF, decoupled): 131.7 singlet;
86.0 singlet

^{31}P NMR (ppm in THF, ^{1}H coupled): 131.9 triplet J [^{31}P-^{1}H] = 33.5 Hz
86.6 singlet

6.3.2. Synthesis of Trans-dichloro,bis[bis(dimethylphosphino)ethane]-iron(II)[38]

Based on the literature method[9] iron (II) dichloride tetrahydrate (4.5g, 22.6 mmol) was dissolved in dry degassed methanol (100 ml) under nitrogen in a 250 ml round bottom flask. The methanol-water azeotropic mixture was removed under reduced pressure at 30°C. This procedure was repeated four times. The anhydrous iron (II) dichloride was washed with dry, degassed toluene and dried at 30°C under reduced pressure. Elemental analysis confirmed that the beige powder was anhydrous iron (II) chloride (2.7g, 93%).

Anhydrous iron (II) dichloride (2.6g, 20.3 mmol) was suspended in dry, degassed THF (100 ml) under nitrogen in a 250 ml round bottom flask fitted with a serum cap. The inert atmosphere was maintained throughout the experiment. Bis-1,2-[dimethylphosphino]ethane (DMPE; 6.7g, 44.7 mmol) was added to the vigorously stirred solution using standard syringe techniques. Initially a red solution formed, rapidly changing to a dark green solution. The solvent was removed under reduced pressure leaving a green powder. Trans-dichloro, bis[bis(dimethyl-phosphino)ethane]iron(II), $Fe(DMPE)_2Cl_2$, was precipitated as a green powder from dry degassed petroleum ether (40/60°C) using dry degassed toluene, yield 5.2g (60% from anhydrous iron (II) dichloride).

Trans-dichloro,bis[bis(dichlorophosphino)ethane]iron(II), $Fe(DCPE)_2Cl_2$, was prepared analogously as a red powder. Yield 14.6g (52% From anh. $FeCl_2$).

Data

i. Anhydrous Iron (II) Dichloride

EA; found (required): %Fe 38.96 (44.53); %Cl 43.56 (55.47).

ii. Trans-dichloro,bis[bis(dimethylphosphino)ethane]iron(II)

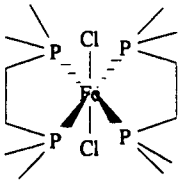
^{31}P NMR (ppm in pentane): 58.5 singlet.

EA; found (required): %Fe 15.42 (13.00); %C 31.55 (33.75); %H 7.16 (7.55); %Cl 17.31 (16.60).

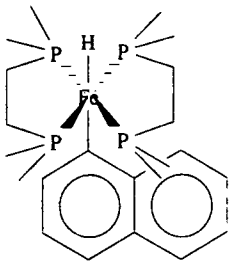
iii. Trans-dichloro,bis[bis(dichlorophosphino)ethane]iron(II)

^{31}P NMR (ppm in pentane): 73.2 singlet.

EA; found (required): %Fe 9.63 (9.46); %C 7.26 (8.14); %H 1.69 (1.37) %Cl 31.95 (60.05); %P 21.64 (20.99).



[38]



[39]

6.3.3. Synthesis of Trans-hydrido,2-Naphthyl,bis[bis(dimethylphosphino)-ethane]iron(II) [39]

Following the literature methods[8-13], trans-dichloro,bis[bis-1,2-(dimethyl-phosphino)ethane]iron(II) (1.9g, 4.43 mmol) was dissolved in dry degassed THF (40 ml) under nitrogen in a 100 ml round bottom flask fitted with a serum cap. Sodium naphthalide solution (10 ml, 7 mmol) was added dropwise to the stirred emerald green iron complex solution using standard syringe techniques. The dark green colour of each drop was discharged as the colour of the iron solution turned orange-red and then started to darken. After complete addition the resulting dark orange solution was stirred at ambient temperature for two hours. Under reduced pressure the volatile components were removed leaving trans-hydrido,2-naphthyl,bis[bis(dimethylphosphino)ethane]iron(II), $HFe(DMPE)_2Np$, as a yellow-orange solid. The product was extracted with dry degassed pentane (3 x 30 ml), subsequently removed under reduced pressure to isolate a yellow powder (1.6g, 74% from $Fe[DMPE]_2Cl_2$).

^{31}P NMR (ppm in pentane): 68.9 singlet

^{1}H NMR (ppm in pentane): -12.6 singlet,

FT-IR (cm^{-1} in pentane) ν_{FeH}: 1717.9 vw (16 scans at 2 cm^{-1} resolution)

Figure 6.4: ^{31}P NMR Spectrum of $HFe(DMPE)_2Np$

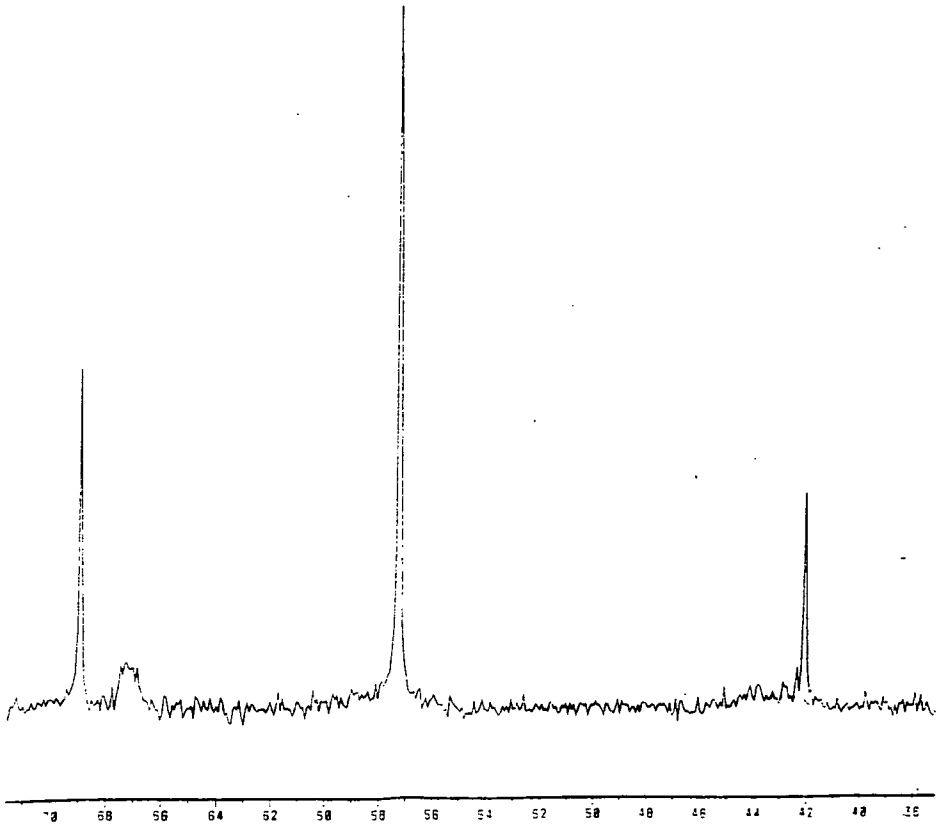
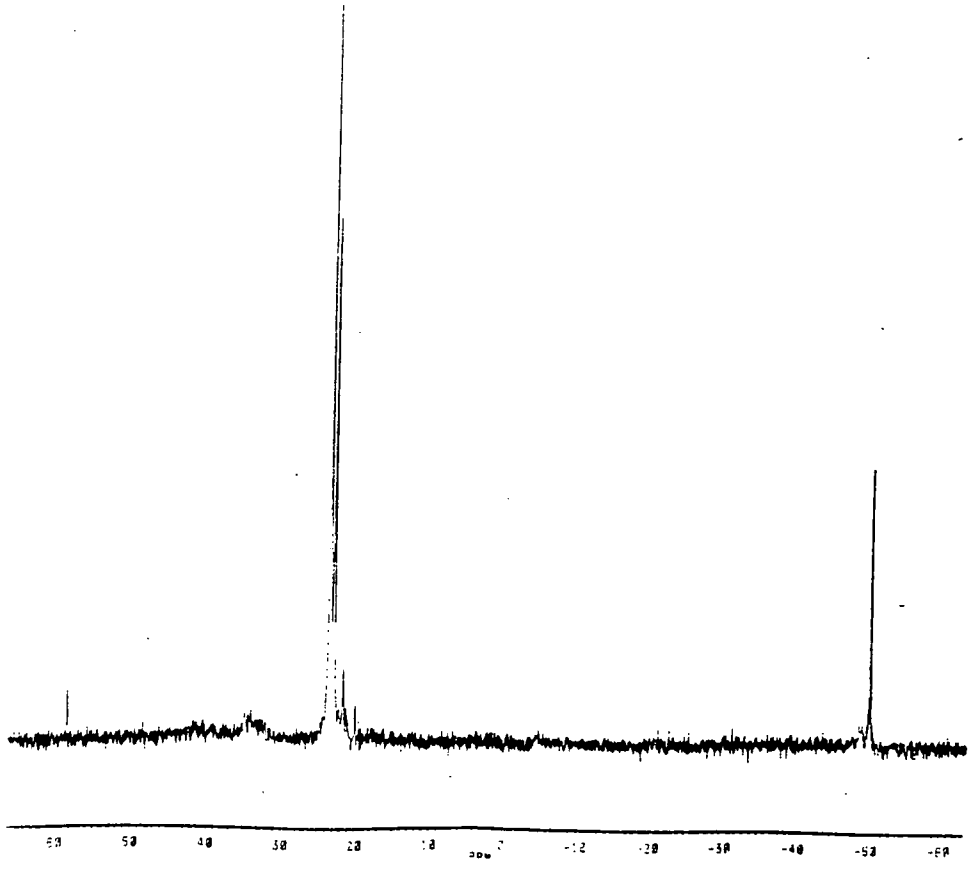


Figure 6.5: ^{31}P NMR Spectrum of $NbFe(DMPE)_2Np$



6.3.4. Reactions of Trans-hydrido,2-naphthyl,bis[bis(dimethylphosphino)-ethane]iron(II) with 2-Norbornyldichlorophosphine

Trans-hydrido,2-naphthyl,bis[bis(dimethylphosphino)ethane]iron(II) (0.5g, 1.03 mmol) dissolved in dry degassed THF (40 ml) was stirred under nitrogen in a 250 ml two neck round bottom flask fitted with a 100 ml pressure equalising dropping funnel. The apparatus was cooled in an ice-bath while the pressure equalising dropping funnel was charged with freshly distilled 2-norbornyldichlorophosphine (0.5g, 2.54 mmol) and dry degassed THF (70ml). The iron complex solution was stirred rapidly during the dropwise addition of the dichlorophosphine solution forming a pale yellow solution. This was stirred at ambient temperature for three hours, filtered to remove any solid oxidation products and concentrated under reduced pressure. The resulting pale yellow solution (approximately 10 ml) was cooled in a fridge. No solid product was recovered until all the volatile components had been removed under reduced pressure yielding a yellow-brown powder:

^{31}P NMR (ppm in pentane):	23.6	doublet	J [^{31}P-^{31}P] = 54.6 Hz
	-50.3	singlet	

6.4. Molybdenum Phosphine Complexes

6.4.1. Introduction

Unusual phosphine complexes have recently been prepared from chlorophosphines and pentacarbonyltungsten hydride[5]. Using the dichlorophosphines produced during this work, the synthesis of some other novel molybdenum-phosphine complexes was attempted. Hydridotricarbonyl-cyclopentadienylmolybdenum and the sodium salt can be readily synthesised[14] from molybdenum hexacarbonyl. Therefore these starting materials were prepared and their reaction with 2-norbornyldichlorophosphine investigated. A control reaction between cyclopentadienyl sodium and phosphorus trichloride was also studied. Trisacetonitriletricarbonylmolybdenum was also synthesised and the reaction with a dichlorophosphine monitored by FT-IR.

6.4.2. Reaction of Cyclooctyldichlorophosphine with Cyclopentadienyl Sodium

Freshly distilled cyclopentadiene (23.9g, 0.36 mol) was diluted in dry degassed THF (100 ml) under nitrogen in a two neck round bottom flask. The solution was stirred and cooled in an ice-bath. Small pieces of sodium (8.49g, 0.36 mol) were added to the cyclopentadiene solution against a counter-current of nitrogen. The solution slowly turned pink and effervesced as hydrogen was evolved. After complete addition the solution was stirred at ambient temperature for 24 hours. Excess sodium was removed from the pink cyclopentadienyl sodium solution (approximately 3.5M) by filtration.

Cyclooctyldichlorophosphine (10g, 47 mmol) in dry degassed THF (50 ml) under nitrogen was cooled in a two neck 100ml round bottom flask fitted with a serum cap. With vigorous stirring, cyclopentadienyl sodium solution (12 ml, 42 mmol) was added dropwise using standard syringe techniques. The pink colour of each drop was discharged to give a yellow solution and cloudy white suspension. The solution was stirred at ambient temperatures and a sample analysed by ^{31}P NMR. After 24 hours a second NMR spectrum showed no further reaction had occurred. Excess cyclopentadienyl sodium solution (20 ml, 72 mmol) was added dropwise to the reaction mixture. The yellow colour deepened, although ^{31}P NMR showed no further reaction had occurred.

The solution was tested with triethylamine, ethanol in triethylamine and sodium to determine the reactivity of the product. Each reaction was monitored by ^{31}P NMR but no changes were observed in the spectra:

^{31}P NMR (in THF) of reaction between	δ (ppm)
Cyclooctyldichlorophosphine + cyclopentadienyl sodium	135.2 singlet 89.5 singlet
Cyclooctyldichlorophosphine + excess cyclopentadienyl sodium	134.3 singlet
many peaks between	4 - -11
and	-31 - -41

A control experiment replacing cyclooctyldichlorophosphine with phosphorus trichloride was also performed. A golden yellow, apparently air-stable, powder (7.7g) was isolated. The powder was insoluble in water, alcohol, toluene, chlorinated and alkane solvents. The order of addition of the reactants was reversed so cyclopentadienyl sodium solution was always in excess. A bright

yellow solid was isolated, identical to the one above. Thus the order of addition of the reactants apparently did not affect the nature of the reaction products:

EA: %C 28.44; %H 3.64; %P 13.67
ratio C:H:P, 5.27:8.25:1

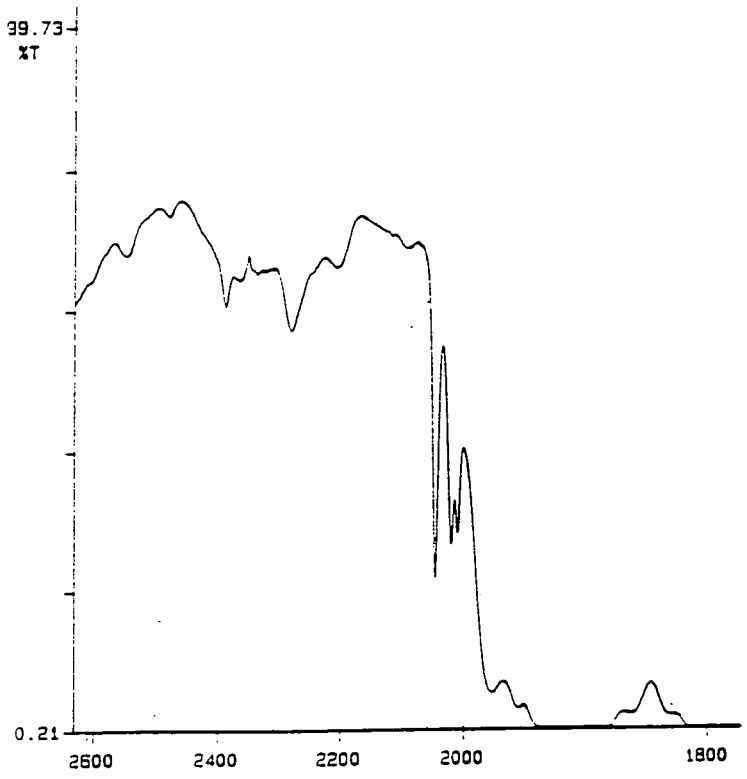
MS; EI: 166 $[C_5H_5PCl_2]^+$; 149 unassigned
CI: 102 $[HPCl_2]^+$; 91 unassigned

6.4.3. Synthesis of Sodium Tricarbonylcyclopentadienylmolybdenum and Hydridotricarbonylcyclopentadienylmolybdenum

Cyclopentadiene solution (sodium [1.9g, 82.6 mmol] in cyclopentadiene [6.1g, 0.92 mmol]) in THF (100 ml) was prepared under a nitrogen atmosphere in a 250 ml round bottom flask fitted with a reflux condenser. Following literature methods[14], molybdenum hexacarbonyl (8.04g, 30.5 mmol) was added to the flask and the mixture heated under reflux for 24 hours producing a pale yellow solution. Photolytic decomposition of molybdenum compounds was minimised by enclosing the apparatus in aluminium foil. Solid decomposition products were removed by filtration at ambient temperature. The FT-IR spectrum, recorded between 2200 and 1700 cm^{-1} (16 scans at 2 cm^{-1} resolution), of sodium tricarbonylcyclopentadienyl-molybdenum solution, $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, exhibited peaks at 2046.9 (vs) and 2010.8 (m) cm^{-1}.

Approximately half (55 ml) of this solution was transferred to a 250 ml round bottom flask under nitrogen using standard syringe techniques. Maintaining the inert atmosphere, glacial acetic acid (2.5 ml, 43.7 mmol) was added dropwise to the rapidly stirred solution, precipitating hydridotricarbonyl-cyclopentadienylmolybdenum, $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, as a white solid. The IR spectrum of the molybdenum hydride in solution showed peaks at 2021.6 (s) and 1954.8 (w) cm^{-1}, although the sample also contained significant amounts of the sodium salt, as shown in Figure 6.6. The solid was removed by filtration, dried under a nitrogen stream and used without further purification.

Figure 6.6: FT-IR Spectrum of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ and the Sodium salt



6.4.4. Reaction of Tricarbonylcyclopentadienylmolybdenum Complexes with 2-Norbornyldichlorophosphine

Sodium tricarbonylcyclopentadienylmolybdenum solution under nitrogen was diluted with dry degassed THF and cooled in an ice-bath. With rapid stirring, 2-norbornyldichlorophosphine (2.5g, 12.7 mmol) was added dropwise to the solution against a gentle counter-current of nitrogen, to maintain the inert atmosphere. Reaction occurred almost immediately, the solution turning dark red. An IR spectrum, recorded between 2650 and 1700 cm^{-1} (16 scans at 2 cm^{-1} resolution) and shown in Figure 6.7, exhibited peaks at 2012.3 (w), 1954.1 (vs) and 1912.1 (s) cm^{-1}. After being stirred at ambient temperature for five hours no further reaction had occurred, confirmed by IR. Therefore excess 2-norbornyl-dichlorophosphine (2.5g, 12.7 mmol) was added to the reaction mixture and the solution was heated under reflux for 10 hours. An IR spectrum, shown in Figure 6.8, of the resulting dark red/brown solution showed peaks at 1974.4 (vs) and 1909.2 (s) cm^{-1}.

Figure 6.7: FT-IR Spectrum of the Reaction of Hydridotricarbonyl-cyclopentadienylmolybdenum with 2-Norbornyldichlorophosphine

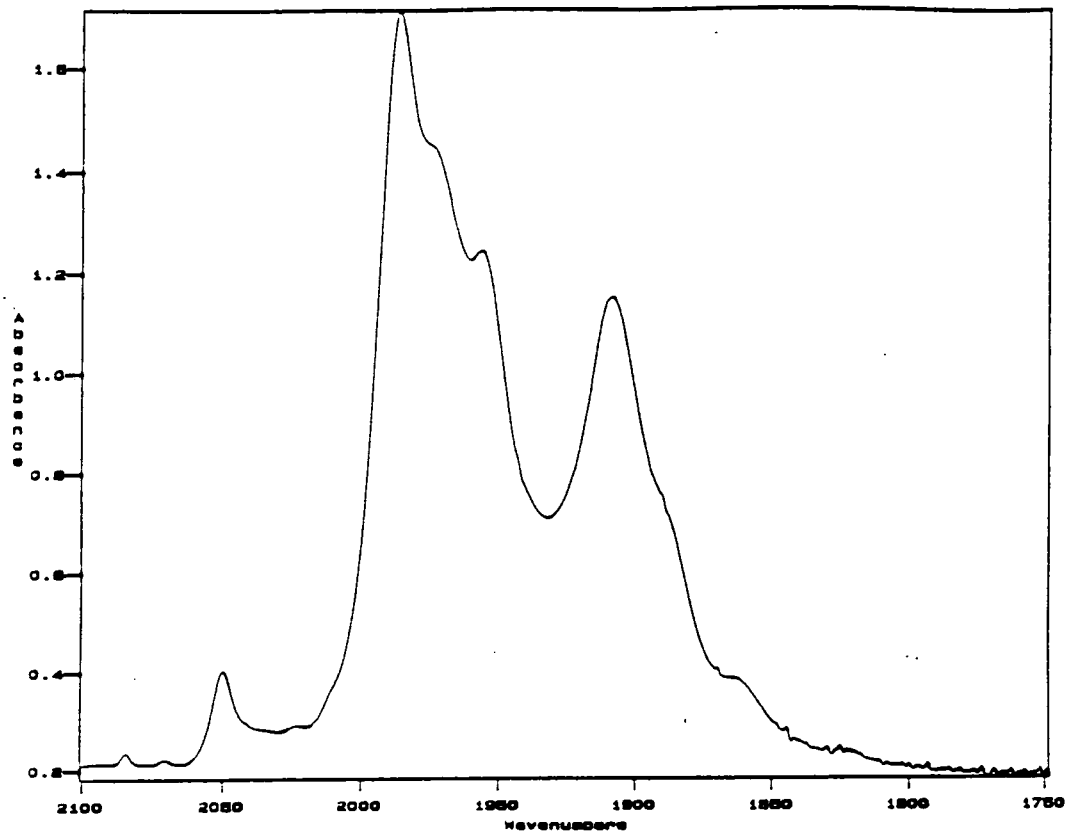
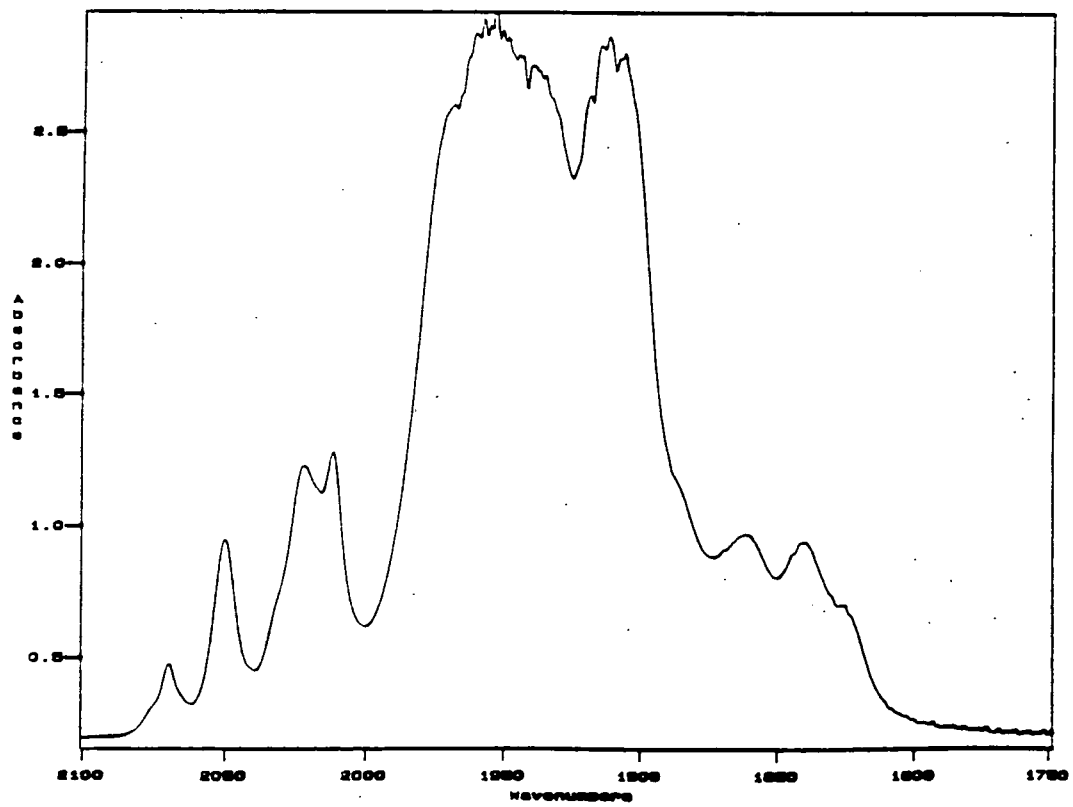


Figure 6.8: IR Spectrum of the Reaction of Hydridotricarbonylcyclopenta-dienylmolybdenum with excess 2-Norbornyldichlorophosphine



This experiment was repeated using hydridotricarbonyl-cyclopentadienylmolybdenum suspended in THF (100 ml). Similar peaks in the IR spectrum were observed, showing the reaction had proceeded identically to that with the sodium salt.

6.4.5. Reaction of Trisacetonitriletricarbonylmolybdenum with 2-Norbornyldichlorophosphine

Molybdenum hexacarbonyl (4.05g, 8.9 mmol) was heated under reflux in freshly distilled dry degassed acetonitrile (150 ml) under nitrogen in a 250 ml foil-covered round bottom flask fitted with a reflux condenser. After cooling to ambient temperature the pale yellow/green solution of trisacetonitriletricarbonyl-molybdenum[15-8] was filtered to remove any decomposition products. With rapid stirring the filtrate was cooled in an ice-bath and 2-hexyldichlorophosphine (1.47g, 7.86 mmol) added dropwise against a gentle counter-current of nitrogen. No reaction was observed until the reaction mixture was heated under reflux, forming a red/purple solution. After cooling to ambient temperature the volatile components were removed under reduced pressure and the dark red residue dissolved in chloroform. The IR spectrum showed peaks at 2004 (w), 1924 (s) and 1903 (s) cm^{-1}.

6.5. Discussion

6.5.1. Palladium Phosphine Complexes

Alkene complexes of palladium (II) dichloride undergo facile substitution by phosphine ligands forming an equilibrium mixture of cis- and trans-isomers in solution. Cis-isomers are apparently the more stable, although only one isomer is usually isolated[19]. In solution the amount of trans-isomer decreases as the phosphine σ-basicity increases, although the steric effects of bulky phosphines favour trans-isomer formation. Many studies[20] of the isomerism process suggest a halide displacement mechanism operates, the intermediate being stabilised by excess phosphine or solvent. Interestingly the diene ring in dichloro(η^4-cyclooctadiene)palladium (II) adopts a boat-boat conformation, and may even isomerise to the 1,4-isomer[21].

^{31}P NMR provides an elegant method for discriminating between cis- and trans-isomers, the former resonating at higher frequency because they form stronger π-bonds[22]. Similarly strong σ-donating phosphines generate a

downfield shift from the free phosphine resonance. Observed chemical shift effects in ^{31}P NMR spectra are caused by the hybridisation, oxidation state, π-bonding strength and bond angles of the phosphorus centre, in addition to the electronegativity of the phosphorus substituents, which is the major factor. ^{31}P-^{31}P coupling constants, transmitted through the metal centre, are much stronger[22] in trans-diphosphines than the cis- analogues. Their magnitude is due to stereochemical and phosphorus substituent effects, bulky and electronegative groups increasing the coupling constant. Chiral phosphines were not resolved before their reaction with the palladium centre, therefore enantiomeric product mixtures would be present. The mixture will consist of an enantiomeric pair and a meso-isomer, each isomer resonating at a slightly different frequency in the ^{31}P NMR.

Phosphines are regarded as soft bases, readily forming complexes with the later transition metals, especially those in lower oxidation states, because they can accept excess electron density. However amine ligands are softer bases than the corresponding phosphines, being more polarisable, and so would be expected to preferentially form complexes with palladium (II) centres, because the platinum metals form stronger complexes with softer ligands. Experimental evidence, using a mixture of 2-norbornyldimethylphosphine and triethylamine, substantiated this theory as no resonances derived from a metal-phosphine complex were observed in the ^{31}P NMR spectrum. Analogously palladium complexes using aminophosphines derived from piperazine could not be studied using ^{31}P NMR. Interestingly mixed phosphine-nitrile ligands preferentially coordinate to palladium dichloride[23] via the phosphorus centre because the nitrile centre is a harder ligand. Other aminophosphine complexes have been used in catalytic processes[24,25].

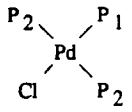
Although no reaction between the palladium centre and phosphine was observed using ^{31}P NMR at room temperature, complexes were readily formed when the solution was gently heated. Normally the initial products did not react further with time at elevated temperatures, although a little dark solid sometimes precipitated from the solution. This is believed to be a decomposition product. Similarly significant amounts of phosphine oxides were detected after prolonged heating of the solution. However, the initial products from some samples did react further over 12 hours at 80°C. These products either resulted from an isomerism or oxidation process or were new complexes, but could not be characterised.

^{31}P NMR studies of palladium phosphines in this work were complicated by significant phosphine impurity, because the metal centre was not sufficiently selective to form complexes with the major phosphine component only. Each complex generates separate multiplets in the spectrum, therefore many resonances were observed. Occasionally these could not be resolved and the reaction could not be followed or analysed using ^{31}P NMR. Thus the spectra were too complicated to interpret accurately, and no conclusions concerning the nature of the products can be drawn. The number of different species present prevented accurate assignment of the observed multiplets. Many doublets were observed in each reaction mixture, and these must arise from ^{31}P-^{31}P coupling. However, each doublet represents the signal from one phosphorus atom in a complex containing two non-equivalent phosphorus ligands. Therefore a second doublet at a different frequency, but having an identical coupling constant, will be produced by the second phosphorus atom. In some samples only one doublet is noted, suggesting that the resonances are not genuinely coupled but are two singlets of similar chemical shift. Additional data, derived from purer samples, is necessary to interpret these spectra. Experiments at various temperatures between 20°C and 80 °C were studied to increase the selectivity of the reaction, however the products were similar in every reaction and independent of the reaction temperature. Only the rate of reaction was found to vary.

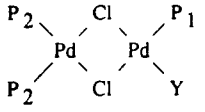
Most of the experimental multiplets were doublets at lower frequency than the free phosphine, caused by ^{31}P-^{31}P coupling of non-equivalent phosphines through the P-M-P bond, or through the diphosphine backbone[26]. Singlets were generated by complexes possessing identical phosphines. Palladium phosphine coupling was not observed. ^{105}Pd (22% abundance, $I=5/2$) is the only NMR active isotope. However no satellites could be resolved from the background noise.

Triplets, at lower frequency, were also occasionally observed in the spectra, as shown in Figures 6.1 and 6.2. These must be caused by coupling between a single phosphine group in a different chemical environment to two other, identical, phosphine groups. Thus at least three phosphine groups must be present on the palladium centre, or on a dichloro-bridged palladium dimer. Four coordinate $PdClL_3$ [40] complexes (L = phosphorus ligand) contain two phosphine groups cis- to chlorine and one trans-, and would therefore be expected to generate a triplet. These complexes are known[19,20] to be formed as intermediates during isomerism between cis- and trans-isomers. Formation of a 5-coordinate palladium species is not favoured, so $PdCl_2L_3$ complexes (L = phosphorus ligand) are unlikely to be detected, even as transient species. Dichloro-bridged palladium dimers [41] could also generate a triplet if the

phosphorus centres couple through the electron deficient Pd-Cl-Pd bridges. Two triplets, with similar coupling constants, would be observed if four phosphines are attached to the dimer (Y=P):



[40]



[41]

Y = P or Cl

Observed ^{31}P-^{31}P coupling constants could not be used to discriminate between cis- and trans-isomers and enantiomeric pairs because accurate interpretation of the spectra was not possible. Larger coupling constants indicate a trans-isomer, although the precise chemical composition of the complex was unknown. Similarly smaller coupling constants show cis-isomers are present, but the exact nature of the complex is unknown.

Thus, although many multiplets were observed for each palladium phosphine system, the spectra could not be reliably interpreted. This profusion of multiplets was caused by the presence of cis- and trans-isomers of enantiomeric pairs derived from many non-equivalent phosphines, due to impurities in the phosphine solution. Therefore many very similar palladium-phosphine complexes were present in the mixture. Nevertheless, very few complexes with identical phosphines were formed, detected as singlets, preventing accurate analysis and characterisation of the products in solution. Triphosphine complexes, the possibility of dimeric palladium species and bridging and ring-chelated diphosphines also complicated the spectra. Some monodentate bis-diphosphine complexes were also observed, having a singlet at 180 ppm due to the non-coordinated phosphorus atom.

Chiral phosphines were not resolved before their reaction with the palladium centre. Therefore, for the complex $PdCl_2L_2$ (where L = chiral phosphine ligand) many isomers are possible. In addition to the cis- and trans-isomers, stereoisomers may also be detected by ^{31}P NMR. These consist of an enantiomeric pair of R,R and S,S isomers and the meso-isomer. Thus many separate multiplets may be observed for a single 'pure' complex. Furthermore, chiral impurities in the phosphine solution will also produce many slightly different complexes, significantly complicating the spectra and hence preventing their interpretation.

No solid products were isolated from these reactions because too many similar species were present in small quantities. Therefore complexes of

sufficient purity for further analysis, such as X-ray structure determination, could not be obtained.

On coordination the phosphorus resonance changes dramatically relative to that of the free ligand. This difference is known as the coordination chemical shift (Δ). Chelate ring formation also predictably affects the chemical shift for the complex, the ring contribution is defined as Δ_R. Many investigations concerning these parameters have been attempted[26-28], although the theoretical aspects are not clear. Usually 4- and 6-membered chelate rings shield the phosphorus centre, although 5-membered rings cause deshielding.

The reaction of dichloropalladium di(2-hexyldichlorophosphine) and the cyclohexane analogue with 1,4-butanediol were investigated. The former complex generated a triplet at 161.6 ppm (J [^{31}P-^{31}P] = 50.6 Hz) and the latter a singlet at 157.2 ppm. Both reactions resulted in many palladium and phosphine oxidation products because triethylamine could not be used to neutralise the hydrogen chloride formed during the reaction. Both spectra showed no similarity to the palladium di(alkyl 1,4-butylphosphite) spectra obtained from the phosphite and $PdCl_2$[COD]. Although this observation cannot be readily explained, coordination of a chiral phosphine, such as 2-hexyldichlorophosphine, to the palladium centre would produce three resonances, derived from the R,R; S,S and meso complexes. Coordination of a phosphine oxide to the metal is also possible.

Conclusion

Although the dichloro(diene)palladium complex readily reacted with phosphines at elevated temperature forming the bisphosphine complex, the reaction was not very discriminating because impure phosphine starting materials prevented selective formation of specific complexes and hence assignment of the ^{31}P NMR spectra. Much higher levels of phosphine purity are required before these reactions can yield pure complexes. However the system studied shows great potential, as many di(alkene)palladium (0) complexes[29,30] are also accessible. Similar experiments with Platinum (II) or (0) complexes could be studied, providing more detailed information concerning the metal-phosphine interaction and stereochemistry.

6.5.2. Iron Phosphine Complexes

Alkylsodium reagents react with chlorophosphines producing alkylphosphines. Similarly, sodium naphthalide reacted readily with

chlorophosphines, the green colour immediately discharging on addition to the chlorophosphine solution. An insoluble yellow solid was isolated from the experiment with bis-1,2-[dichlorophosphino]ethane. Mass spectroscopy suggested dimeric or oligomeric species of the type $[X_2PCH_2CH_2P(X)CH_2CH_2PX_2]$ where X = Cl or 2-naphthyl had formed, although this seems unlikely. A similar reaction with cyclooctyldichlorophosphine produced a yellow dialkylchlorophosphine or alkylarylchlorophosphine solution, as determined by ^{31}P NMR.

Iron (II) chloride tetrahydrate could be readily dehydrated in methanol, although water ligands are lost sequentially, and with increasing difficulty, from the metal centre. Elemental analysis of the anhydrous complex suggested complete dehydration had not occurred, although the remaining water of crystallisation did not significantly affect the subsequent experiments. Because iron (II) compounds are rapidly oxidised in air, all manipulations were carried out under an inert atmosphere of nitrogen, using dry degassed solvents. $Fe(DMPE)_2Cl_2$ [38] rapidly formed as a green powder when DMPE was added to anhydrous iron (II) chloride in THF. Initially a red solvated iron species was observed, although this rapidly reacted with the phosphine, precipitating the product. Similarly the dichlorophosphino analogue was also prepared as a red powder, and was apparently more air-stable than the free ligand. Lord Lewis[31] has prepared Trans-dichloro,bis[bis-1,2-(di-n-butylphosphino)ethane]iron(II), $Fe(DBPE)_2Cl_2$, using similar methods, and has investigated a variety of related σ-acetylide complexes.

Sodium naphthalide reacts with $Fe(DMPE)_2Cl_2$ in THF producing an iron hydride [39] as a very air-sensitive orange solution. This complex reacted in situ with a dilute 2-norbornyldichlorophosphine solution generating two new peaks in the ^{31}P NMR spectrum. The singlet at -50 ppm is characteristic of a free trialkylphosphine, showing the chlorophosphine had displaced at least one of the four bound phosphorus atoms from the coordination sphere of the iron centre. However the second phosphorus centre of the diphosphine may still be coordinated to the iron complex, DMPE becoming a monochelated ligand. Displacements of bulky diphosphines from the metal centre by better ligands is known to occur in these iron dichloride bis-diphosphine systems[32]. A doublet at 23.6 ppm (J [^{31}P-^{31}P] = 54.6 Hz, coupling between the phosphorus atoms of DMPE and 2-norbornyldichlorophosphine) is also observed, caused by the new iron dichlorophosphine complex. This suggests displacement of naphthalene has occurred, generating a non-rigid 5-coordinate trigonal bipyramidal iron complex, which is capable of undergoing limited Berry twist rearrangement. Loss of

naphthalene from [39] producing the highly reactive [$Fe(DMPE)_2$] is known to occur[11]:

1. $[Fe(DMPE)_2]Cl_2 + NaNp \rightarrow HFe(DMPE)_2Np$
2. $HFe(DMPE)_2Np \rightarrow [Fe(DMPE)_2] + NpH$
3. $[Fe(DMPE)_2] + NbPCl_2 \rightarrow (NbPCl_2)Fe(DMPE)_2$

Therefore although 2-norbornyldichlorophosphine is bound to the iron atom, probably in the classical mode, insufficient detailed information concerning the nature of the bonding interaction can be obtained. The aim of the experiment was to replace the hydride with an alkylchlorophosphine unit. However, although no hydride resonances are observed in either ^{31}P or ^{1}H NMR, displacement of DMPE and probably naphthalene from the iron centre has also occurred. Thus more detailed studies of this system are required to unambiguously characterise the final iron complex.

At ambient temperature dichloroiron-phosphine complexes are paramagnetic in solution[32,33], although facile loss of one coordinated phosphine atom is possible and is believed to be responsible for NMR signal sharpening at lower temperatures.

Trans-dichloro,bis[bis(dimethylphosphino)ethane]iron(II), $Fe(DMPE)_2Cl_2$, is a very versatile intermediate. In the presence of a strong reducing agent, such as sodium borohydride, a η^2-dihydrogen cationic complex is formed[34]. Under ethene this complex liberates dihydrogen forming a η^2-ethene cationic complex.

$$Fe(DMPE)_2Cl_2 + NaBH_4 \rightarrow [HFe(DMPE)_2(H_2)]^+$$
$$[HFe(DMPE)_2(H_2)]^+ + C_2H_4 \rightarrow [HFe(DMPE)_2(C_2H_4)]^+$$

Deprotonation of the cationic iron-ethene complex by base yields the neutral complex[35], and reaction of the dihydrogen cationic complex with halide produces trans,bis[bis(dimethylphosphino)ethane]iron (II) chloride hydride[36] which was thought to bind dihydrogen. However, the chelate ring opens, destroying the complex.

Conclusion

Trans-dichloro,bis[bis(dimethylphosphino)ethane]iron(II) and the 2-naphthyl hydride derivative were prepared in a one-pot synthesis and the reaction

with a chlorophosphine examined. The aim of this work was to study the reaction of the iron hydride with chlorophosphines. However the iron complex displaced naphthalene prior to substitution by the chlorophosphine, probably generating a 5-coordinate iron-phosphine complex. DMPE relieved the steric strain around the metal centre by acting as a monochelate ligand. These iron hydride systems are very susceptible to oxidative addition. A variety of diphosphine complexes are documented and their properties have been previously investigated. This preliminary work indicates that the research is worth pursuing, to investigate the effects of the novel phosphines produced in this work.

6.5.3. Molybdenum Phosphine Complexes

Cyclopentadienyl sodium reacted very vigorously with phosphorus-chlorine bonds. To moderate the reaction, the reagents were frequently cooled in an ice-bath. ^{31}P NMR showed cyclooctyldichlorophosphine formed a dialkylchlorophosphine[37] (δ = 135.2 ppm), cyclooctylcyclopentadienylchloro-phosphine, and a second major product (at 89.5 ppm). Many trialkylphosphines were also observed between -31 and -41 ppm, although these products were not fully characterised. Other peaks between 4 and -11 ppm suggest arylphosphines are present, although this would seem unlikely under the experimental conditions.

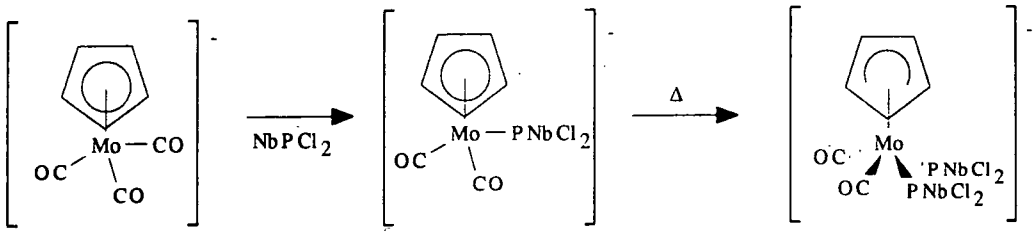
Phosphorus trichloride reacted with cyclopentadienyl sodium precipitating a golden yellow solid. Elemental analysis and mass spectroscopy suggest this product is cyclopentadienyldichlorophosphine or a phosphorus polymer. However due to its insolubility and air-stability a phosphorus (V) species such as the phosphine oxide is a more likely identity, although the characteristic ν_{PO} was not observed. Dimerisation of cyclopentadiene ring may produce a bicyclic derivative, such as $C_{10}H_{10}(PCl_2)_2$. Therefore phosphorus trichloride oxidised during the reaction whereas, surprisingly, cyclooctyldichlorophosphine did not. Although cyclopentadiene π-complexes of phosphines are known[38], an aluminium catalyst is required to abstract halogen from the phosphorus centre generating a very unstable phosphorus cationic species, so a similar reaction is unlikely to occur in this study:

$$(C_5H_5)PRCl + AlCl_3 \rightarrow [(C_5H_5)PR][AlCl_4]$$

Hydridotricarbonylcyclopentadienylmolybdenum and the sodium salt were readily prepared in good yield using the standard literature method[14], although some decomposition of the molybdenum complexes occurred. A significant molar excess of cyclopentadienyl sodium solution was used in the

syntheses, causing some problems in purifying and analysing reaction products. However IR spectra of the products were in good agreement with literature values[14,39]. The sodium salt exists as an ion-pair in THF[40] and is susceptible to nucleophilic substitution. With triphenylstannyl chloride, a (triphenyltin)tricarbonylcyclopentadienyl-molybdenum complex is formed[41]. η^5-Cyclopentadiene complexes are very stable and tend not to 'slip' to an η^3- or η^1-structure. The ring itself is normally inert to both nucleophilic and electrophilic substitution[42].

2-Norbornyldichlorophosphine reacted readily with both cyclopentadienyl-molybdenum tricarbonyls forming similar products. Some products associated with the reaction of cyclopentadienyl sodium and chlorophosphines were also detected. The aim of these reactions was to form a non-classical, 3-electron donor, molybdenum-phosphorus interaction, without using the phosphorus lone-pair orbital, caused by loss of sodium chloride or hydrogen chloride from the complex. However comparison of the experimental IR spectra with literature data[39] shows the initial product was probably a 'piano-stool' dicarbonylcyclopentadienylmolybdenum phosphine complex. This product reacted further at elevated temperatures, possibly involving cyclopentadiene ring slip to η^3, although the product could not be fully characterised. Thus the phosphine displaced a carbonyl ligand rather than attacking the hydride or ring. ^{31}P NMR spectra of the samples showed poor resolution, caused by a low signal-to-noise ratio, and slight product decomposition, preventing accurate interpretation. A postulated reaction scheme is shown below:



Another widely used activated molybdenum system is trisacetonitrile-tricarbonylmolybdenum[15-8]. Reaction of this complex with a chlorophosphine formed a fac-tricarbonylmolybdenum triphosphine similar to those reported previously[39]. IR spectra of this species were very similar to those obtained from the analogous reaction of the cyclopentadiene complex, surprisingly suggesting displacement of the dienyl ring may have occurred.

Conclusion

Without a more comprehensive study, and more thorough analysis, of this molybdenum system no firm conclusions concerning the nature of the reaction can be drawn. Apparently chlorophosphines prefer to behave as classical ligands, displacing carbonyl groups. Thus the molybdenum-hydride bond probably did not react with chlorophosphines, and only the classical ligand properties of the phosphine were exhibited. Previous work[43] has shown metal-phosphorus 3-electron donor double bonds can be formed by decarbonylating metallophosphanes such as $(C_5H_5)Mo(CO)_3)PR_2$, so this area of study is well worth pursuing.

6.6. Conclusion

Dichloro(η^4-1,5-cyclooctadiene)palladium (II) was prepared in good yield from $PdCl_2$ and the reactions with a variety of novel phosphines studied by ^{31}P NMR. Although the dichloro(diene)palladium complex readily reacted with phosphines at 80°C, impure phosphine starting materials prevented selective formation of the intended complexes, a mixture of many similar complexes being observed. Therefore detailed assignment of the spectra was not possible. Purification of the phosphines is thus essential, although problematic, before pure palladium-phosphine complexes can be produced and isolated. However despite these problems the system studied shows great potential, and constitutes an area of significant interest for future work.

Trans-dichloro,bis[bis(dimethylphosphino)ethane]iron(II) and the 2-naphthyl hydride derivative were prepared from anhydrous $FeCl_2$ permitting their reaction with 2-norbornyldichlorophosphine to be investigated. Displacement of naphthalene from the complex resulted in formation of the 5-coordinate iron phosphine complex. However products from the attempted reaction of the chlorophosphine with the metal hydride, producing a 3-electron donor metal-phosphine bond, were not detected. Other phosphines synthesised during this study may activate the iron centre towards oxidative addition of simple molecules, potentially acting as homogeneous catalysts.

Similarly the molybdenum hydride $(C_5H_5)Mo(CO)_3)H$ and the sodium salt were synthesised from $Mo(CO)_6$ and cyclopentadienyl sodium, but did not interact with 2-norbornyldichlorophosphine generating a 3-electron donor interaction. Although the results are not conclusive, the molybdenum-hydride bond apparently did not react with chlorophosphines, as a new piano-stool

dicarbonylcyclopentadienyl-molybdenum phosphine complex was generated. Therefore chlorophosphines prefer to behave as classical ligands with both iron and molybdenum hydrides, donating two electrons and displacing labile or carbonyl groups. Thus only the classical ligand properties of the chlorophosphine were exhibited and no metal-phosphorus double bonds were formed, which was the major aim of the work.

Sodium complexes of cyclopentadiene and naphthalene reacted rapidly and exothermically with chlorophosphines. The former anion reacted with cyclooctyldichlorophosphine producing cyclooctylcyclopentadienylchlorophosphine. Excess cyclopentadienyl sodium did not replace the remaining chlorine atom, probably for steric reasons. With phosphorus trichloride, cyclopentadienyldichlorophosphine or the oxide was formed as a yellow solid. Surprisingly polymeric phosphines were formed during the reaction between sodium naphthalide and bis-1,2-(dichlorophosphino)ethane. However, these could not be fully characterised even by mass spectroscopy. A dialkylchlorophosphine formed from the analogous reaction with cyclooctyldichlorophosphine, however the exact chemical composition of this product was not established.

Much of the work described in this chapter provides a solid foundation for future studies, although inconclusive results prevented rigorous analysis and unambiguous determination of some product structures. However a more detailed and systematic investigation of each system would permit some interesting and unusual chemistry to be investigated, and the reaction products precisely characterised.

6.7. References

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CHAPTER 7:

CONCLUSIONS

Phosphines are important transition metal ligands because their electronic and steric properties can be altered systematically and predictably. Diphosphines provide additional control at the metal centre, and are thus widely used to stabilise transition metal complexes, such as homogeneous catalysts. Recently chiral phosphines have been used to confer chiral properties on transition metal complexes, allowing asymmetric syntheses and stereospecific catalytic processes, producing enantiomerically pure products.

7.1. Chlorophosphine Synthesis

Many novel alkyldichlorophosphines and bis-1,2-[dichlorophosphino]-alkanes were prepared from white phosphorus, phosphorus trichloride and an alkene under high temperature and pressure conditions. A reaction temperature of 240°C was employed, frequently generating pressures in excess of 100 atm. During the reaction a black polymeric material was also produced, complicating isolation and purification of the products, although no alkenes were recovered from the autoclave after the reaction. A wide variety of alkenes were used as the substrate: chain alkenes, cyclic alkenes, dienes and terpenes, although in every reaction the yield of monophosphine was greater than that of diphosphine. A new stereocentre is produced at the α-carbon of unsymmetric alkenes during the reaction.

Many chlorophosphines were produced in each reaction and were difficult to isolate and purify. The reaction products were distilled under reduced pressure producing clear viscous oils. Characterisation of the products was achieved using ^{31}P, ^{13}C NMR, MS and elemental analysis. The NMR spectra provided a wealth of information and were usually sufficiently detailed to unambiguously characterise the products. ^{31}P-^{13}C coupling constants were vital in determining the position of each carbon atom relative to phosphorus. Sample impurity and decomposition complicated elemental analysis, inaccurate non-reproducible results often being obtained. Therefore MS was used to prove the assigned structure.

Simple chain alkenes readily reacted forming the expected products, although the diphosphine yield decreased as the molecular mass and steric size of the substrate increased. Invariably the monophosphine was the Markownikoff-type (2-alkyl) addition product. Haloalkenes reacted in a dangerous and unpredictable manner, generating very high pressures and damaging the autoclave's copper gasket. Cyclic alkenes also reacted under the high pressure and

temperature conditions, the equatorial or trans,diequatorial conformation being adopted by the product ring system. Both the endo- and exo-isomers of 2-norbornyldichloro-phosphine were observed, in a ratio of 1:3 (endo:exo), but could not be separated.

Cyclopentadiene and 2,5-norbornadiene reacted analogously to their mono-alkene derivatives, undergoing 1,2-addition. Slight differences in the ^{13}C NMR spectra of 2-norbornyldichlorophosphine derived from the parent mono-alkene and diene were observed, although these were probably caused by sample impurities. Double bond isomerisation (conjugation) in 1,5-cyclooctadiene, under the reaction conditions, produced the 1,4-diphosphine. No 1,2-diphosphine was isolated from this reaction. Butadiene may have dimerised under the high temperature and pressure conditions forming cyclooctadiene. This reaction may be mediated by phosphorus because one possible product is a 1,4-bridged cyclooctane ring, probably 9,10-dichloro-9,10-diphosphabicyclo[4.2.2]decane. A second, more probable, product is dichloro-2,2'-diphospholane, although detailed analysis failed to unambiguously characterise this product. A similar product was not detected in the reaction with 1,5-cyclooctadiene. Additional products from the butadiene reaction included both 1,2- and 1,4-diphosphines.

Natural product terpenes isomerised and interconverted under the reaction conditions generating many chemically similar products, detected by ^{31}P NMR. These chiral products could not be separated, even using a high resolution distillation column. Therefore they could not be separated or characterised. Styrene generated many products under the reaction conditions, although benzene and toluene did not react, suggesting ring aromaticity is not destroyed during the reaction. Similarly, the C-N triple bond in acetonitrile did not undergo reaction in the autoclave.

Monophosphines are apparently formed by a simple radical mechanism, hydrogen atoms adding across the double bond before the phosphorus dichloride unit. Diphosphine synthesis is more complex. An intermediate chloroalkyldichlorophosphine species is formed by the insertion of the alkene into phosphorus trichloride. Subsequent reaction of this intermediate with white phosphorus and phosphorus trichloride generates the diphosphine. This postulated mechanism is supported by literature and experimental evidence. A second suggested mechanism, involving diphosphorus tetrachloride as the reactive species, is thought unlikely but cannot be discounted.

7.2. Phosphine Ligand Synthesis

Dichlorophosphines are versatile precursors in organophosphorus chemistry, undergoing facile conversion into a wide variety of phosphines and phosphites suitable for chelation. Dimethylphosphines and diethylphosphites were readily prepared using organometallic and 'active hydrogen' methods respectively. Reactions with alcohols produced inseparable mixtures. The high boiling points precluded separation of the components by distillation. 1,4-Butanediol produced three chemically similar products including a 1,3,2-phosphepane ring. The products from reactions with piperazine also could not be purified. Although some of the secondary products could not be fully characterised, the structure of the parent dichlorophosphine was unambiguously determined.

7.3. FT-IR of Group Manganese Carbonyl Halide Phosphines

Using the A_1 carbonyl stretching frequency of manganese tetracarbonyl bromide phosphine complexes an electronic parameter ($^{Mn}\chi$) relating to the ligand strength of the phosphine could be calculated. The values indicate the ligand strength of each phosphine relative to PPh_3. A systematic, but not exhaustive, study showed substituent electronegativity determined the value of $^{Mn}\chi$, more electronegative substituents (such as chloride) increasing the calculated values. Molecular mass of the parent alkyl group also increased $^{Mn}\chi$, therefore steric effects of the phosphine also affected the values obtained. ^{31}P NMR studies of both manganese and rhenium complexes were complicated by poor spectral resolution and long scan-times were necessary to acquire the data.

7.4. Synthesis of other Metal Phosphine Complexes

Dichloro(η^4-1,5-cyclooctadiene)palladium (II) was prepared from $PdCl_2$, and the reactions with various phosphines studied. However, phosphine impurity prevented characterisation of the products because of the large number of similar complexes formed. $Fe(DMPE)_2Cl_2$, formed from $FeCl_2$, readily reacted with sodium naphthalide forming an iron hydride. However reaction of the Fe-H bond with chlorophosphines was prevented by loss of naphthalene from the complex. Therefore only a 5-coordinate, $M(L_2)_2L'$, complex was isolated. Similarly phosphine substitution of a carbonyl group in the molybdenum complex $(C_5H_5)Mo(CO)_3H$ was preferred to reaction of the molybdenum-hydride. Further

reaction of the product occurred, generating a dicarbonyl-η^3-cyclopentadienyl-molybdenum phosphine complex. However, the products were not fully characterised. The sodium salt of the molybdenum complex reacted similarly to the hydride, as detected by NMR and IR.

7.5. Conclusion

Many unusual and novel mono- and diphosphines were prepared, characterised and studied. Dichlorophosphines were readily synthesised from white phosphorus, phosphorus trichloride and an alkene in good yield. Although the phosphorus starting materials are hazardous, requiring special precautions, and the reaction involves very forcing conditions, the high temperature and pressure reaction offers several advantages over other synthetic methods. These include a single-step one-pot synthesis, handling fewer hazardous materials in a controlled environment and production of novel and chiral organophosphines from readily available inexpensive starting materials. The phosphorus-chlorine bonds of these precursors react with many organometallic and active hydrogen compounds forming phosphines suitable for the synthesis of coordination compounds.

Many metal complexes of these phosphines were prepared. Manganese-carbonyl-bromide-phosphine complexes were examined, using FT-IR, to determine the electronic parameter of the phosphine. Dichloropalladium-phosphine complex formation was followed using ^{31}P NMR. However, phosphine impurity prevented detailed assignment of the spectra. Iron and molybdenum hydrides both formed mixed phosphine complexes with chlorophosphines, rather than complexes containing non-classical, 3-electron donor, metal-phosphine interactions.

APPENDIX 1:

INSTRUMENTAL PARAMETERS

1. Bruker AC250 NMR Spectrometer

5.9 Tesla Oxford Instruments magnet.

All dichlorophosphine samples were recorded as a neat liquid, other phosphine samples and metal-phosphine complexes were dissolved in chloroform, unless otherwise stated.

1.1 ^{31}P NMR

Reference (external):	1% H_3PO_4
Scan Frequency:	101.256 MHz
Sweep Width:	62500.000 MHz
Pulse Width:	3.5 μs
Line Broadening:	1.000 Hz

1.2. ^{13}C NMR

Reference (external)	TMS
Scan Frequency:	62.896 MHz
Sweep Width:	15151.515 Hz
Pulse Width:	3.5 μs
Line Broadening:	0.500 Hz
Decoupling:	Walz, noise broad-band decoupling

2. Bruker AMX 500 NMR Spectrometer

11.9 Tesla Oxford Instruments magnet.

All samples were dissolved in chloroform, unless otherwise stated.

2.1. ^{13}C NMR

Reference (external):	TMS
Scan Frequency:	125.763 MHz
Sweep Width:	7575.76 Hz
Pulse Width:	12.5 μs
Line Broadening:	5.0 Hz

3. Mattson Alpha Centauri FT-IR Spectrometer

PC-FIRST spectral interpretation package

Data Type:	Absorbance
Detector:	DTGS
Apodisation:	Triangular
Phase Correction:	Phaseapod
Iris size:	25%
Amplifier Gain:	1

3.1. Manganese Pentacarbonyl Bromide Spectra

Range:	2200 - 1800 cm^{-1}
Resolution:	2 cm^{-1}
No. of Sample Scans:	16
No. of Background Scans:	16

3.2. Iron Diphosphine Spectra

Range:	1800 - 1600 cm^{-1}
Resolution:	2 cm^{-1}
No. of Sample Scans:	16
No. of Background Scans:	16

3.3. Cyclopentadienylmolybdenum Tricarbonyl Spectra

Range:	2200 - 1700 cm^{-1}
Resolution:	2 cm^{-1}
No. of Sample Scans:	16
No. of Background Scans:	16

4. VG Analytical 7070E Mass Spectrometer

Electron Impact (EI) spectra were recorded at 70 eV.
Chemical Ionisation (CI) spectra were recorded using NH_3 as reagent gas.

5. Elemental Analysis

5.1. CHN Analysis was performed using a Carlo Erba Elemental Analyser 1106

5.2. Phosphorus Analysis

Acid digestion of the sample with perchloric and sulphuric acids was followed by dilution with a colouring agent consisting of ammonium molybdate and vanadate. Comparison of the intensity of UV absorption of this solution at 420 nm with a reference colouring agent solution allowed the phosphorus component to be calculated.

5.3. Chlorine Analysis

Combustion of the sample in oxygen, followed by potentiometric titration of the product with silver nitrate allowed the phosphorus content to be calculated.

APPENDIX 2:

COLLOQUIA, LECTURES AND SEMINARS

FROM INVITED SPEAKERS

Bold type indicates lectures attended

1. October 1992 - July 1993

October 15 — Dr. M. Glazer & Dr. S. Tarling, Oxford University & Birbeck College
It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation.

October 20 — **Dr. H.E. Bryndza, Du Pont Central Research**
Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.

October 22 — Prof. A. Davies, University College, London
The Albert-Ingold Lecture: The Behaviour of Hydrogen as a Pseudo-metal.

October 28 — Dr J.K. Cockcroft, University of Durham
Recent Developments in Powder Diffraction.

October 29 — **Dr. J. Emsley, Imperial College, London**
The Shocking History of Phosphorus.

November 4 — **Dr. T.P. Kee, University of Leeds**
Synthesis and Coordination Chemistry of Silylated Phosphites.

November 5 — Dr. C.J. Ludman, University of Durham
Explosions, A demonstration Lecture.

November 11 — Prof. D. Robins, Glasgow University
Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits.

November 12 — Prof. M.R. Truter, University College, London
Luck and Logic in Host-Guest Chemistry.

November 18 — Dr. R. Nix, Queen Mary College, London
Characterisation of Heterogeneous Catalysts.

November 25 — Prof. Y. Vallee, University of Caen
Reactive Thiocarbonyl Compounds.

November 25 — **Prof. L.D. Quin, University of Massachusetts, Amherst**
Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.

November 26 — Dr. D. Humber, Glaxo, Greenford
AIDS - The Development of a Novel Series of Inhibitors of HIV.

December 2 — Prof. A.F. Hegarty, University College, Dublin
Highly Reactive Enols Stabilised by Steric Protection.

December 2 — **Dr. R.A. Aitken, University of St. Andrews**
The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$.

December 3 — **Prof. P. Edwards, Birmingham University**
The SCI Lecture: What is a Metal.

December 9 — Dr. A.N. Burgess, ICI Runcorn
The Structure of Perfluorinated Ionomer Membranes.

January 20 — Dr. D.C. Clary, University of Cambridge
Energy Flow in Chemical Reactions.

January 21 — Prof. L. Hall, Cambridge
NMR, Window to the Human Body.

January 27 — Dr. W. Kerr, University of Strathclyde
Development of the Pauson-Khand Annulation Reaction: Organocobalt Mediated Synthesis of Natural and Unnatural Products.

January 28 — Prof. J. Mann, University of Reading
Murder, Magic and Medicine.

February 3 — Prof. S.M. Roberts, University of Exeter
Enzymes in Organic Synthesis.

February 10 — **Dr. D. Gillies, University of Surrey**
NMR and Molecular Motion in Solution.

February 11 — **Prof. S. Knox, Bristol University**
The Tilden Lecture: Organic Chemistry at Polynuclear Centres.

February 17 — **Dr. R.W. Kemmitt, University of Leicester**
Oxatrimethylenemethane Metal Complexes.

February 18 — Dr. I. Fraser, ICI Wilton
Reactive Processing of Composite Materials.

February 22 — Prof. D.M. Grant, University of Utah
Single Crystals, Molecular Structure and Chemical Shift Anisotropy.

February 24 — Prof. C.J.M. Stirling, University of Sheffield
Chemistry on the Flat-Reactivity of Ordered Systems.

March 10 — **Dr. P.K. Baker, University College of North Wales, Bangor**
Chemistry of Highly Versatile 7-Coordinate Complexes.

March 11 — Dr. R.A.Y. Jones, University of East Anglia
The Chemistry of Wine Making.

March 17 — Dr. R.J.K. Taylor, University of East Anglia
Adventures in Natural Product Synthesis.

March 24 — Prof. I.O. Sutherland, University of Liverpool
Chromogenic Reagents for Cations.

May 13 — Prof. J.A. Pople, Carnegie-Mellon University, Pittsburgh
The Boys-Rahman Lecture: Applications of Molecular Orbital Theory.

May 21 — **Prof. L. Weber, University of Bielefeld**
Metallo-phospha Alkenes as Synthons in Organometallic Chemistry.

June 1 — Prof. J.P. Konopelski, University of California, Santa Cruz

Synthetic Adventures with Enantiomerically Pure Acetals.

June 2 — Prof. F. Ciardelli, University of Pisa
Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins.

June 7 — Prof. R.S. Stein, University of Massachusetts
Scattering Studies of Crystalline and Liquid Crystalline Polymers.

June 16 — Prof. A.K. Covington, University of Newcastle
Use of Ion-Selective Electrodes as Detectors in Ion Chromatography.

June 17 — Prof. O.F. Nielson, H.C. Orsted Institute, University of Copenhagen
Low-Frequency IR and Raman Studies of Hydrogen-Bonded Liquids.

2. October 1991 - July 1992

October 17 — Dr. J.A. Salthouse, University of Manchester
Son et Lumiere, A Demonstration Lecture.

October 31 — **Dr. R. Keeley, Metropolitan Police Forensic Science**
Modern Forensic Science.

November 6* — **Prof. B.F.G. Johnson, Edinburgh University**
Cluster-surface Analogies.

November 7 — Dr. A.R. Butler, St. Andrews University
Traditional Chinese Herbal Drugs: A Different Way of Treating Disease.

November 13* — **Prof. D. Gani, St. Andrews University**
The Chemistry of PLP-Dependant Enzymes.

November 20* — Dr. R. More O'Ferrall, University College, Dublin
Some Acid-Catalysed Rearrangements in Organic Chemistry.

November 28 — Prof. I.M. Ward, IRC in Polymer Science, University of Leeds
The SCI Lecture: The Science and Technology of Oriented Polymers.

December 4* — **Prof. R. Grigg, University of Leeds**
Palladium-Catalysed Cyclisation and Ion-Capture Processes.

December 5 — Prof. A.L. Smith, ex-Unilever
Soap, Detergents and Black Puddings.

December 11* — **Dr. W.D. Cooper, Shell Research**
Colloid Science, Theory and Practice.

January 22* — **Dr. K.D.M. Harris, St. Andrews University**
Understanding the Properties of Solid Inclusion Compounds.

January 29* — Dr. A. Holmes, Cambridge University
Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products.

January 30 Dr. M. Anderson, Shell Research
Recent Advances in the Safe and Selective Chemical Control of Insect Pests.

February 12* **Prof. D.E. Fenton, Sheffield University**
Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.

February 13 Dr. J. Saunders, Glaxo Group Research
Molecular Modelling in Drug Discovery.

February 19* **Prof. E.J. Thomas, Manchester University**
Applications of Organostannanes to Organic Synthesis.

February 20 **Prof. E. Vogel, University of Cologne**
The Musgrave Lecture: Porphyrins: Molecules of Interdisciplinary Interest.

February 25 **Prof. J.F. Nixon, University of Sussex**
The Tilden Lecture: Phosphaalkynes: New Building Blocks in Inorganic and Organometallic Chemistry.

February 26* Prof. M.L. Hitchman, Strathclyde University
Chemical Vapour Deposition.

March 5 Dr. N.C. Billingham, University of Sussex
Degradable Plastics, Myth or Magic.

March 11* **Dr. S.E. Thomas, Imperial College, London**
Recent Advances in Organoiron Chemistry.

March 12 Dr. R.A. Hann, ICI Imagedata
Electronic Photography: An Image of the Future.

March 18* Dr. H. Maskill, University of Newcastle
Concerted or Stepwise Fragmentation in a Deamination-type Reaction.

April 7 Prof. D.M. Knight, University of Durham
Interpreting Experiments: The Beginning of Electrochemistry.

May 13 Dr. J-C. Gehet, Ciba Geigy, Basel
Some Aspects of Industrial Agrochemical Research.

3. October 1990 - July 1991

October 11 Dr. W.A. MacDonald, ICI Wilton
Materials for the Space Age.

October 22* **Dr. M. Bochmann, University of East Anglia**
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.

October 26* Prof. R. Soulen, South Western University, Texas
Preparation and Reactions of Bicycloalkenes.

October 31* Dr. R. Jackson, University of Newcastle

New Synthetic Methods: α-Amino Acids and Small Rings.

November 1 **Dr. N. Logan, Nottingham University**
Rocket Propellants.

November 6* **Dr. P. Kocovsky, Uppsala University**
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals.

November 7* **Dr. D. Gerrard, BP**
Raman Spectroscopy for Industrial Analysis.

November 8 Dr. S.K. Scott, University of Leeds
Clocks, Oscillations and Chaos.

November 14* Prof. T. Bell, SUNY, Stoney Brook, USA
Functional Molecular Architecture and Molecular Recognition.

November 21 Prof. J. Pritchard, Queen Mary and Westfield College, London
Copper Surfaces and Catalysts.

November 28* Dr. B.J. Whitaker, University of Leeds
Two-Dimensional Velocity Imaging of State Selected Reaction Products.

November 29 Prof. D. Crout, Warwick University
Enzymes in Organic Synthesis.

December 5* **Dr. P.G. Pringle, Bristol University**
Metal Complexes with Functionalised Phosphines.

December 13 Prof. A.H. Cowley, University of Texas
New Organometallic Routes to Electronic Materials.

January 15 Dr. B.J. Alder, Lawrence Livermore Labs., California
Hydrogen in all its Glory.

January 17 **Dr. P. Sarre, Nottingham University**
Comet Chemistry.

January 24 **Dr. P.J. Sadler, Birkbeck College, London**
Design of Inorganic Drugs: Precious Metals, Hypertension and HIV.

January 30* **Prof. E. Sinn, Hull University**
Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of (Metalloproteins and other) Macromolecules.

January 31 Dr. D. Lacey, Hull University
Liquid Crystals.

February 6* **Dr. R. Bushby, University of Leeds**
Biradicals and Organic Magnets.

February 14 Dr. M.C. Petty, Durham University
Molecular Electronics.

February 20*	**Pro. B.L. Shaw, University of Leeds** Syntheses with Coordinated, Unsaturated Phosphine Ligands.
February 28	**Dr. J. Brown, University of Oxford** Can Chemistry Provide Catalysts Superior to Enzymes?
March 6*	Dr. C.M. Dobson, University of Oxford NMR Studies of Dynamics in Molecular Crystals.
March 7	**Dr. J. Markam, ICI Pharmaceuticals** DNA Fingerprinting.
April 24	**Dr. R.R. Schrock, Massachusetts Institute of Technology** Metal-Ligand Multiple Bonds and Metathesis Initiators.
April 25	Prof. T. Hudlicky, Virginia Polytechnic Institute Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.
June 20	Prof. M.S. Brookhart, University of North Carolina Olefin Polymerisations, Oligomerisations and Dimerisations using Electrophilic Late Transition Metal Catalysts.
July 29	Dr. M.A. Brimble, Massey University, NZ Synthetic Studies Towards the Antibiotic Griseusin-A.

* Invited specially for the postgraduate training programme