Cyclic triphosphenium ions and related species

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Cyclic Triphosphenium Ions and Related Species

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Declaration

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Abstract

A series of cyclic triphosphenium ions containing three adjacent phosphorus atoms linked by a hydrocarbon backbone has been synthesised. They vary in ring size (four- to seven-membered rings), substituents on the four-coordinate phosphorus atoms, and organic backbone, and have been characterised by ^{31}P NMR spectroscopy. Variable temperature studies probing the mechanism of formation of cyclic triphosphenium ions from a reaction of PX_3 with a diphosphane have shown a three-step mechanism: (i) the addition of PX_3 to the diphosphane to form an acyclic intermediate, (ii) cyclisation to afford a heterocycle with a halogen still bonded to the central P atom, and (iii) removal of the halogen to afford the cyclic triphosphenium ion.

The syntheses of P_C-alkyl and aryl derivatives of cyclic triphosphenium ions using two different methods are described. Direct ethylation of a cyclic triphosphenium ion using ethyl triflate is only possible when the substituents on the four-coordinate phosphorus atoms are small *e.g.* Et. Synthesis of P_C-alkyl and aryl derivatives with larger substituents on the four-coordinate P atoms, and/or P_C, have been achieved *via* reaction of a diphosphane with a dichlorophosphane in the presence of $AlCl_3$ or $SnCl_2$. A series of tetraphosphonium ions containing four adjacent P atoms linked by an organic backbone has also been synthesised. These derivatives have been characterised using ^{31}P NMR spectroscopy and where possible X-ray diffractions studies and elemental analyses. The P-P bonds in these derivatives are typical values for single bonds.

The synthesis of Pt(II) complexes containing cyclic triphosphenium ions has been achieved to afford *cis* and/or *trans* isomers *via* reaction of a cyclic triphosphenium ion with *trans*-$[Pt(PR_3)Cl(\mu Cl)]_2$. However, if the cyclic triphosphenium ion contains phenyl groups on both of the four-coordinate phosphorus atoms, ring scission followed by complexation of the diphosphane to Pt is observed. In the Pt(II) complexes containing cyclic triphosphenium ions, an unusually small $^1J_{Pt\text{-}P}$ value to the phosphenium central P (981-1267 Hz) suggests that the bond between the phosphenium central P atom and the Pt centre is long. Hydrolysis reactions of several Pt(II) complexes containing chlorophosphane ligands have been monitored by ^{31}P NMR spectroscopy.

Publications

- Keith B. Dillon, Andrés E. Goeta, Judith A. K. Howard, Philippa K. Monks, Helena J. Shepherd and Amber L. Thompson, *"Alkyl and aryl dicationic derivatives of cyclic triphosphenium ions" Dalton Trans.*, 2008, 1144

- Alice J. Boyall, Keith B. Dillon, Philippa K. Monks and Jennifer C. Potts, "*Reaction of a cyclic triphosphenium ion with triflic acid and SnX_2 (X = Br or Cl): A ^{31}P NMR study*" *Heteroatom Chemistry*, 2007, **18**, 609

- Keith B. Dillon and Philippa K. Monks, "*The mechanism of formation of cyclic triphosphenium ions; detection of transient intermediates in solution.*" *Dalton Trans.*, 2007, 1420.

- Alice J. Boyall , Keith B. Dillon , Judith A. K. Howard, Philippa K. Monks and Amber L. Thompson, "*Novel (n + 1 + 1) cycloaddition reactions; the formation of cyclic tetraphosphonium dications with four linked phosphorus atoms and an organic backbone*" *Dalton Trans.*, 2007, 1374.

- Jenny D. Burton, Robert M. K. Deng, Keith B. Dillon, Philippa K. Monks and Richard J. Olivey, "*Protonation of some cyclic triphosphenium ions*" *Heteroatom Chemistry*, 2005, **16**, 447.

- Keith. B. Dillon, Philippa. K. Monks, Richard J. Olivey, Hans H. Karsch "*The identification of some novel four-membered ring cyclic triphosphenium ions in solution*" Heteroatom Chemistry, 2004, **15**, 464.

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Abbreviations

Ar	2,4,6-tris(trifluoromethyl)phenyl
Ar'	2,6-bis(trifluoromethyl)phenyl
Ar''	2,4-bis(trifluoromethyl)phenyl
biphep	2,2'-bis(diphenylphosphino)-1,1'-biphenyl
Cpent	cyclopentyl
Cy	cyclohexyl
d	doublet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
dcpe	1,2-bis(dichlorophosphino)ethane
dcypb	1,4-bis(dicyclohexylphosphino)butane
dcype	1,2-bis(dicyclohexylphosphino)ethane
dcypm	bis(dicyclohexylphosphino)methane
dcypp	1,3-bis(dicyclohexylphosphino)propane
dedppe	(1-diethylphosphino-2-diphenylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
depp	1,3-bis(diethylphosphino)propane
DFT	density functional theory
dippb	1,4-bis(di-isopropylphosphino)butane
dippf	1,1'-bis(di-isopropylphosphino)ferrocene
dippp	1,3-bis(di-isopropylphosphino)propane
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dpdtbpf	(1-diphenyl-1'-ditertiarybutylphosphino)ferrocene
dpfppe	1,2-bis(dipentafluorophenylphosphino)ethane
dppb	1,4-bis(diphenylphosphino)butane
dppben	1,2-bis(diphenylphosphino)benzene
dppdmx	9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene

dppe	1,2-bis(diphenylphosphino)ethane
dppE	*cis*-bis(diphenylphosphino)ethene
dppf	1,1'-bis(diphenylphosphino)ferrocene
dpph	1,6-bis(diphenylphosphino)hexane
dppm	bis(diphenylphosphino)methane
dppme	1,1-bis{diphenylphosphanyl)methyl]ethene
dppox	bis(α,α-diphenylphosphino)-o-xylene
dppp	1,3-bis(diphenylphosphino)propane
dpppe	1,5-bis(diphenylphosphino)pentane
dtbpf	1,1'-bis(di-tertiarybutylphosphino)ferrocene
dtbpox	bis(α,α'-di-t-butylphosphino)-o-xylene
Ethyl triflate	ethyltrifluoromethanesulfonate
HOMO	highest occupied molecular orbital
HOMO-1	second highest occupied molecular orbital
m	multiplet
Methyl triflate	methyltrifluoromethanesulfonate
Morph	N-morpholino
NBO	non-bonding orbital
NLMO	natural localised molecular orbital
NMR	nuclear magnetic resonance
Phenyl triflate	phenyltrifluoromethanesulfonate
RT	room temperature
s	singlet
t	triplet
^{t}Bu	tertiary butyl
tetraphos	tetrakis(diphenylphosphinomethyl)methane
THF	tetrahydrofuran
tht	tetrahydrothiophene
TMEDA	tetramethylethylenediamine
Triflic acid	trifluoromethanesulfonic acid
triphos2	tris(diphenylphosphinomethyl)ethane

Table of Contents

Chapter 1: ..... - 6 -
Introduction ..... - 6 -
1.1 What are cyclic triphosphenium ions? ..... - 6 -
1.2 Synthesis of cyclic triphosphenium ions ..... - 7 -
1.2.1 Synthesis of four-membered ring cyclic triphosphenium ions ..... - 9 -
1.2.2 Synthesis of five-membered ring cyclic triphosphenium ions ..... - 10 -
1.2.3 Synthesis of six-membered ring cyclic triphosphenium ions ..... - 15 -
1.2.4 Synthesis of seven-membered ring cyclic triphosphenium ions ..... - 19 -
1.2.5 Synthesis of eight-membered ring cyclic triphosphenium ions ..... - 21 -
1.2.6 Synthesis of nine-membered ring cyclic triphosphenium ions ..... - 22 -
1.3 Bonding in cyclic triphosphenium ions – DFT calculations ..... - 23 -
1.4 Reactions of cyclic triphosphenium ions ..... - 24 -
1.4.1 Protonation reactions ..... - 24 -
1.4.2 Alkylation reactions ..... - 28 -
1.4.2.1 Methylation reactions ..... - 30 -
1.4.2.2 Ethylation reactions ..... - 31 -
1.4.3 Deprotonation using DBU ..... - 32 -
1.4.4 Synthesis of phosphamethine cyanine salts ..... - 33 -
1.4.5 Reactions with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ ..... - 34 -
1.5 Acyclic triphosphenium ions ..... - 39 -
1.6 Neutral P(I) cycles ..... - 41 -
1.7 Tetraphosphonium, tetraphosphenium ions and other diphosphonium cations containing four adjacent phosphorus atoms ..... - 43 -
1.8 References ..... - 47 -

Chapter 2: ..... - 50 -
Synthesis and Characterisation of Some Cyclic Triphosphenium Ions ..... - 50 -
2.1 Introduction ..... - 50 -
2.2 Synthesis of a four-membered ring cyclic triphosphenium ion from dcypm ..... - 51 -
2.3 Synthesis of some five-membered ring cyclic triphosphenium ions from depe, dcype, dppe and dmpe ..... - 52 -
2.4 Synthesis of some six-membered ring cyclic triphosphenium ions from depp, dcypp, dippp, dippf and dpdtbpf ..... - 54 -
2.5 Synthesis of some seven-membered ring cyclic triphosphenium ions from dcypb, dppb and dippb ..... - 59 -
2.6 Conclusions ..... - 61 -
2.7 Experimental ..... - 61 -
2.8 References ..... - 66 -

Chapter 3: ..... - 67 -
Investigation into the Mechanism of Formation of Cyclic Triphosphenium Ions ..... - 67 -
3.1 Introduction ..... - 67 -
3.2 Detection of transient intermediates in the synthesis of the depp cyclic triphosphenium ion using PX_3 (X = Cl or Br) ..... - 68 -
3.3 Detection of transient intermediates in the synthesis of the depe cyclic triphosphenium ion using PX_3 (X = Cl or Br) ..... - 73 -
3.4 Detection of transient intermediates in the synthesis of the dippp cyclic triphosphenium ion using PX_3 (X = Cl or Br) ..... - 74 -
3.5 Detection of transient intermediates in the synthesis of the dcypp cyclic triphosphenium ion using PX_3 (X = Cl or Br) ..... - 77 -
3.6 Attempts to detect transient intermediates in the synthesis of the dppe, dcype, dippb and dcypb cyclic triphosphenium ions using PX_3 (X = Cl or Br) ..... - 79 -
3.7 Conclusions ..... - 80 -
3.8 Experimental ..... - 81 -
3.9 References ..... - 84 -

Chapter 4: ..... - 85 -
Synthesis and Characterisation of P-Alkyl and P-Aryl Derivatives of Cyclic Triphosphenium Ions ..... - 85 -
4.1 Introduction ..... - 85 -
4.2 Synthesis of P_C-alkyl and P_C-aryl derivatives – A direct method ..... - 87 -
4.2.1 Synthesis of P_C-methyl derivatives ..... - 87 -
4.2.2 Synthesis of P_C-ethyl derivatives ..... - 88 -
4.2.3 Attempted synthesis of P_C-phenyl derivatives ..... - 89 -
4.3 Synthesis of P_C-alkyl and P_C-aryl derivatives – An indirect method ..... - 89 -
4.3.1 Derivatives of the depe cyclic triphosphenium ion ..... - 89 -
4.3.2 Derivatives of the dppe cyclic triphosphenium ion ..... - 92 -
4.3.3 P_C-ethyl derivatives of other cyclic triphosphenium ions ..... - 94 -
4.3.4 Other P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions. - 96 -
4.3.5 Mechanism of formation of P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions ..... - 98 -
4.4 Molecular structures of some P-alkyl derivatives of cyclic triphosphenium ions ..... - 101 -
4.5 Conclusions ..... - 107 -
4.6 Experimental ..... - 109 -
4.7 References ..... - 113 -

Chapter 5: ..... - 115 -
Synthesis and Characterisation of Some Cyclic Tetraphosphonium Ions ..... - 115 -
5.1 Introduction ..... - 115 -
5.2 Synthesis of tetraphosphonium ions from dppm ..... - 116 -
5.3 Synthesis of tetraphosphonium ions from dcypm ..... - 120 -
5.4 Synthesis of tetraphosphonium ions from dppe ..... - 123 -
5.5 Synthesis of tetraphosphonium ions from other diphosphanes ..... - 124 -
5.6 Attempted synthesis of a 'mixed' tetraphosphonium ion ..... - 126 -
5.7 Molecular structures of cyclic tetraphosphonium ions derived from dppm and dcypm ..... - 128 -
5.8 Conclusions ..... - 133 -
5.9 Experimental ..... - 134 -
5.10 References ..... - 137 -

Chapter 6: ..... - 139 -
Synthesis and Characterisation of Some Pt(II) Complexes of Cyclic Triphosphenium Ions ..... - 139 -
6.1 Introduction ..... - 139 -
6.2 Synthesis of Pt(II) complexes containing five-membered ring cyclic triphosphenium ions ..... - 141 -
6.2.1 Reaction of the depe cyclic triphosphenium ions 2a and 2b with *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ and *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ ..... - 141 -
6.2.2 Reaction of the dcype cyclic triphosphenium ion, 3b, with *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ and *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ ..... - 144 -
6.2.3 Reaction of the dppe cyclic triphosphenium ion, 4a, with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ ..... - 146 -
6.3 Synthesis of Pt(II) complexes containing six-membered ring cyclic triphosphenium ions ..... - 147 -
6.3.1 Reactions of the depp cyclic triphosphenium ion, 6a and 6b, with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ ..... - 147 -
6.3.2 Reactions of the dcypp cyclic triphosphenium ions 7a and 7b with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ ..... - 149 -
6.3.3 Reactions of the dippp cyclic triphosphenium ions 8a and 8b with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ ..... - 152 -
6.4 Synthesis of Pt(II) complexes containing seven-membered ring cyclic triphosphenium ions ..... - 155 -
6.4.1 Reactions of the dcypb cyclic triphosphenium ions 11a and 11b with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ ..... - 155 -
6.4.2 Reactions of the dippb cyclic triphosphenium ions 13a and 13b with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ ..... - 158 -
6.5 Reactions of diphosphanes and cyclic triphosphenium ions containing a ferrocene backbone with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ ..... - 160 -
6.6 Synthesis of Pt(II) complexes containing chlorophosphanes ..... - 164 -
6.6.1 Synthesis and characterisation of the parent Pt(II) complexes..... - 166 -

6.6.1.1 Reactions of *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ with PCl_3 ..... - 166 -
6.6.1.2 Reactions of *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ with $PR'Cl_2$ ..... - 168 -
6.6.1.3 Reactions of *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ with PR'_2Cl ..... - 172 -
6.6.1.4 Molecular structures of the parent Pt(II) complexes containing chlorophosphane ligands ..... - 177 -
6.6.2 Investigation into the hydrolysis of Pt(II) chlorophosphane complexes - 180 -
6.6.2.1 Hydrolysis of Pt(II) chlorophosphane complexes through exposure to air and 'wet' solvents ..... - 182 -
6.6.2.1.1 Hydrolysis of $PtCl_2(PEt_3)(PCl_3)$ - Synthesis of *cis*-$PtCl_2(PEt_3)[P(OH)_3]$ ..... - 182 -
6.6.2.1.2 Hydrolysis of $PtCl_2(PEt_3)(PR'Cl_2)$ – Attempted synthesis of *cis*-$PtCl_2(PEt_3)[PR'(OH)_2]$ ..... - 185 -
6.6.2.1.3 Hydrolysis of $PtCl_2(PEt_3)(PR_2'Cl)$ – Attempted synthesis of *cis*-$PtCl_2(PEt_3)[PR_2'(OH)]$ ..... - 187 -
6.6.2.2 Hydrolysis reactions using 2-aminobenzyl alcohol ..... - 190 -
6.6.2.2.1 Hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ using 2-aminobenzyl alcohol - Synthesis of *cis*-$PtCl_2(PEt_3)[PCl_2(OH)]$ and *cis*-$PtCl_2(PEt_3)[PCl(OH)_2]$ ..... - 191 -
6.6.2.2.2 Hydrolysis of *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ using 2-aminobenzyl alcohol ..... - 195 -
6.6.2.2.3 Hydrolysis of *cis*-$PtCl_2(PEt_3)(PR_2'Cl)$ using 2-aminobenzyl alcohol ..... - 198 -
6.7 Conclusions ..... - 201 -
6.8 Experimental ..... - 206 -
6.8.1 Three-stage synthesis of *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ ..... - 206 -
6.8.2 Synthesis of *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ – An alternative method ..... - 208 -
6.8.3 Synthesis of *trans*-[Pt(PPh_2Me)Cl(μ-Cl)]$_2$ dimer ..... - 208 -
6.8.4 Synthesis of *trans*-[Pt($PPhMe_2$)Cl(μ-Cl)]$_2$ dimer ..... - 209 -
6.8.5 Synthesis of Pt(II) complexes containing cyclic triphosphenium ions ..... - 209 -
6.8.6 Synthesis of parent Pt(II) complexes containing chlorophosphanes ..- 211 -
6.8.7 Hydrolysis reactions ..... - 212 -
6.9 References ..... - 217 -

Chapter 7: ..... - 220 -
Future Work ..... - 220 -
7.1 Cyclic triphosphenium ions coordination chemistry ..... - 220 -
7.2 P-alkyl and P-aryl derivatives ..... - 221 -
7.3 Tetraphosphonium ions ..... - 222 -
7.4 Tetraphosphenium ions ..... - 224 -
7.5 Potential applications in catalysis ..... - 226 -
7.6 Hydrolysis reactions ..... - 227 -
7.7 References ..... - 227 -

The following appendices may be found on the accompanying CD

Appendix 1: ..... - 228 -
Synthesis, Reactivity and Coordination Properties of $2,6\text{-}(CF_3)_2C_6H_3\text{-}P(OCH_2)_2$ ..... - 228 -
A.1 Introduction ..... - 228 -
A.2 Synthesis of $2,6\text{-}(CF_3)_2\text{-}C_6H_3\text{-}P(OCH_2)_2$ ..... - 229 -
A.3 Reaction of $2,6\text{-}(CF_3)_2\text{-}C_6H_3\text{-}P(OCH_2)_2$ with Selenium ..... - 231 -
A.4 Coordination studies using $2,6\text{-}(CF_3)_2\text{-}C_6H_3\text{-}P(OCH_2)_2$ ..... - 232 -
A.4.1 Reaction with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ ..... - 232 -
A.4.2 Reaction with *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ ..... - 234 -
A.4.3 Reaction with *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ ..... - 237 -
A.5 Conclusions ..... - 240 -
A.6 Experimental ..... - 241 -
A.7 References ..... - 243 -

Appendix 2: ..... - 244 -
Calculating coupling constants for AA'XX' systems observed in Chapter 5 ..... - 244 -

Appendix 3: ..... - 246 -
Compound Numbering Sheets ..... - 246 -

Chapter 1:

Introduction

1.1 What are cyclic triphosphenium ions?

Cyclic triphosphenium ions were first reported in 1982 by Schmidpeter *et al.*.[1] They are positively charged heterocycles containing three adjacent phosphorus atoms linked to form a ring by a hydrocarbon backbone (Figure 1.1). The two 'outer' phosphorus atoms each have two aryl or alkyl substituents, whereas the central phosphorus atom is 'bare,' and is in the +1 formal oxidation state.

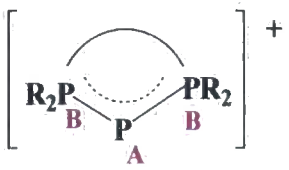


Figure 1.1: The general structure of a cyclic triphosphenium ion

The favoured representation features the positive charge delocalised over all three phosphorus atoms (Figure 1.2). X-ray diffraction studies carried out on some isolated

cyclic triphosphenium ions have shown that the phosphorus-phosphorus bond lengths are intermediate between values for a single and a double phosphorus-phosphorus bond.[1-6]

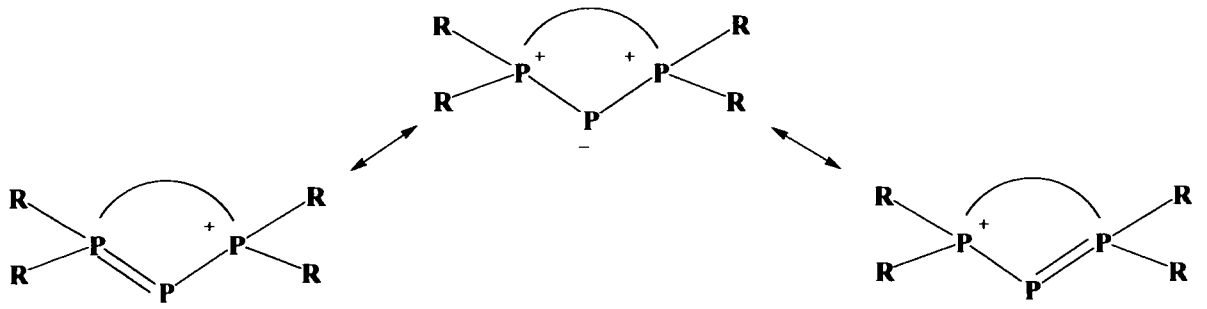


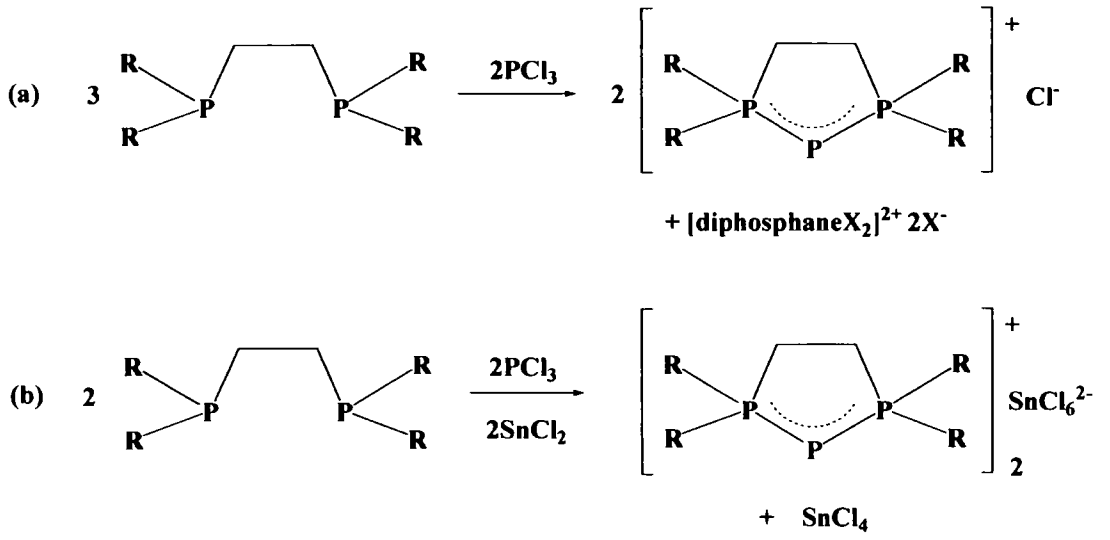
Figure 1.2: Resonance forms of cyclic triphosphenium ions

These heterocyclic triphosphenium ions are readily characterised using $^{31}P\{^{1}H\}$ NMR spectroscopy, as they present a triplet at very low frequency corresponding to P_A and a doublet at higher frequency corresponding to P_B. The $^{1}J_{P\text{-}P}$ coupling constant is usually in the region of 400-500 Hz.

These heterocycles are interesting not only because they provide a quick and easy route to low coordinate phosphorus compounds, but because they have different steric and electronic properties compared to traditional phosphane ligands. For example, the structure of a cyclic triphosphenium ion differs from those of traditional phosphanes, with steric bulk being located one atom further away from the donor P atom.

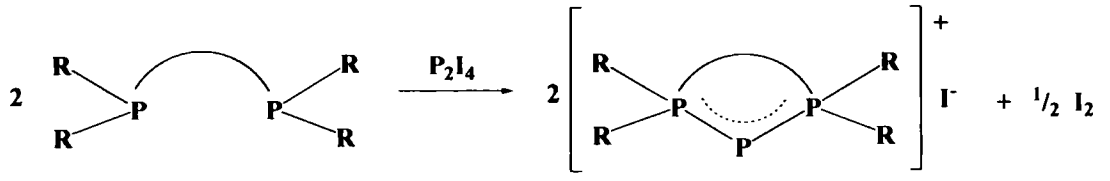
1.2 Synthesis of cyclic triphosphenium ions

The two most commonly used synthetic routes involve reacting a diphosphane with a phosphorus trihalide, with or without tin(II) halide (Scheme 1.1). The advantage in using the tin(II) halide is that only one phosphorus-containing product is afforded.



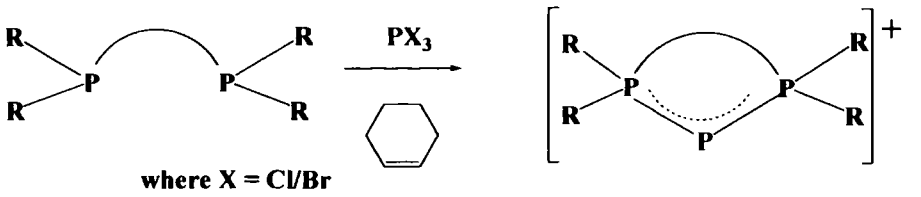
Scheme 1.1: (a) 3:2 reaction between a diphosphane and PX_3 and (b) 1:1:1 reaction between a diphosphane, PX_3 and SnX_2

A variation on these methods was reported by Macdonald *et al.*, involving the disproportionation of P_2I_4 (Scheme 1.2).[4] This method also affords only one phosphorus-containing product, with the other product, I_2, easily removed from the reaction mixture.



Scheme 1.2: Synthesis of cyclic triphosphenium ions from disproportionation of P_2I_4

Recently Macdonald *et al.* have reported a new synthetic method to form chloride and bromide salts of cyclic triphosphenium ions using cyclohexene as a halogen-scavenger (Scheme 1.3).[7] For reactions involving PCl_3 a mixture of other products is formed, including HCl, *cis*-1,2-dichlorocyclohexane and 3-chlorocyclohexene, although, when using PBr_3, the only other product formed is *trans*-1,2-dibromocyclohexane.



Scheme 1.3: Synthesis of cyclic triphosphenium ions using cyclohexene as a halogen-scavenger

Since their discovery in 1982,[1] many different cyclic triphosphenium ions have been synthesised which vary in ring size, hydrocarbon backbone and substituents on the four-coordinated phosphorus atoms.

1.2.1 Synthesis of four-membered ring cyclic triphosphenium ions

Although four-membered rings are generally thought to be unstable species, several four-membered ring cyclic triphosphenium ions have now been reported (Table 1.1). δP_A for the cyclic triphosphenium ions containing nitrogen and methyl substituents is at higher frequency than observed for other cyclic triphosphenium ions. Another interesting point is that for all the four-membered cyclic triphosphenium ions the $^1J_{P\text{-}P}$ coupling constants are much lower compared to those in the larger rings, except for the dmpm cyclic triphosphenium ion.

Attempts to form a four-membered ring from dppm and PCl_3 (with and without $SnCl_2$) were unsuccessful.[3] Some colour changes were noted, but there were no NMR data to support the formation of the ring. The $^{31}P\{^1H\}$ NMR data suggested that two phenyl groups had been replaced by chlorine, as one of the products appeared to be $Cl_2PCH_2PPh_2$ (δP_{Ph} -25.3 ppm, δP_{Cl} 187.8 ppm, $^2J_{P\text{-}P}$ = 141 Hz).[8]

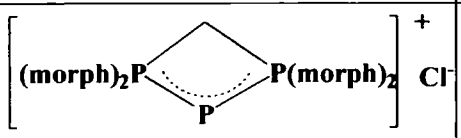
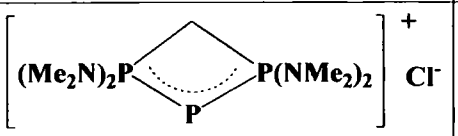
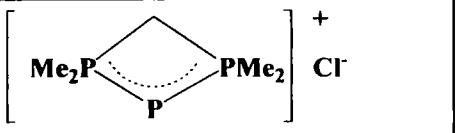
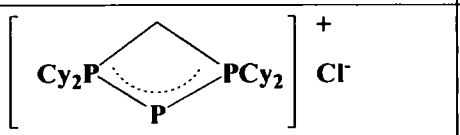
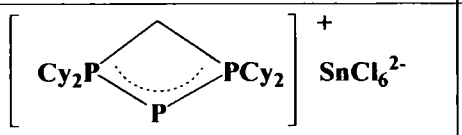
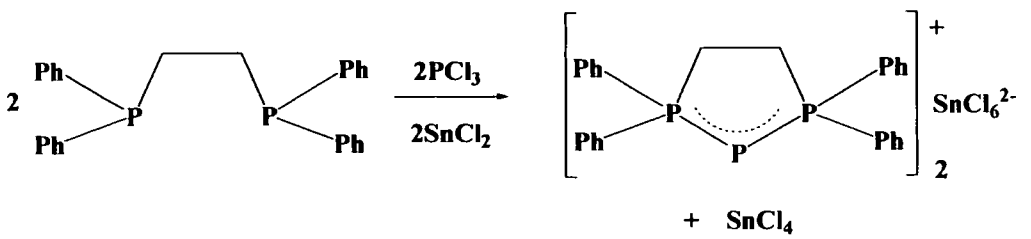
Cyclic triphosphenium ion	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Reference
	-90.0	56.0	347	9
	-126.0	56.0	358	9
	-153.7	21.3	452	10
	-214.6	45.1	333	10
	-216.1	45.4	331	10

Table 1.1: $^{31}P\{^1H\}$ NMR literature data for four-membered cyclic triphosphenium ions

1.2.2 Synthesis of five-membered ring cyclic triphosphenium ions

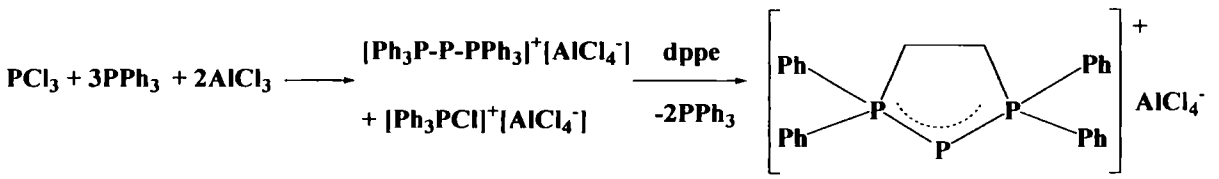
The first cyclic triphosphenium ion was synthesised from the diphosphane dppe in 1982 by Schmidpeter *et al.* (Scheme 1.4).[1]



Scheme 1.4: The synthesis of the first cyclic triphosphenium ion

The $^{31}P\{^{1}H\}$ NMR spectrum showed the characteristic doublet and triplet (δP_A = -231.6 ppm, δP_B = 63.8 ppm, $^{1}J_{P\text{-}P}$ = 448.9 Hz). Colourless crystals were collected; X-ray diffraction studies showed that the ring had an envelope conformation, and the two P-P bond lengths were intermediate between single and double bond lengths [2.128(2) Å and 2.122(1) Å]. This suggested that the positive charge was delocalised over all three phosphorus atoms.

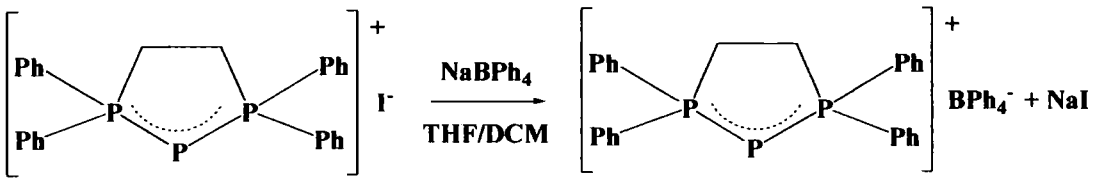
An alternative synthesis for this five-membered cyclic triphosphenium ion was reported by Schmidpeter *et al.* in 1985, *via* a hexaphenyltriphosphenium tetrachloroaluminate species (Scheme 1.5).[1, 11] The $^{31}P\{^{1}H\}$ NMR data obtained for this species were consistent with the previous synthesis (δP_A = -232.0 ppm, δP_B = 64.4 ppm, $^{1}J_{P\text{-}P}$ = 451.5 Hz).[1]



Scheme 1.5: The alternative route to form the 1,1,3,3-tetraphenyl-1λ^5,2λ^3,3λ^5-triphospholenyl cation

Further studies into reactions to form the 1,1,3,3-tetraphenyl-1λ^5,2λ^3,3λ^5-triphospholenyl cation from dppe have since been carried out. One study involved the synthesis of the dppe cyclic triphosphenium ion using PX_3 (where X=Cl, Br, I) with and without the use of SnX_2. The $^{31}P\{^{1}H\}$ NMR data showed little variation in the chemical shifts or coupling constants when using the different trihalides indicating that there is little/no ion-pair interactions.[3]

In 2003 Macdonald *et al.* reported that the cyclic triphosphenium ion made from dppe and PI_3 would react with $Na[BPh_4]$, where the iodide counter-ion is exchanged with the tetraphenyl borate (Scheme 1.6).[4] Again the $^{31}P\{^{1}H\}$ NMR data showed little change in the chemical shift of the central phosphorus atom, suggesting that there is little interaction between the cation and anion when in solution.



Scheme 1.6: Reaction between the ring formed from dppe and PI_3 and $Na[BPh_4]$

The molecular structures of several salts of the dppe cyclic triphosphenium ion have now been reported. [1, 5, 7] For each salt the P-P bond lengths are very similar and are intermediate between those for single and double P-P bonds (Table 1.2).

	$X^- =$			
	$SnCl_6^{2-}$	I^-	BPh_4^-	Br^-
P(1)-P(2)	2.122(1)	2.1263(17)	2.1166(6)	2.1231(9)
P(2)-P(3)	2.128(2)	2.1315(18)	2.1293(6)	2.1308(9)
P(1)-C(5)	1.821(5)	1.821(5)	1.8164(17)	1.818(2)
P(3)-C(4)	1.820(4)	1.826(5)	1.8430(16)	1.817(2)
P(1)-P(2)-P(3)	88.9(1)	88.37(7)	86.52(2)	88.37(3)
Reference	1	5	5	7

Table 1.2: Selected bond lengths and angles for some dppe cyclic triphosphenium ion salts

Other five-membered cyclic triphosphenium ions have been synthesised from dppE,[3] depe,[2] dppben,[2] dmpe,[2] and dcype.[10] The $^{31}P\{^1H\}$ NMR data obtained for each cyclic triphosphenium ion are in good agreement with those reported for Schmidpeter's original ring (Table 1.3).[1]

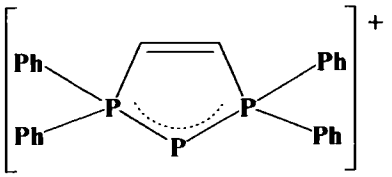
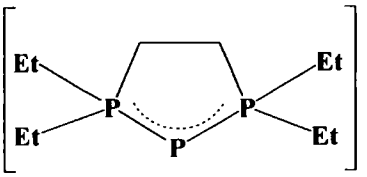
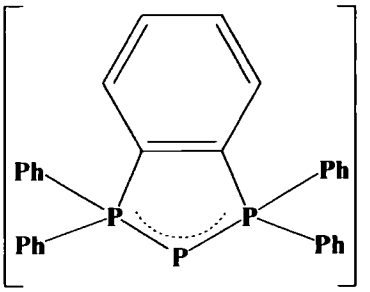
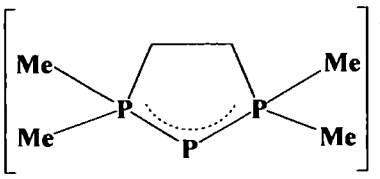
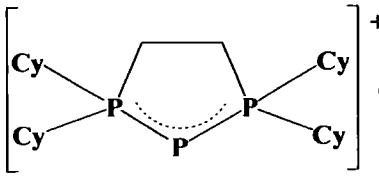
Cyclic triphosphenium ion		δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Ref.
	Cl-	-248.4	473	71.9	3
	Br-	-247.6	473	71.8	
	I-	-246.9	473	70.9	
	$SnCl_6^{2-}$	-247.6	473	71.2	
	$SnBr_6^{2-}$	-247.1	472	71.5	
	Cl^-	-269.2	81.6	441	2
	Cl^-	-212.8	57.6	453	2
	Cl^-	-212.9	60.4	430	2
	Cl^-	-289.6	87.3	457	10

Table 1.3: $^{31}P\{^1H\}$ NMR literature data for five-membered cyclic triphosphenium ions

X-ray diffraction studies were carried out on crystals obtained from the reaction between dppben and PCl_3, and the resulting molecular structure is shown in Figure 1.3.[2]

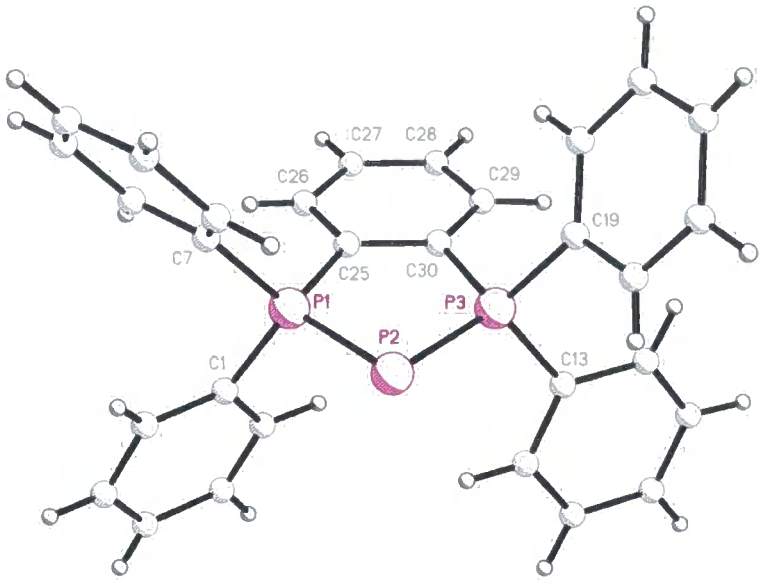


Figure 1.3: Molecular structure of the cyclic triphosphenium ion derived from dppben and PCl_3[2]

The benzene backbone gives the five-membered ring a planar conformation. As with Schmidpeter's dppe ring system, the P-P bond lengths (2.124 Å and 2.122 Å) are intermediate between normal single P-P (2.20-2.25 Å)[12] and double P-P bond lengths (2.00-2.03 Å).[12]

Another five-membered cyclic triphosphenium ion was synthesised from the diphosphane dedppe to afford an unsymmetrical ring (Figure 1.4).[2] Similar to the other ring systems, there was little difference in the chemical shifts or coupling constants when synthesising the ring from PCl_3, PBr_3, or PI_3, with or without SnX_2 (Table 1.4).

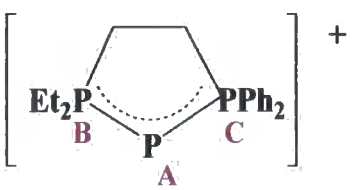


Figure 1.4: The five-membered ring synthesised from dedppe

System	δP_A, ppm	δP_B, ppm	δP_C, ppm	$^1J_{PA-PB}$, Hz	$^1J_{PA-PC}$, Hz	$^2J_{PB-PC}$, Hz
dedppe, PCl_3	-251.0	78.0	67.1	431	460	10.4
dedppe, PBr_3	-251.0	78.9	67.0	433	461	10.4
dedppe, PI_3	-249.6	78.2	66.7	435	461	9.6
dedppe, PCl_3, $SnCl_2$	-251.0	81.3	69.4	434	466	9.6

Table 1.4: $^{31}P\{^1H\}$ NMR literature data for the dedppe ring

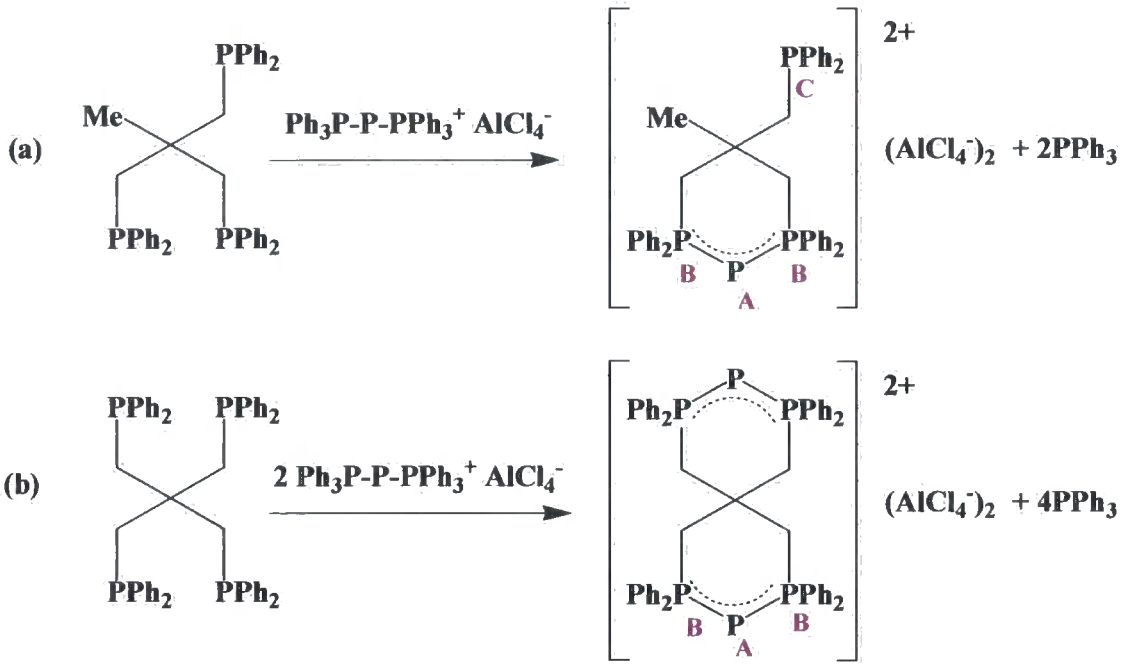
Other diphosphanes that could potentially form five-membered heterocycles, such as dcpe[6] and dpfppe,[18] were reacted with phosphorus trihalides. However there was no $^{31}P\{^1H\}$ NMR evidence for the formation of the rings. This suggests that ring formation is not favoured by the presence of very electronegative groups on the diphosphane.

1.2.3 Synthesis of six-membered ring cyclic triphosphenium ions

The first six-membered cyclic triphosphenium ions were reported by Schmidpeter *et al.* in 1985.[11] They were made from the diphosphanes triphos2 (a tridentate ligand) and tetraphos (a tetradentate ligand) (Scheme 1.7, Table 1.5).

diphosphane	δP_A, ppm	δP_B, ppm	δP_C, ppm	$^1J_{PA-PB}$, Hz
triphos2	-242.8	19.5	-30.2	444
tetraphos	-249.6	17.6	-	441

Table 1.5: $^{31}P\{^1H\}$ NMR data for two six-membered cyclic triphosphenium ions



Scheme 1.7: 6-membered rings from (a) triphos2 and (b) tetraphos

Other six-membered cyclic triphosphenium ions have since been synthesised from dppme, dppp, dppf, dcypp, depp and dppNap. The $^{31}P\{^{1}H\}$ NMR data obtained for each of these rings are consistent with those reported for other cyclic triphosphenium ions (Table 1.6).

For the reaction between dppf, PCl_3 and $SnCl_2$, the triplet corresponding to the central phosphorus atom in the resulting cyclic triphosphenium ion, P_A, was at higher frequency compared with those for other cyclic triphosphenium ions. However this is probably due to the ferrocene backbone, which has different electronic properties to the other diphosphanes previously used to synthesise cyclic triphosphenium ion.

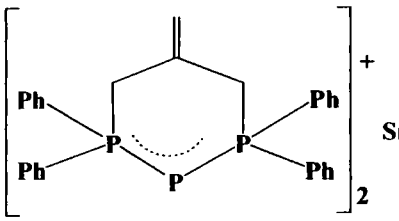
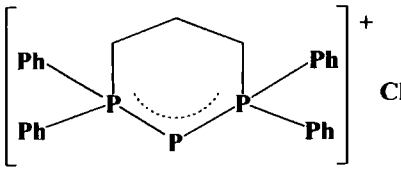
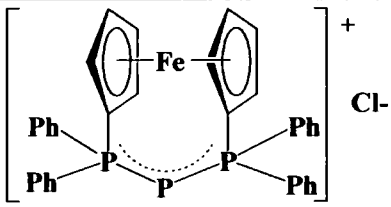
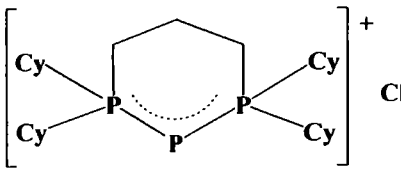
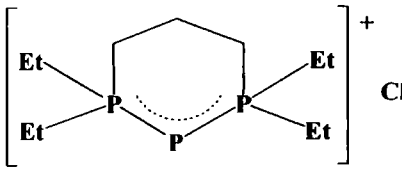
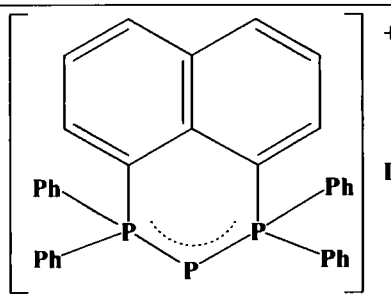
Cyclic triphosphenium ion	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Reference
	-213.4	23.0	431	13, 14
	-209.4	23.1	424	3, 5, 7, 14
	-135.4	33.3	496	14, 15
	-293.3	36.5	456	14, 16
	-253.5	30.4	417	14, 16, 17
	-216.0	26.0	392	6, 14

Table 1.6: $^{31}P\{^1H\}$ NMR literature data for six-membered cyclic triphosphenium ions

When the reaction was carried out between depp and PCl_3, two sets of doublets and triplets were seen in the $^{31}P\{^1H\}$ NMR spectrum (Table 1.7). This suggested that two rings had formed, although on standing the doublet and triplet at 42.7 ppm and –103.2 ppm disappeared. This second doublet and triplet were initially assigned to impurities.

δP, ppm	$^1J_{P\text{-}P}$, Hz	Multiplicity
42.7	351	d
30.4	417	d
-103.2	351	t
-253.5	417	t

Table 1.7: $^{31}P\{^1H\}$ NMR literature data for the reaction between depp and PCl_3

Crystals were isolated from a reaction between dppp, PCl_3 and $SnCl_2$. Single crystal X-ray diffraction studies were carried out, and the resulting molecular structure is shown in Figure 1.5.[3]

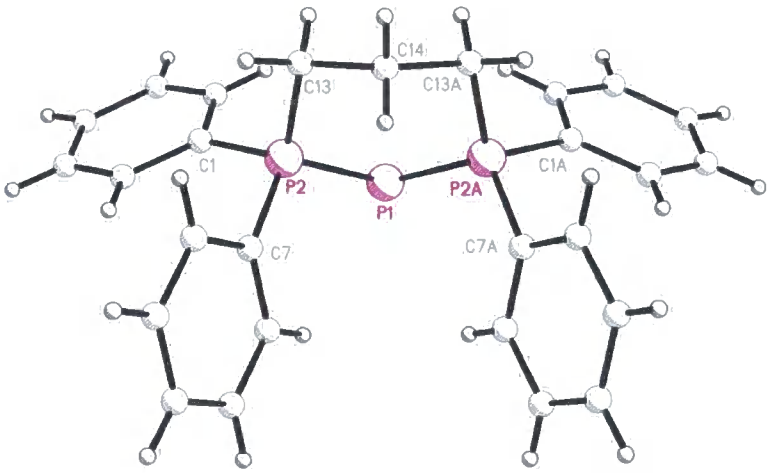


Figure 1.5: Molecular structure of the cyclic triphosphenium ion formed from dppp, PCl_3 and $SnCl_2$[3]

The molecular structures of several other salts of the dppp cyclic triphosphenium ion have been reported.[3, 5, 7, 18] The P-P bond lengths are very similar for each salt, showing that the counter-ion has little effect on the crystallographic parameters for the cation (Table 1.8).

X^-	P(1)-P(2)	P(2)-P(3)	P(1)-C(5)	P(3)-(C4)	P(1)-P(2)-P(3)	Reference
$SnCl_6^{2-}$	2.132(1)	2.132(1)	1.815(3)	1.815(3)	96.44(6)	3
$AlCl_4^-$	2.1529(5)	2.1310(5)	1.8146(13)	1.8143(13)	95.579 (18)	18
I^-	2.1318(6)	2.1203(6)	1.8068(16)	1.8112(16)	97.77(2)	5
BPh_4^-	2.1224(13)	2.1326(14)	1.807(3)	1.804(3)	93.98(5)	5
PF_6^-	2.122(2)	2.113(2)	1.811(6)	1.815(6)	97.19(9)	5
$GaCl_4^-$	2.1276(12)	2.1211(12)	1.815(3)	1.816(3)	93.76(5)	5
Br-	2.1138(11)	2.1262(11)	1.801(3)	1.807(3)	98.30(4)	7
HCl_2^-	2.1254(8)	2.1132(8)	1.811(2)	1.814(2)	96.70(3)	7

Table 1.8: Selected bond lengths and angles for isolated dppp cyclic triphosphenium ion salts

1.2.4 Synthesis of seven-membered ring cyclic triphosphenium ions

The first seven-membered cyclic triphosphenium ion was reported by Byers *et al.* in 1999.[3] The diphosphane dppb was reacted with PCl_3 to form the seven-membered equivalent of Schmidpeter's first ring. Further work on seven-membered ring cyclic triphosphenium ions has been carried out using the diphosphanes dppox, dtbpox, dcypb and biphep. The $^{31}P\{^1H\}$ NMR data for each ring show a triplet at low frequency, a doublet at higher frequency and a large $^1J_{P\text{-}P}$ (Table 1.9).

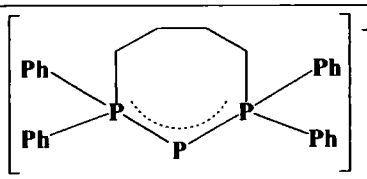
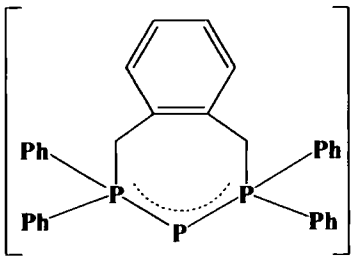
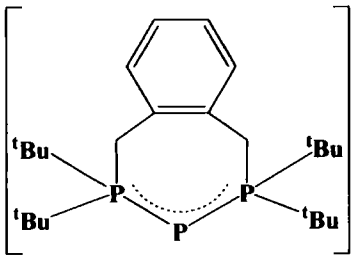
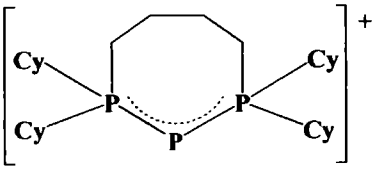
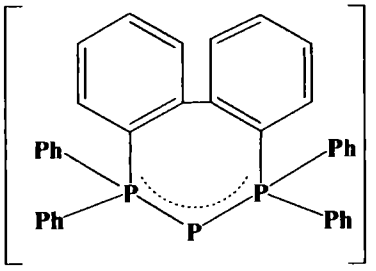
Cyclic triphosphenium ion	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Reference
 Cl^-	-210.9	34.3	455	3
 Cl^-	-214.5	25.1	436	2
 Cl^-	-237.5	45.5	565	19
 Cl^-	-258.7	47.4	486	17
 $SnCl_6^{2-}$	-153.6	29.9	432	20

Table 1.9: $^{31}P\{^1H\}$ NMR data for cyclic triphosphenium ions formed from dppb, dppox, dtbpox and dcxpb

1.2.5 Synthesis of eight-membered ring cyclic triphosphenium ions

Dillon *et al.* reported the synthesis of an eight-membered cyclic triphosphenium ion in 2000.[21] This was made using dpppe with PCl_3, as an eight-membered analogue to Schmidpeter's original ring. However the $^{31}P\{^1H\}$ NMR spectrum showed two sets of doublets and three sets of triplets, unlike previously synthesised cyclic triphosphenium ions. The synthesis was repeated but only two doublets and triplets were observed (Table 1.10).

δP, ppm	Multiplicity	$^1J_{P\text{-}P}$, Hz
30.2	d	465
29.3	d	465
-198.1	t	467
-215.8	t	466

Table 1.10: $^{31}P\{^1H\}$ NMR data obtained from the reaction of dpppe with PCl_3

The data obtained suggested that a monomer and a dimer had formed (Figure 1.6). It was proposed that the third triplet observed could be due to the 'open-end' form of the dimer.

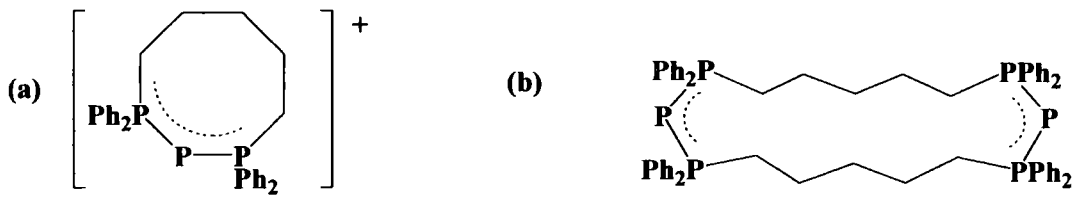


Figure 1.6: Possible products from the reaction of dpppe and PCl_3 (a) monomer, (b) dimer

Another eight-membered cyclic triphosphenium ion was synthesised from the diphosphane dppdmx.[20] The $^{31}P\{^1H\}$ NMR spectrum shows a triplet at low frequency and a doublet at higher frequency corresponding to P_A and P_B respectively, and a large $^1J_{P\text{-}P}$ (Table 1.11).

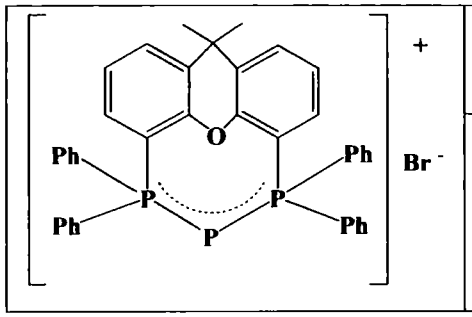
	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz
	-112.2	26.1	553

Table 1.11: $^{31}P\{^1H\}$ NMR data obtained for the dppdmx cyclic triphosphenium ion as its bromide salt

1.2.6 Synthesis of nine-membered ring cyclic triphosphenium ions

Attempts to synthesise a nine-membered cyclic triphosphenium ion using the diphosphane dpph with PCl_3 afforded three products. The $^{31}P\{^1H\}$ NMR spectrum showed three sets of doublets and triplets (Table 1.12). These were assigned to monomer, dimer and open chained species with a singlet corresponding to the ends of the chain (Figure 1.7).[21]

δP, ppm	Multiplicity	$^1J_{P-P}$, Hz
30.5	d	463
30.3	d	468
23.2	d	423
-11.5	s	-
-197.8	t	468
-198.5	t	463
-209.1	t	423

Table 1.12: $^{31}P\{^1H\}$ NMR literature data for the formation of a nine-membered ring (plus dimer and open chain) synthesised from dpph and PCl_3

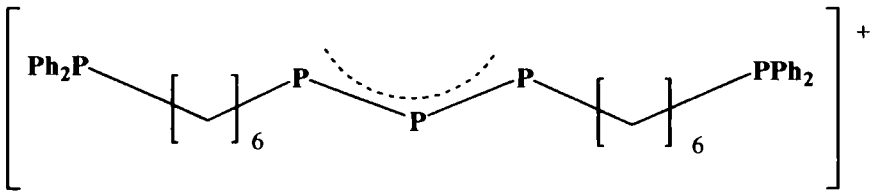


Figure 1.7: The proposed structure of the open chain species

1.3 Bonding in cyclic triphosphenium ions – DFT calculations

Examination of the frontier orbitals of the model compound $[(dmpe)P]^+$ by Macdonald and Ellis has provided further insight into the electronic structure of cyclic (and acyclic) triphosphenium ions. The results obtained suggest that there is a 'lone pair' orbital on the central phosphorus atom (P_A) which is in the P-P-P plane (HOMO-1), and that the HOMO consists mainly of $3p_x$ orbitals on P_A.[5]

The stability of cyclic triphosphenium ions was attributed to stabilisation of the HOMO through back-bonding interactions. Electron density from the $3p_x$ orbitals on P_A is donated to empty anti-bonding orbitals on the four coordinate phosphorus atoms (P_B) (Figure 1.8).[5]

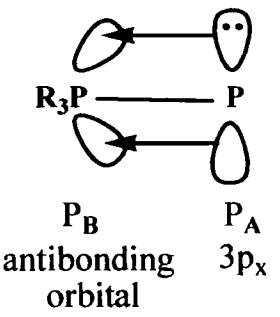


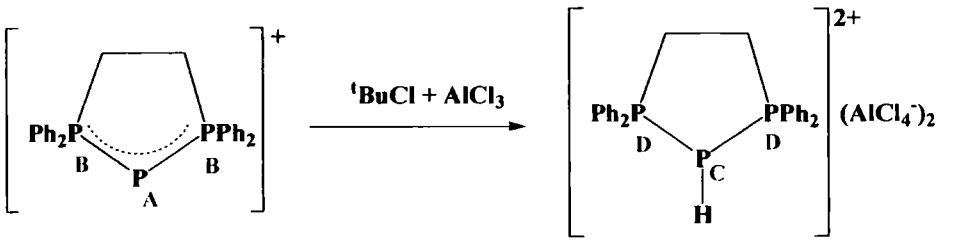
Figure 1.8: Back-bonding interactions between filled $3p_x$ orbitals on P_A and empty anti-bonding orbitals on P_B[5]

NBO population analysis and NLMO calculations were also carried out by Macdonald and Ellis. The results provide evidence for backbonding as there is a decreased population of the $3p_x$ orbital on P_A and there is significant delocalisation of the 'lone pair' orbitals respectively.[5]

1.4 Reactions of cyclic triphosphenium ions

1.4.1 Protonation reactions

The first reported protonation of cyclic triphosphenium ions was carried out by Schmidpeter in 1985.[11] The dppe cyclic triphosphenium ion was reacted with ^{t}BuCl in the presence of aluminium trichloride to afford the P-protonated derivative (Scheme 1.8).



Scheme 1.8: Protonation of the dppe cyclic triphosphenium ion using ^{t}BuCl and $AlCl_3$

There are two possible sources for the proton. One possibility is the abstraction of the proton from ^{t}BuCl to afford an alkene (Scheme 1.9). Since $AlCl_3$ is easily hydrolysed, the alternative source of protons is H_2O or OH^- groups on the surface of the $AlCl_3$.

$$^t\mathrm{BuCl} + \mathrm{AlCl_3} \longrightarrow \mathrm{H^+} + \mathrm{AlCl_4^-} + \mathrm{Me_2C{=}CH_2}$$

Scheme 1.9: Abstraction of a proton from ^{t}BuCl

The $^{31}P\{^{1}H\}$ NMR spectrum of the product showed that the triplet corresponding to the central phosphorus atom (P_C) had shifted to higher frequency (Table 1.13). This is due to deshielding by the proton. The coupling constant decreased compared to that of the cyclic triphosphenium ion, due to the π-bonding being lost. Analogous reactions were carried out with cyclic triphosphenium ions derived from tetraphos, depe, dppben, dppE, dppp and dppb. The $^{31}P\{^{1}H\}$ NMR data for each P-protonated derivatives showed a shift to higher frequency for the triplet (P_C) and a decrease in the $^{1}J_{P\text{-}P}$ compared to those for the parent cyclic triphosphenium ion (Table 1.13).

For the reaction between the dppE ring, $AlCl_3$ and $^{t}BuCl$ an unusual result was reported.[22] Along with the expected doublet and triplet corresponding to the protonated ring, a second doublet and triplet were apparent in the $^{31}P\{^{1}H\}$ NMR spectrum (d, δP 29.9 ppm, t, δP 54.9 ppm, $^{2}J_{P\text{-}P}$ = 25.1 Hz) corresponding to the norbornane-like trication isolated as its $(AlCl_4^-)_3$ salt (Figure 1.9).

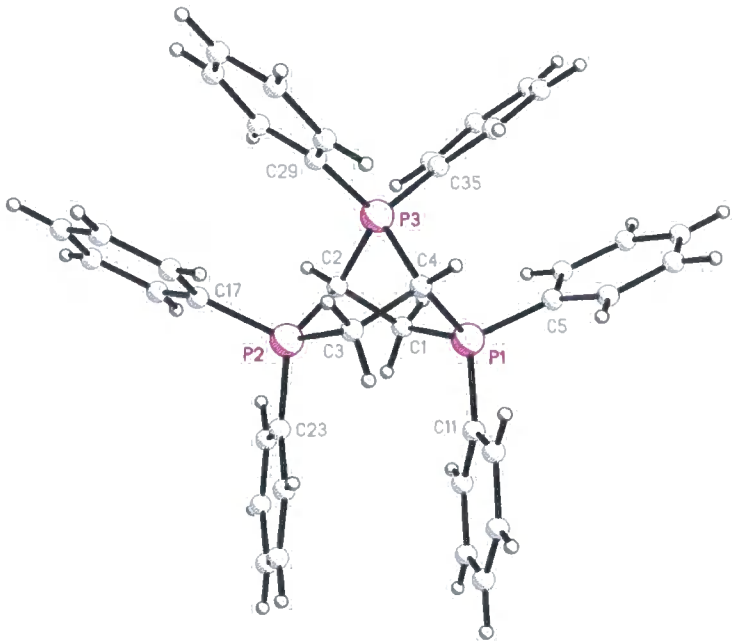


Figure 1.9: Molecular structure of the 1,4,7-tris(diphenylphosphonium) norbornane trication [22]

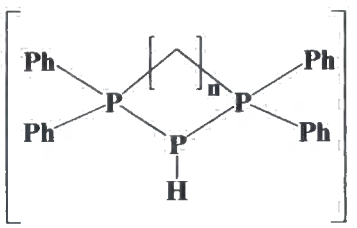
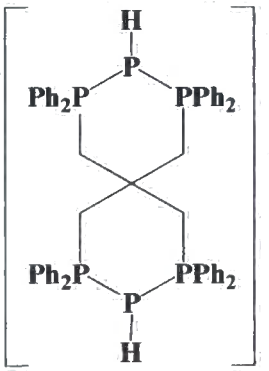
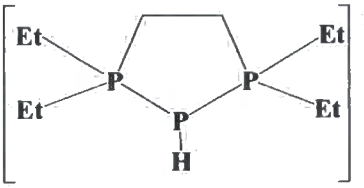
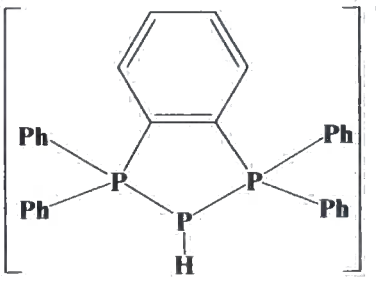
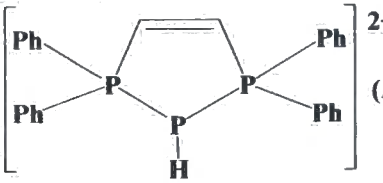
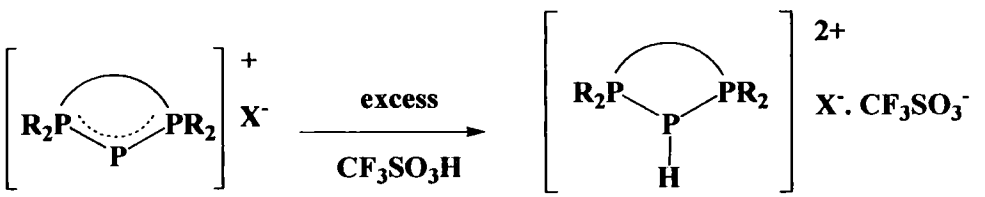
P-protonated cyclic triphosphenium ion		δP_C, ppm	δP_D, ppm	$^1J_{P-P}$, Hz	$^1J_{P-H}$, Hz	Reference
	n=2	-154.5	53.5	240	NR	11, 23
	n=3	-156.2	13.8	226	223	17
	n=4	-134.4	28.6	255	236	17
		-177.0	11.7	232	NR	11, 23
		-183.9	68.0	255	NR	17
		-133.0	42.7	241	219	17
		-157.2	58.1	258	231	17

Table 1.13: $^{31}P\{^1H\}$ and ^{31}P NMR data for some P-protonated cyclic triphosphenium ions using ^{t}BuCl and $AlCl_3$ (NR – not recorded)

Isolation of the nine-membered ring derived from dpph had not been achieved. Addition of $AlCl_3$ and ^tBuCl to a solution containing a mixture of the cyclic triphosphenium ion, the dimer and monomer resulted in the protonation of all three species. Other protonations reactions were attempted, including those for the rings formed from dppox and dppf, although, these proved unsuccessful.[17]

An alternative method to synthesise P-protonated derivatives of cyclic triphosphenium ions was reported by Dillon *et al.* in 2004.[17] This method involved reacting the cyclic triphosphenium ion with triflic acid instead of $AlCl_3$ and ^tBuCl (Scheme 1.10).



Scheme 1.10: Protonation of cyclic triphosphenium ions using triflic acid

The $^{31}P\{^1H\}$ NMR data for P-protonated derivative of cyclic triphosphenium ions using this method were consistent with those previously reported (Scheme 1.10). There was a shift to higher frequency of the triplet corresponding to P_C and a decrease in $^1J_{P\text{-}P}$ compared with those for the parent cyclic triphosphenium ion (Table 1.14).

For cyclic triphosphenium ions derived from dppox, dppf, dpppe and dcypm, attempts to synthesise P-protonated derivatives were unsuccessful. This was attributed to the strength of triflic acid, which caused decomposition of the rings.[17]

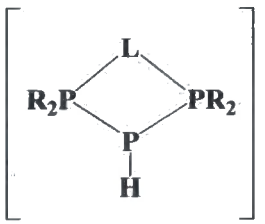
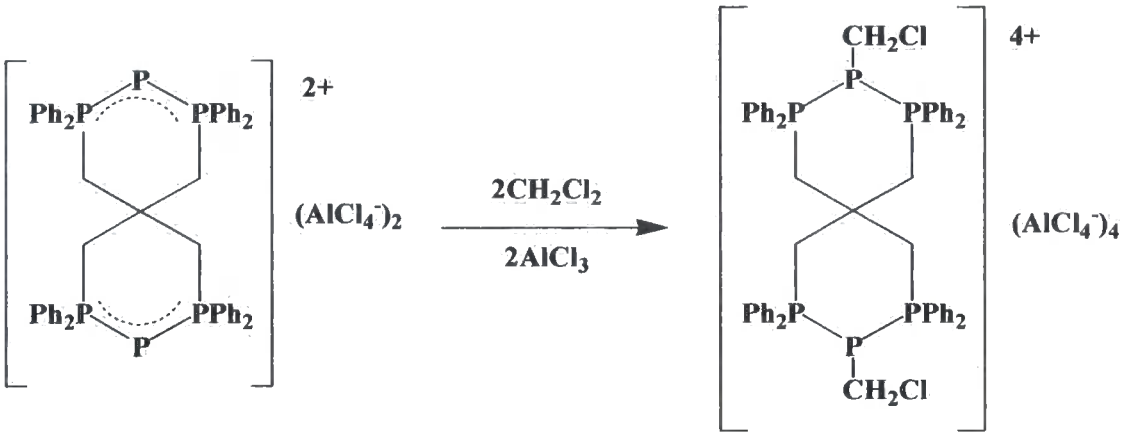
 $X^-.CF_3SO_3^-$		δP_C, ppm	δP_D, ppm	$^1J_{P-P}$, Hz	$^1J_{P-H}$, Hz
R =	L =				
Ph	C_2H_4	-153.1	53.4	241	NR
Ph	C_2H_2	-159.2	58.1	273	NR
Et	C_2H_4	-180.7	72.3	243	230
Et	C_3H_6	-182.0	29.0	232	223
Cy	C_4H_8	-166.5	49.3	276	267
Me	C_2H_4	-148.6	55.7	240	218
Cy	C_2H_4	-203.1	77.6	259	228

Table 1.14: $^{31}P\{^1H\}$ and ^{31}P NMR data for P-protonated cyclic triphosphenium ions synthesised using triflic acid (NR – not recorded)[17]

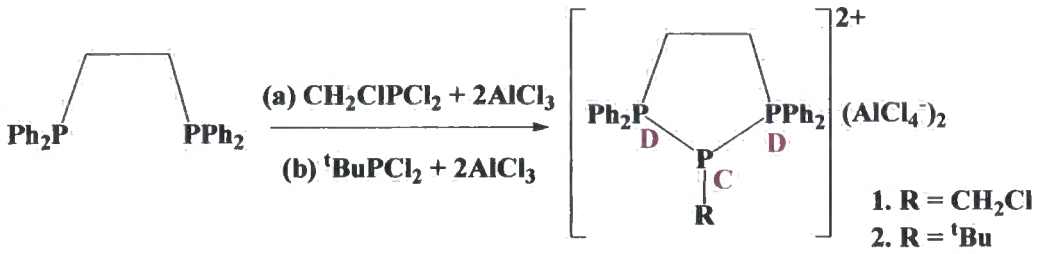
1.4.2 Alkylation reactions

Schmidpeter *et al.* reported the first alkylation of a cyclic triphosphenium ion in 1986.[9] The reaction involved the chloromethylation of the ring formed from tetraphos and PCl_3 (Scheme 1.11).



Scheme 1.11: Chloromethylation of the tetraphos cyclic triphosphenium ion

Similar to the results reported for P-protonation reactions, the $^{31}P\{^{1}H\}$ NMR spectrum showed a shift of the triplet corresponding to P_C and a decrease in $^{1}J_{P\text{-}P}$ compared with those for the triphos cyclic triphosphenium ion (Table 1.15). P-alkyl derivatives were also synthesised by reacting the diphosphane dppe with either CH_2ClPCl_2 or $^{t}BuPCl_2$ to afford P-chloromethyl and P-^{t}Butyl derivatives (Scheme 1.12, Table 1.15).[23]



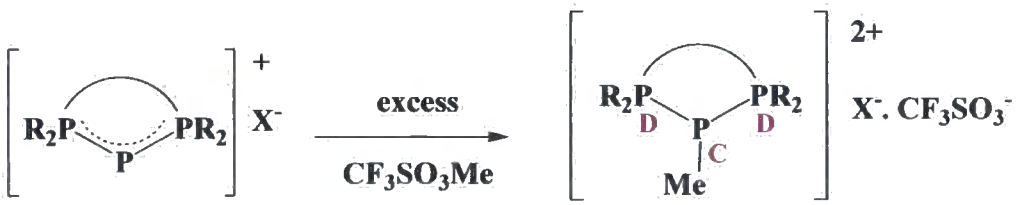
Scheme 1.12: Synthesis of P-chloromethyl and P-^{t}Butyl derivatives of the dppe cyclic triphosphenium ion.

Alkyl derivative	δP_C, ppm	δP_D, ppm	$^1J_{P-P}$, Hz	Reference
triphos-PCH_2Cl	-79.8	8.7	282	11
dppe-PCH_2Cl	-78.0	52.0	282	23
dppe-P^{t}Bu	-79.0	52.0	283	23

Table 1.15: $^{31}P\{^1H\}$ NMR literature data for P-alkylated cyclic triphosphenium ions

1.4.2.1 Methylation reactions

The first attempt to methylate a cyclic triphosphenium ion was carried out by Wilkinson in 2001, which involved reacting the dppe cyclic triphosphenium ion with methyl iodide. This was unsuccessful.[24] However, Dillon *et al.* showed that reaction of cyclic triphosphenium ions with methyl triflate afforded the P-methylated derivatives, although excess methyl triflate was required for 100% conversion (Scheme 1.13, Table 1.16).[14, 25, 26]



Scheme 1.13: Synthesis of P-methyl derivatives of cyclic triphosphenium ions using methyl triflate.

Similar to the $^{31}P\{^1H\}$ NMR data reported for P-protonated and P-alkylated derivatives, upon methylation the triplet corresponding to the central phosphorus (P_C) is shifted to higher frequency. This suggests that for P-protonated and P-alkylated derivatives the central P is effectively deshielded compared with the P(I) centre in cyclic triphosphenium ions. In all cases $^1J_{P-P}$ is decreased, compared with those for the parent cyclic triphosphenium ion probably due to the increased P-P distance upon loss of delocalisation (Table 1.16).

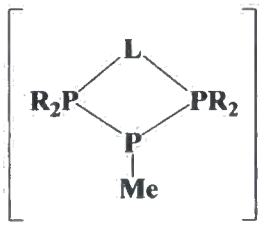
 $X^-.CF_3SO_3^-$		δP_C, ppm	δP_D, ppm	$^1J_{P-P}$, Hz	Reference
R =	L =				
Ph	C_2H_4	-91.3	54.8	284	14, 25
Ph	1,2-C_6H_4	-68.6	45.4	291	14, 25
Ph	C_3H_6	-88.7	12.2	263	14, 25
Ph	C_4H_8	-75.2	30.9	306	14, 25
Ph	1,2-$(CH_2)_2C_6H_4$	-73.4	15.8	298	14, 25
Et	C_2H_4	-98.0	65.7	289	26
Et	C_3H_6	-102.1	28.1	274	26
Cy	C_4H_8	-76.3	43.4	321	26
Cy	CH_2	-35.1	33.6	195	10

Table 1.16: $^{31}P\{^1H\}$ NMR data for P-methyl derivatives of cyclic triphosphenium ions

1.4.2.2 Ethylation reactions

Attempts to synthesis a P-ethyl cyclic triphosphenium ion using ethyl triflate were unsuccessful when the substituents on the four-coordinate P atoms in the cyclic triphosphenium ion were phenyl or cyclohexyl. This was attributed to steric hindrance of the phenyl/cyclohexyl groups, which restricted the approach of the ethyl group to the central phosphorus atom.[26]

However Dillon *et al.* reported the synthesis of two P-ethylated derivatives of cyclic triphosphenium ions where the substituents on the four-coordinate P atoms of the ring were ethyl (Table 1.17).[26] The $^{31}P\{^1H\}$ NMR data for the P-ethyl derivatives, as expected, showed a shift of the triplet corresponding to P_C to higher frequency and a decrease in $^1J_{P-P}$ compared with those for the corresponding parent cyclic triphosphenium ion.

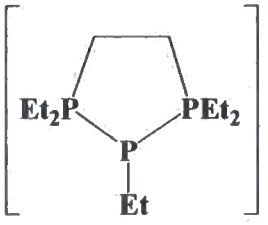
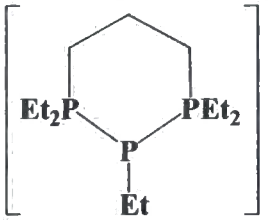
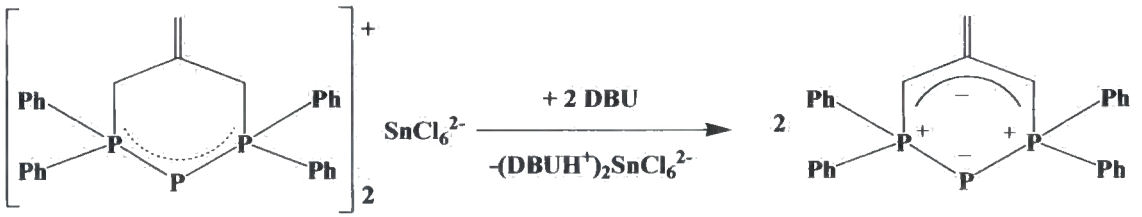
P-Et derivative	δP_C, ppm	δP_D, ppm	$^1J_{P-P}$, Hz
	-89.8	66.1	291
	-89.8	28.6	283

Table 1.17: $^{31}P\{^1H\}$ NMR literature data for the P-ethyl derivatives of the depp and depe cyclic triphosphenium ions[26]

1.4.3 Deprotonation using DBU

Gamper and Schmidbaur reported a reaction between the dppme cyclic triphosphenium ion and DBU (Scheme 1.14). Following deprotonation, isomerisation occurs to afford a neutral phosphinine.[13]



Scheme 1.14: Deprotonation of the dppme cyclic triphosphenium ion using DBU.[13]

$^{31}P\{^1H\}$ NMR data for both the parent cyclic triphosphenium ion and the phosphinine show a shift to lower frequency for both the doublet and triplet resonances (Table 1.18).

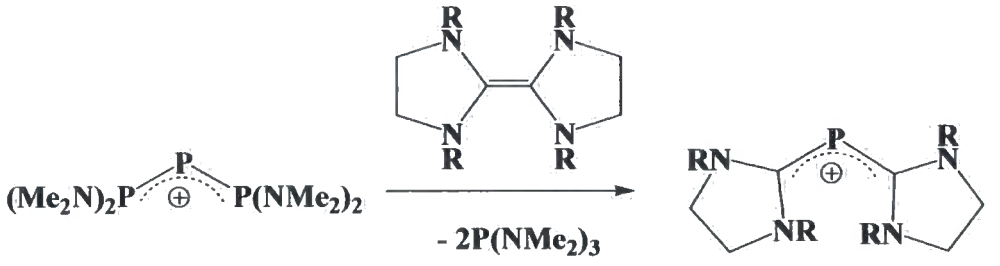
The ^{13}C and ^{1}H NMR data were consistent with those for a methallylic fragment on an sp^2 carbon with a partial negative charge.

System	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz
dppme cyclic triphosphenium ion	-216.4	23.0	431
phosphinine	-232.9	16.1	375

Table 1.18: $^{31}P\{^1H\}$ NMR data for the dppme cyclic triphosphenium ion and the phosphinine synthesised *via* a deprotonation reaction[13]

1.4.4 Synthesis of phosphamethine cyanine salts

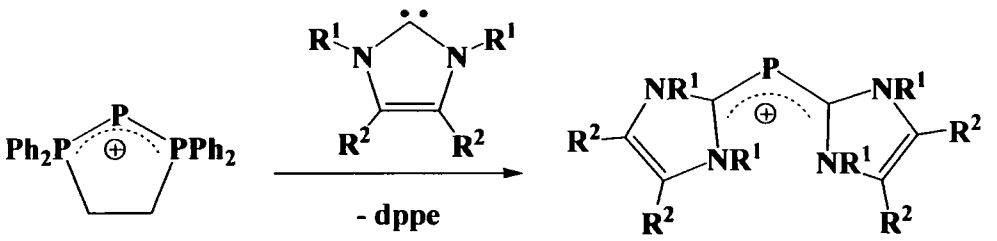
Schmidpeter *et al.* reported in 1983, the synthesis of a phosphamethine cyanine salt through a reaction of an acyclic triphosphenium cation with an electron-rich olefin (Scheme 1.15).[27] The salt formed through insertion of the P(I) centre of the triphosphenium ion into the olefin.



Scheme 1.15: Synthesis of a phosphamethine cyanine salt from a triphosphenium ion and an electron-rich olefin[27]

It has also been demonstrated that reaction of cyclic triphosphenium ions with N-heterocyclic carbenes affords phosphamethine cyanine salts (Scheme 1.16).[28] An alternative route to synthesise the phosphamethine cyanine salt involves reacting the

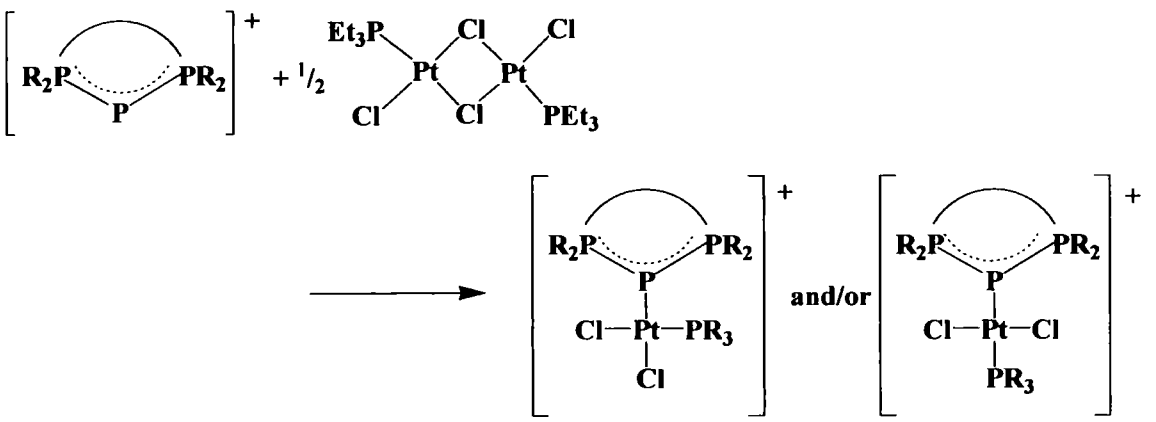
N-heterocyclic carbene with PCl_3. However by using the dppe cyclic triphosphenium ion by-products are easily removed from the reaction mixture, and also a smaller amount of the N-heterocyclic carbene is required.



Scheme 1.16: Synthesis of a phosphamethine cyanine salt from a triphosphenium ion and an N-heterocyclic carbene[28]

1.4.5 Reactions with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

Investigations into the coordination of cyclic triphosphenium ions to form Pt(II) complexes have been carried out by Dillon *et al.*[19] By reacting a cyclic triphosphenium ion with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, it was proposed that the reactions would afford the *cis* and/or *trans* complexes (Scheme 1.17).



Scheme 1.17: Proposed synthesis of Pt(II) complexes containing cyclic triphosphenium ions

The first attempted reaction was between the dppe cyclic triphosphenium ion and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$. The $^{31}P\{^1H\}$ NMR spectrum showed that the main product of the reaction was $[Pt(dppe)(PEt_3)Cl]^+$ and there was no evidence for coordination of the cyclic triphosphenium ion to platinum (Figure 1.10, Table 1.19).

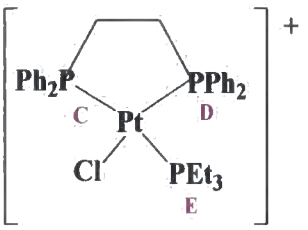


Figure 1.10: Main product of the reaction between *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and the dppe cyclic triphosphenium ion, $[Pt(dppe)(PEt_3)Cl]^+$ **71**

δP, ppm	$^2J_{PC\text{-}PE}$, Hz	$^2J_{PC\text{-}PD}$, Hz	$^2J_{PD\text{-}PE}$, Hz	$^1J_{Pt\text{-}P}$, Hz	Assignment
53.5	368	7	-	2251	P_C
43.7	-	7	17	3537	P_D
17.2	368	-	17	2289	P_E

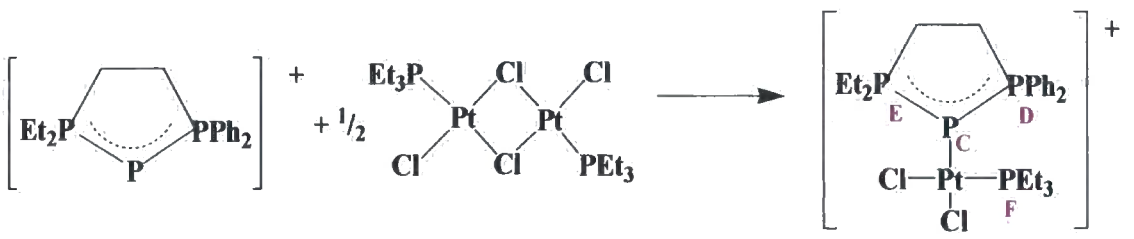
Table 1.19: $^{31}P\{^1H\}$ NMR data for the complex formed in a reaction between dppe and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

Similar results were obtained from the reaction between the dppf cyclic triphosphenium ion and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$. Again the $^{31}P\{^1H\}$ NMR spectrum showed no evidence of coordination of the cyclic triphosphenium ion to platinum, and the main product of the reaction was $[Pt(dppf)(PEt_3)Cl]^+$ (Table 1.20).

δP, ppm	$^2J_{PC-PE}$, Hz	$^2J_{PC-PD}$, Hz	$^2J_{PD-PE}$, Hz	$^1J_{Pt-P}$, Hz	Assignment
23.4	408	15	-	2325	P_C
12.8	-	15	20	3785	P_D
15.8	408	-	20	2362	P_E

Table 1.20: $^{31}P\{^1H\}$ NMR data for the complex formed in a reaction between dppf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

Reaction of the unsymmetrical cyclic triphosphenium ion derived from dedppe with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ was carried out (Scheme 1.18). The $^{31}P\{^1H\}$ NMR data showed that the *cis*-complex had formed (Table 1.21). Upon complexation the triplet corresponding to the central P atom of the cyclic triphosphenium ion (P_C) had shifted to higher frequency, as in the protonation, methylation and ethylation reactions. The $^1J_{Pt-P}$ coupling to the phosphenium central P is unusually small for a one-bond phosphorus–platinum coupling at 1096 Hz. It was suggested that this could be due to a long Pt-P bond, possibly due to the cationic nature of the ligand.



Scheme 1.18: Reaction between the dedppe cyclic triphosphenium ion and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

δP, ppm	Multiplicity	Assignment	$^{1}J_{P-P}$, Hz	$^{2}J_{P-P}$, Hz	$^{1}J_{Pt-P}$, Hz	$^{2}J_{Pt-P}$, Hz
72.9	ddd	P_D	357	30	-	13
50.8	ddd	P_E	366	30	-	11
10.7	s	P_F	363	-	3385	-
-89.5	t(dd)	P_C	360	-	1096	-

Table 1.21: $^{31}P\{^{1}H\}$ NMR data for the complexation of the Pt dimer to the dedppe cyclic triphosphenium ion

Further investigations showed that, if the cyclic triphosphenium ion contains substituents on the four-coordinate phosphorus atoms that are not phenyl, or only phenyl groups on one phosphorus atom, then complexation does take place to afford *cis* and/or *trans* complexes (Scheme 1.18). In all the complexes synthesised the $^{1}J_{Pt-P}$ coupling to the phosphenium central P is unusually small for a one-bond phosphorus–platinum coupling (Table 1.22).[19]

The data obtained from these reactions show that when forming a Pt (II) complex from a cyclic triphosphenium ion with cyclohexyl or any ethyl substituents, the *trans*-complex, the kinetic product, forms first but this then converts to the more thermodynamically stable product, the *cis*-isomer. If all the substituents are tertiary butyl groups then only the *trans*-complex forms, due to steric hindrance. When there are phenyl groups on both four-coordinate phosphorus atoms, the cyclic triphosphenium ion undergoes ring scission, followed by complexation to the platinum.

These experimental results suggest tat the failure to synthesise complexes with phenyl substituents on both four-coordinate P atoms is due to electronic rather than steric effects, with alkyl phosphanes being better donors.

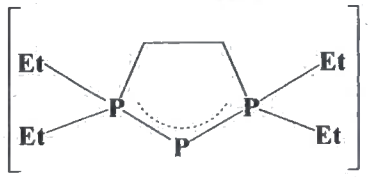
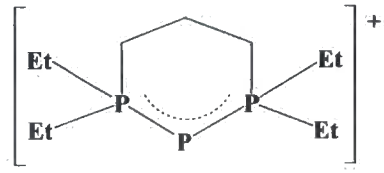
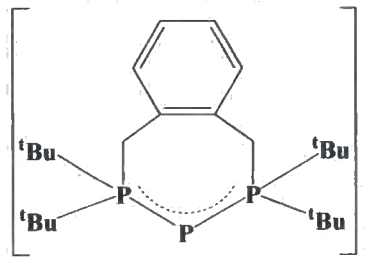
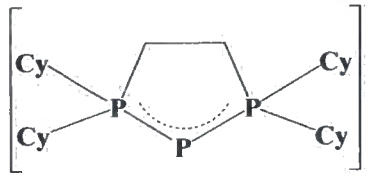
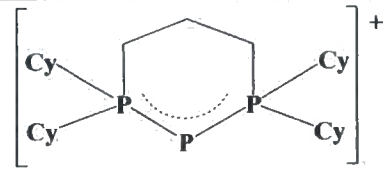
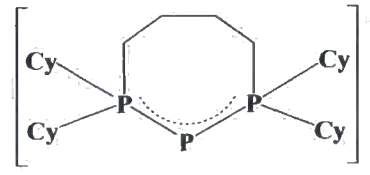
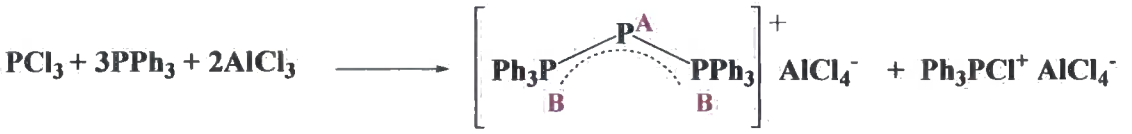
Cyclic triphosphenium ion	δP_C, ppm	δP_D, ppm	δP_E, ppm	$^1J_{Pt\text{-}PC}$ Hz	$^1J_{Pt\text{-}PE}$ Hz	$^1J_{P\text{-}P}$, Hz	$^2J_{P\text{-}P}$, Hz	*cis/ trans*
	-104.3	70.0	11.4	1059	3407	363	-	*cis*
	-102.3	18.9	3.1	1098	3399	340	-	*cis*
	-137.0	25.9	9.6	*	*	348	180	*trans*
	-136.5	50.8	11.4	*	*	549	375	*trans*
	-107.9	69.6	9.0	1097	3430	384	-	*cis*
	-148.2	72.6	16.3	1023	2974	408	321	*trans*
	-102.7	20.3	3.4	*	*	371	-	*cis*
	-152.4	27.4	15.6	*	*	369	255	*trans*
	-78.6	38.5	3.9	1222	3438	420	-	*cis*
	-129.5	42.8	15.0	*	*	426	279	*trans*

Table 1.22: $^{31}P\{^1H\}$ NMR data for Pt(II) complexes containing cyclic triphosphenium ions (* - Pt satellites were weak so *J* values could not be calculated)

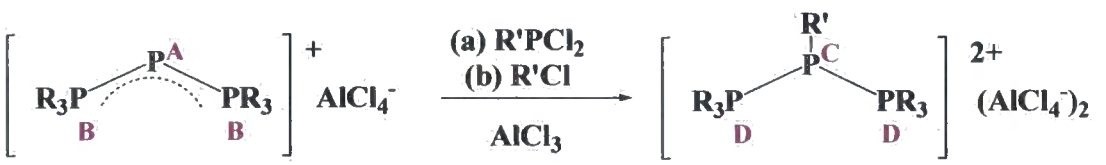
1.5 Acyclic triphosphenium ions

Schmidpeter *et al.* reported the synthesis of acyclic triphosphenium ion in 1985.[29] The reaction between PCl_3, PPh_3 and $AlCl_3$ formed the acyclic triphosphenium ion and a chlorophosphonium salt (Scheme 1.19). The $^{31}P\{^1H\}$ NMR data for this cation were similar to those obtained for the cyclic triphosphenium ions, with a triplet at low frequency, a doublet at higher frequency and a large $^1J_{P\text{-}P}$ (Table 1.23). X-ray diffraction studies confirmed that the P-P bond lengths were intermediate between values for single and double P-P bonds, as in cyclic triphosphenium ions.[29] Many other symmetrical and unsymmetrical acyclic triphosphenium ions have since been reported. The $^{31}P\{^1H\}$ NMR data for these ions are similar to those obtained for the cyclic species (Table 1.23).



Scheme 1.19: Synthesis of an acyclic triphosphenium ion

Schmidpeter also reported the P-protonation and P-alkylation of acyclic triphosphenium ions (Scheme 1.20). The $^{31}P\{^1H\}$ NMR data for the products were consistent with the results obtained for the cyclic analogues, with a shift to higher frequency for P_C and a decrease in $^1J_{P\text{-}P}$ compared with the parent triphosphenium ion (Table 1.24).[23, 29] X-Ray diffraction studies confirmed that the P-P bond lengths were consistent with those for single P-P bonds, indicating a loss of π-bonding between the phosphorus atoms.



Scheme 1.20: Synthesis of P-protonated and P-alkylated acylic triphosphenium ions

L^1	L^2	δP_A, ppm	δP_B, ppm	δP_C, ppm	$^1J_{PA-PB}$, Hz	$^1J_{PA-PC}$, Hz	$^2J_{PB-PC}$, Hz	Ref.
PPh_3	L^1	-174	30	-	502	-	-	29
$PMePh_2$	L^1	-176	-	23	-	480	25	29
PMe_2Ph	L^1	-159	-	12	-	463	26	29
PBu_3	L^1	-229	-	33	-	458	41	29
$PPh_2(NEt_2)$	L^1	-164	-	79	-	501	30	29
$PPh(NEt_2)_2$	L^1	-163	-	64	-	479	27	29
$PPh_2(NHPh)$	L^1	-182	-	47	-	524	27	29
$P(NMe_2)_3$	L^1	-194	-	85	-	493	30	29
$P[N(CH_2)_5]_3$	L^1	-193	-	79	-	497	32	29
$P[O(CH_2)_4N]_3$	L^1	-207	-	78	-	527	32	29
$P(OEt)_3$	L^1	-218	-	82	-	562	15	29
PPh_3	$PMePh_2$	-180	30	-	482	464	-	29
PPh_3	PMe_2Ph	-173	31	-	481	451	-	29
PPh_3	PBu_3	-199	32	-	503	473	-	29
PPh_3	$PPh_2(NEt_2)$	-167	30	-	510	508	-	29
PPh_3	$PPh(NEt_2)_2$	-170	30	-	524	510	-	29
PPh_3	$PPh_2(NHPh)$	-178	29	-	479	498	-	29
PPh_3	$P(NMe_2)_3$	-180	29	-	523	518	-	29
PPh_3	$P[N(CH_2)_5]_3$	-173	29	-	542	560	-	29
PPh_3	$P[O(CH_2)_4N]_3$	-181	28	-	526	566	-	29
PPh_3	$P(OEt)_3$	-196	32	-	437	508	-	29
$P(NMe)_3$*	$P(NMe)_3$	-194	85	-	518	-	-	27

Table 1.23: $^{31}P\{^1H\}$ NMR literature data for acyclic triphosphenium ions $[L^1P_AL^2]AlCl_4^-$ where δP_B corresponds to a PPh_3 ligand (* reaction carried out with $NaBPh_4$ instead of $AlCl_3$)

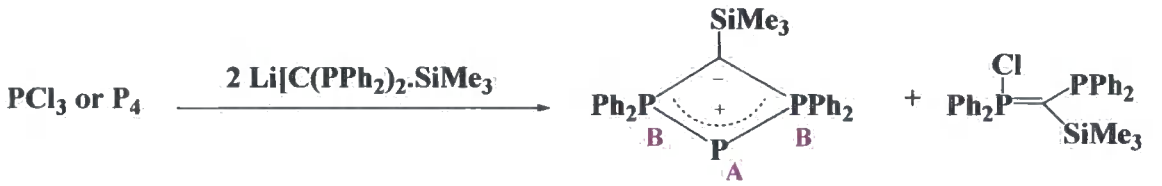
PR_3	R'	Preparation	δP_C, ppm	δP_D, ppm	$^1J_{PC-PD}$, Hz	$^1J_{P-H}$, Hz
PPh_3	H	(b)	-120	23	286	236
PPh_3	Me	(b)	-48	23	330	-
PPh_3	CH_2Cl	(a) and (b)	-41	25	330	-
PPh_3	Et	(b)	-37	22	334	-
PPh_3	^{i}Pr	(b)	-23	21	354	-
PPh_3	Ph	(a)	-28	24	358	-
$PMePh_2$	H	(b)	-121	18	261	230
$PMePh_2$	CH_2Cl	(b)	-38	20	305	-
PMe_2Ph	H	(b)	-116	18	255	227
PMe_2Ph	CH_2Cl	(b)	-31	21	300	-
PBu_3	H	(b)	-146	38	277	233
PBu_3	CH_2Cl	(b)	-39	39	319	-

Table 1.24: $^{31}P\{^1H\}$ NMR literature data for P-protonated and P-alkylated derivatives of acyclic triphosphenium ions[23]

1.6 Neutral P(I) cycles

Karsch *et al.* reported the synthesis of some neutral P(I) cycles from reactions between diphosphinomethanides and PCl_3. Depending on the substituents on the diphosphinomethanide and the reaction stoichiometry and conditions, rings of various sizes were synthesised.[30-33]

A neutral four-membered ring was synthesised from a reaction between PCl_3 (or P_4) with $Li[C(PPh_2)_2(SiMe_3)]$ at low temperatures (Scheme 1.21, Table 1.25).[30, 33]



Scheme 1.21: Synthesis of a neutral four-membered cycle

With methyl groups on the carbanion, and by changing the ratio of PCl_3 to diphosphinomethanide to 1:3, neutral six- and eight-membered rings were synthesised (Figure 1.11, Table 1.25).[31,33]

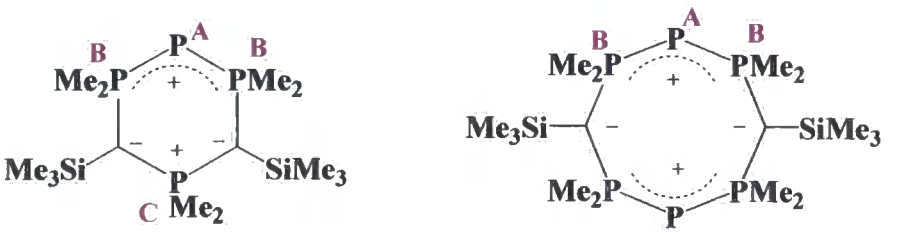


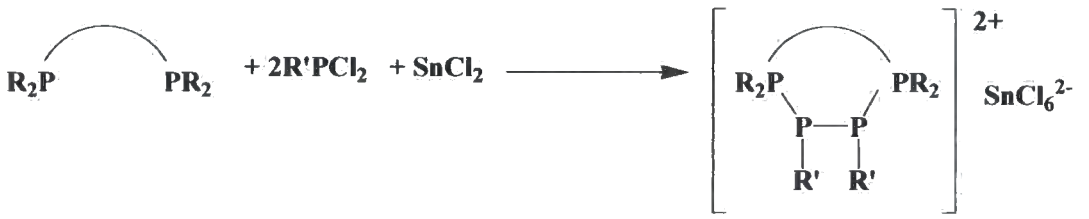
Figure 1.11: Six- and eight-membered neutral P(I) cycles

Ring size	δP_A, ppm	δP_B, ppm	δP_C, ppm	$^1J_{PA\text{-}PB}$, Hz	Reference
4	-86.3	20.2	-	261	30
6	-140.4	5.5	13.5	348	31
8	-109.5	7.9	-	251	33

Table 1.25: $^{31}P\{^1H\}$ NMR literature data for some neutral P(I) cycles.

1.7 Tetraphosphonium, tetraphosphenium ions and other diphosphonium cations containing four adjacent phosphorus atoms

Tetraphosphonium ions, first reported in 2007, are heterocycles containing four adjacent phosphorus atoms, which can be synthesised in a novel (n + 1 + 1) cycloaddition reaction, (Scheme 1.22).[34] Although this is not a formal cylcoaddition, the end product resembles a cycloaddition product and is described as such in the literature.[34] Several tetraphosphonium ions were synthesised using this method (Table 1.26).



Scheme 1.22: General synthetic route for cyclic tetraphosphonium ions

Diphosphane	R' =	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
dppb	Et	-64.7	29.4	289.2	-95.1	263.1	64.0
biphep	Et	-55.9	30.1	321.0	-77.2	121.7	12.5
dppdmx	Et	-41.9	28.5	309.5	-86.5	202.4	123.8
dppe	Et	-73.6	27.3	297.5	-48.1	87.5	2.7

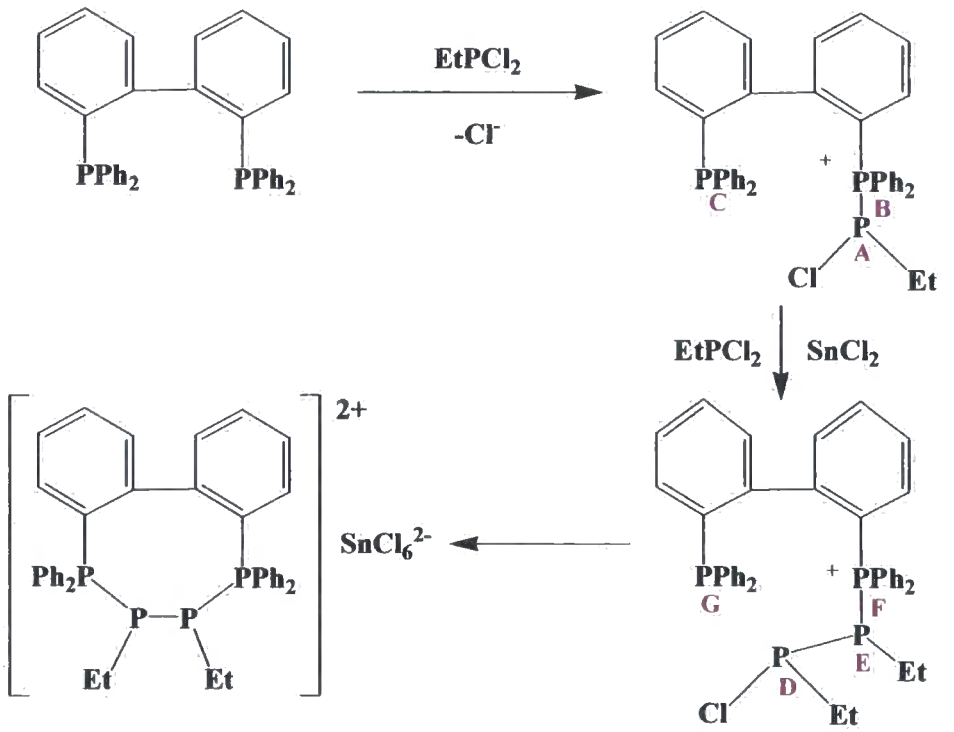
Table 1.26: $^{31}P\{^1H\}$ NMR literature data for some cyclic tetraphosphonium ions

In the reaction between biphep, $EtPCl_2$ and $SnCl_2$, transient intermediates were detected in the $^{31}P\{^1H\}$ NMR spectra recorded soon after the addition of the chlorophosphane (Table 1.27). The first step in the mechanism of formation necessarily involved the addition of the $EtPCl_2$ to the diphosphane to form an acyclic intermediate. $^{31}P\{^1H\}$ NMR data suggested

that the next step involved the formation of an unsymmetrical intermediate. Cyclisation could then take place to afford the tetraphosphonium ion (Scheme 1.23).

P atom	δ^{31}P, ppm	$^{1}J_{P\text{-}P}$, Hz
P_G	-13.3 s	-
P_D or P_F	13.4 d	320
P_D or P_F	12.9 d	300
P_E	-14.3 t[b]	317

Table 1.27: $^{31}P\{^{1}H\}$ NMR literature data for the unsymmetrical intermediate in the formation of the biphep cyclic tetraphosphonium ion ([b] broad)



Scheme 1.23: Proposed mechanism for cyclic tetraphosphonium ions derived from biphep

X-ray diffraction studies on the cyclic tetraphosphonium ion derived from biphep showed that the P-P bond lengths were typical values for single P-P bonds (2.218(2) – 2.235(2) Å). The molecular structure is shown in Figure 1.12.[34]

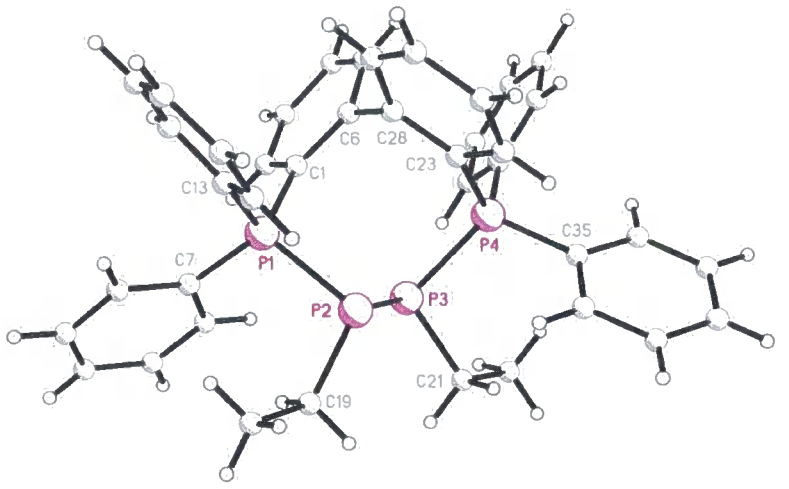
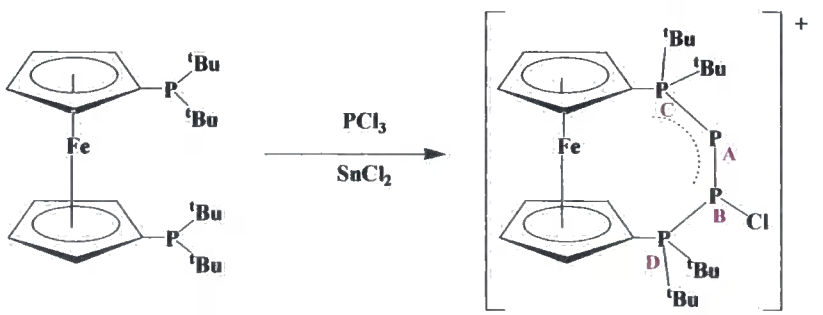


Figure 1.12: Molecular structure of the biphep cyclic tetraphosphonium ion[34]

Further investigation into the synthesis of heterocycles containing four adjacent phosphorus atoms has been carried out by Dillon *et al.*, including the synthesis of the first cyclic tetraphosphenium ion (Scheme 1.24).[35] The cyclic tetraphosphenium ion contains four adjacent phosphorus atoms, and similar to cyclic triphosphenium ions, one of the central phosphorus atoms is 'bare' and in the +1 formal oxidation state. This cationic species has not been isolated but has been characterised using $^{31}P\{^{1}H\}$ NMR spectroscopy, including 2D spectra (Table 1.28).



Scheme 1.24: Synthesis of a cyclic tetraphosphenium ion derived from dtbpf

	δ, ppm	J_{P-P}, Hz
P_A	-92.0	$^1J_{AB} = 410$, $^1J_{AC} = 515$, $^2J_{AD} = 26$
P_B	143.6	$^1J_{AB} = 413$, $^1J_{BD} = 525$, $^2J_{BC} = 66$
P_C	62.8	$^1J_{AC} = 516$, $^2J_{BC} = 66$
P_D	38.1	$^1J_{BD} = 526$, $^2J_{AD} = 33$

Table 1.28: $^{31}P\{^1H\}$ NMR data for the cyclic tetraphosphenium ion derived from dtbpf

Although many acylic diphosphonium cations are known,[6, 23, 36-40] the only examples of homocyclic diphosphonium cycles were reported by Schmutzler[41] and Burford[42] containing four and six phosphorous atoms (Figure 1.13). The four-membered ring was synthesised in a reaction of 2,6-dimethoxyphenyl(trimethyl)stannane with chlorodifluorophosphane forming the dication with two Me_3SnF_2 counter-ions, whereas the six-membered cycle was synthesised in a reaction between a cyclopolyphosphine $((PhP)_5)$, PPh_2Cl and $GaCl_3$. In both the four- and six-membered cycles the P-P bond lengths are typical values for single P-P bonds, between 2.231 Å and 2.232 Å and between 2.217(2) Å and 2.242(2) Å respectively .[41, 42]

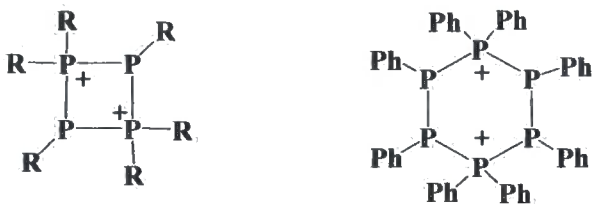


Figure 1.13: Four-[41] and six-[42] membered homocyclic diphosphonium cations

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[40] D. Schomburg, G. Bettermann, L. Ernst, and R. Schmutzler, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 975.

[41] L. Heuer, L. Ernst, R. Schmuzler, and D. Schomburg, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 1507.

[42] J. J. Weigand, N. Burford, M. D. Lumsden, and A. Decken, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 6733.

Chapter 2:

Synthesis and Characterisation of Some Cyclic Triphosphenium Ions

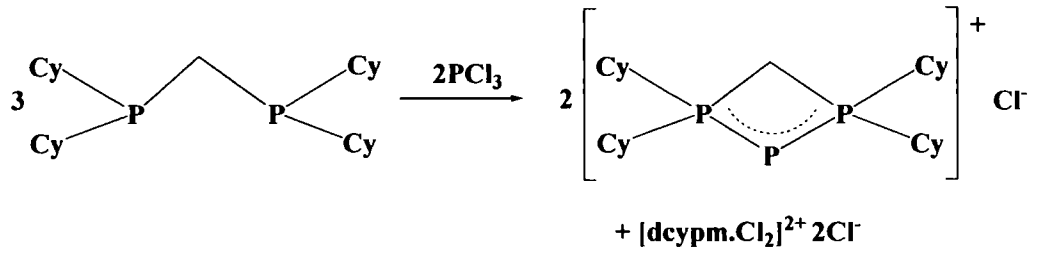
2.1 Introduction

Since their discovery in 1982 by Schmidpeter *et al.*[1] many different cyclic triphosphenium ions have been synthesised which vary by ring size, substituents on the outer two phosphorus atoms, or their hydrocarbon backbone.[2-13] The well-established methods of preparation are *via* a one pot reaction to give high yields, and provide a quick and easy route to the formation of these low coordinate phosphorus compounds.

It is the ease of preparation and the possibility of tuning these novel heterocycles that make them so attractive as potential ligands. This chapter details the synthesis and characterisation of a range of cyclic triphosphenium ions. This will allow an in-depth study into the reactivity and coordination properties of these novel heterocycles. By having a variety of different ring sizes, with different backbones and with different substituents on the outer, four-coordinate P atoms, we could investigate the effect on the reactivity of these novel heterocycles and also their coordination to metal centres.

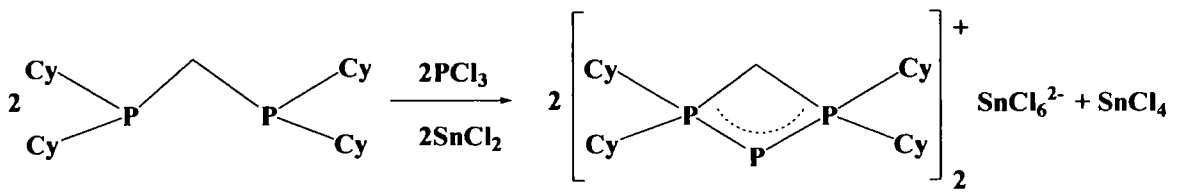
2.2 Synthesis of a four-membered ring cyclic triphosphenium ion from dcypm

Using the diphosphane dcypm, the cyclic triphosphenium ion (**1a**) was prepared according to a literature procedure (Scheme 2.1). The product displayed a characteristic triplet at δP = -216.0 ppm and doublet δP = 45.4 ppm ($^1J_{P\text{-}P}$ = 331 Hz) in its ^{31}P {^1H} NMR spectrum.[9]



Scheme 2.1: Synthesis of the dcypm cyclic triphosphenium ion (**1a**)

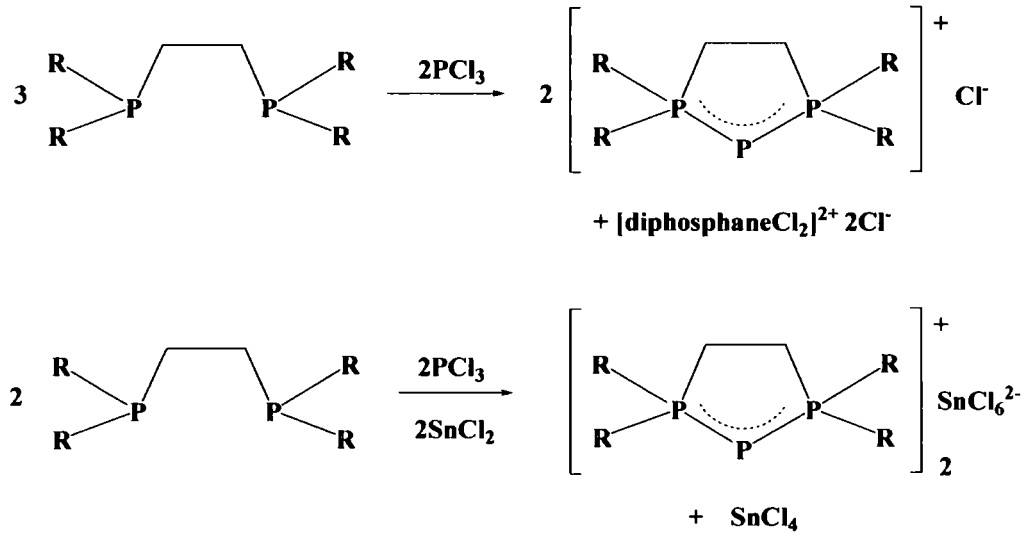
This same cyclic triphosphenium ion was also synthesised as a hexachlorostannate (**1b**) (Scheme 2.2). Again the product displayed a characteristic doublet at δP = 45.4 ppm and triplet δP = -215.2 ppm ($^1J_{P\text{-}P}$ = 333 Hz) in its ^{31}P {^1H} NMR spectrum.[9] There is a small difference in shift compared with **1a** as the counter-ion has changed from $2Cl^-$ to $SnCl_6^{2-}$ indicating that there is little interaction between the anion and cation.



Scheme 2.2: Synthesis of the dcypm cyclic triphosphenium ion using $SnCl_2$ (**1b**)

2.3 Synthesis of some five-membered ring cyclic triphosphenium ions from depe, dcype, dppe and dmpe

Four different five-membered cyclic triphosphenium ions were synthesised using previously reported literature procedures. With the exception of the cyclic triphosphenium ion derived from dmpe, these heterocycles were synthesised both as their chloride and hexachlorostannate salts (Scheme 2.3). Cyclic triphosphenium ions were also synthesised from dppe as a tetrachloroaluminate salt (**4d**), and from depe as a bromide salt (**2c**).



Scheme 2.3: Synthesis of five-membered ring cyclic triphosphenium ions (**2a-5a**)

During the synthesis of the depe cyclic triphosphenium ion, extra resonances were observed in the $^{31}P\{^{1}H\}$ NMR spectrum recorded only 15 minutes after the addition of PCl_3. These extra resonances were attributed to transient intermediates, and will be discussed in greater detail in Chapter 3. Upon standing for 12 hours the reactions had gone to completion. The $^{31}P\{^{1}H\}$ NMR data for the depe cyclic triphosphenium ions **2a-2c**, are in good agreement with those previously reported (Table 2.2).[7, 14] The only other signals in the spectra were assigned to residual PCl_3 (s, 220.3 ppm),[15] and in the synthesis of the chloride salt, $[depe.Cl_2]^{2+}2Cl^-$ (s, 109.9 ppm, **2ax**) and the bromide salt, $[depe.Br_2]^{2+}2Br^-$ (s, 95.2 ppm, **2cx**).[14]

The cyclic triphosphenium ion containing cyclohexyl groups on the four coordinate P atoms, synthesised from dcype, was also obtained both as its chloride, **3a**, and hexachlorostannate salt, **3b**. The $^{31}P\{^{1}H\}$ NMR data for the chloride salt showed the expected doublet and triplet with a large $^{1}J_{P\text{-}P}$ (Table 2.1).[9] The hexachlorostannate salt showed similar NMR parameters, with a small change in shift attributed to the change of counter ion.[16, 17]

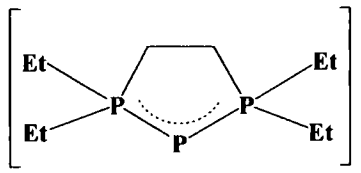
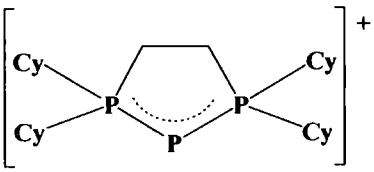
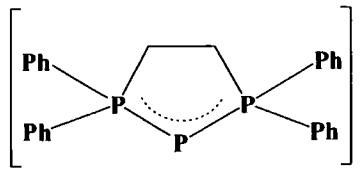
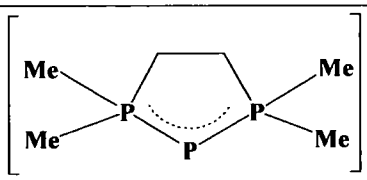
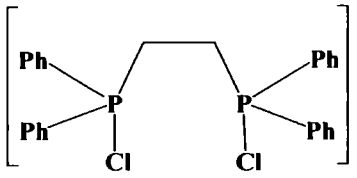
Cyclic triphosphenium ion		X=	δP_A, ppm	δP_B, ppm	$^{1}J_{P\text{-}P}$, Hz	Reference
	**2a**	Cl	-269.7	81.5	441	7
	2b	$SnCl_6^{2-}$	-268.3	81.3	440	7
	2c	Br^-	-268.8	81.4	441	*
	**3a**	Cl	-289.3	87.2	457	9
	3b	$SnCl_6^{2-}$	-289.0	87.2	455	*
	**4a**	Cl	-230.0	65.0	450	6
	4b	$SnCl_6^{2-}$	-229.3	64.9	449	1
	4d	$AlCl_4^-$	-229.7	65.0	450	3
	**5a**	Cl	-213.4	60.5	430	7

Table 2.1: $^{31}P\{^{1}H\}$ NMR data for five-membered ring cyclic triphosphenium ions (* previously unreported)

Cyclic triphosphenium ions were also synthesised from dppe with Cl^- (**4a**), $SnCl_6^{2-}$ (**4b**) and $AlCl_4^-$ (**4d**) as the counter-ions. The $^{31}P\{^1H\}$ NMR spectra showed a doublet and triplet with large values $^1J_{P\text{-}P}$ for each compound , in good agreement with Schmidpeter's results, and those reported since (Table 2.1).[1, 6, 8] In each case the cyclic triphosphenium ion was obtained as the major product of the reaction, although a small amount of the chlorinated diphosphane was present in each case (Table 2.2).



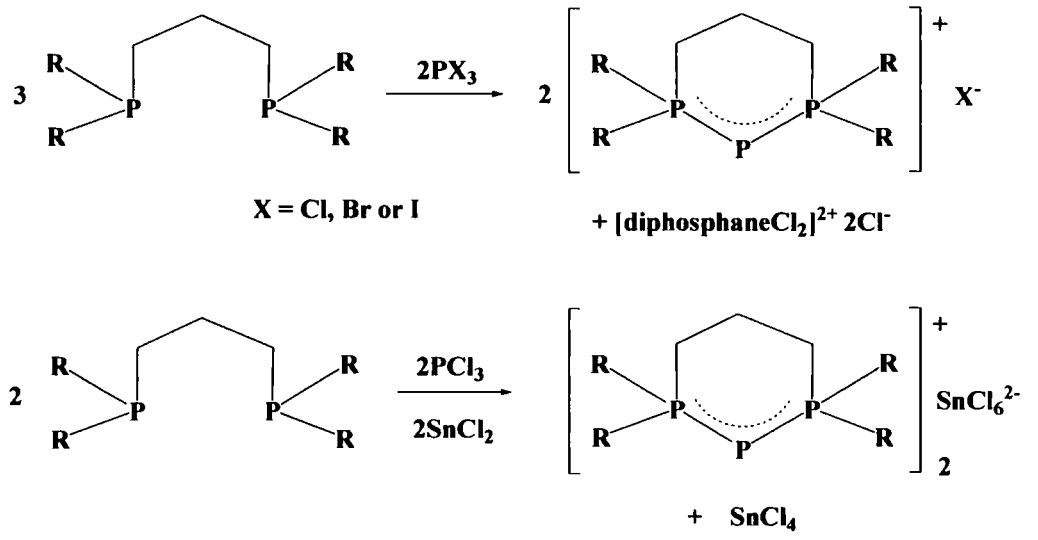
X=	Compound number	δP, ppm
$2Cl^-$	**4ax**	76.2
$SnCl_6^{2-}$	**4bx**	77.3
$(AlCl_4^-)_2$	**4dx**	76.1

Table 2.2: $^{31}P\{^1H\}$ NMR data for chlorinated dppe with various counter-ions

The synthesis of the dmpe-derived cyclic triphosphenium ion often resulted in precipitation of the product before a solution spectrum could be obtained, especially when attempting to synthesise the hexachlorostannate salt. As a result of this, the ring was only synthesised as a chloride salt (**5a**) using a dilute solution. The $^{31}P\{^1H\}$ NMR spectra of the solution showed a characteristic doublet and triplet resonances, with their shifts, and the magnitude of $^1J_{P\text{-}P}$, in good agreement with those previously reported (Table 2.1).[7]

2.4 Synthesis of some six-membered ring cyclic triphosphenium ions from depp, dcypp, dippp, dippf and dpdtbpf

Five six-membered ring cyclic triphosphenium ions, including three new ones, were synthesised as their chloride and hexachlorostannate salts with the exception of the dippf cyclic triphosphenium ion which formed only the chloride salt (Scheme 2.5). Bromide salts for the depp, dippp and dcypp cyclic triphosphenium ions, and the iodide salt of the depp cyclic triphosphenium ion were also synthesised.



Scheme 2.5: Synthesis of six-membered ring cyclic triphosphenium ions (**6a-10c**)

The synthesis of the depp cyclic triphosphenium ion to form the chloride (**6a**), hexachlorostannate (**6b**), bromide (**6c**) and iodide salts (**6e**), showed extra resonances in the $^{31}P\{^{1}H\}$ NMR spectrum recorded only a short time after the addition of PX_3. These extra resonances correspond to the formation of transient intermediates and will be discussed in greater detail in Chapter 3. Upon standing overnight, the reactions went to completion to give the desired cyclic triphosphenium ions, **6a- 6c** and **6e**. The characteristic doublet and triplet, and large magnitude of $^{1}J_{P-P}$ attributed to these compounds were observed (Table 2.3).[12, 14] In both cases, the only other resonance present in the $^{31}P\{^{1}H\}$ NMR spectra corresponded to the halogonated diphosphane (s, 109.6 ppm, **6ax**;[14] s, 79.6 ppm, **6bx**; s 94.9 ppm, **6cx**; s 104.3 ppm, **6ex**), where the significant difference in shift can be attributed to the change of counter-ion (Figure 2.1).[16, 17]

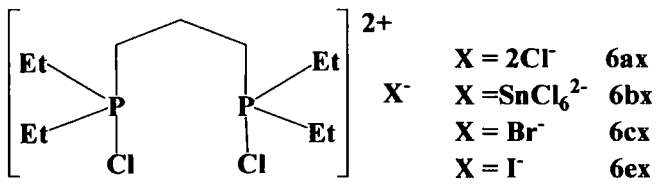


Figure 2.1: By-product of the synthesis of the depe cyclic triphosphenium ion

The synthesis of the dcypp cyclic triphosphenium ion was carried out to form the chloride (**7a**), hexachlorostannate salt (**7b**) and bromide salt (**7c**). In each case doublet and triplet resonances with large values of $^{1}J_{P\text{-}P}$ were observed, which were in good agreement with previously reported data.[16] In the solution NMR spectra obtained from the synthesis of the chloride salt, two other species were also observed (s, 104.9 ppm; s, 21.8 ppm) which were assigned to dcypp tetrachloride (**7ax**)[14], and dcypp dioxide (this resonance was also visible in the $^{31}P\{^{1}H\}$ NMR spectrum of the starting material as an impurity)[18]. In the synthesis of the bromide salt, formation of the dcypp tetrabromide (**7cx**) also occurred (s, 97.3 ppm).

Cyclic triphosphenium ions were also synthesised from dippp as chloride (**8a**), hexachlorostannate (**8b**) and bromide salts (**8c**). For the reaction between dippp and PCl_3, a $^{31}P\{^{1}H\}$ NMR spectrum recorded as soon as possible after reactant mixing showed resonances corresponding to intermediates in the formation of the cyclic triphosphenium ion. This will be discussed in detail in Chapter 3. Upon standing overnight, the $^{31}P\{^{1}H\}$ NMR spectrum showed, as expected, doublet and triplet resonances with large $^{1}J_{P\text{-}P}$ values corresponding to the desired cyclic triphosphenium ion (Table 2.3). These data are consistent with those for other cyclic triphosphenium ions.[2-13] Also apparent was a singlet (115.0 ppm), assignable to the dippp tetrachloride (**8ax**).[14] The reactions to form the hexachlorostannate and bromide salts showed no evidence of any intermediates, only the peaks corresponding to the cyclic triphosphenium ions, and the formation of $[dipppBr_2]^{+}2Br^{-}$ (**8cx**) in the synthesis of the bromide salt (s, 108.1 ppm).

The second previously unreported cyclic triphosphenium ion was synthesised from the diphosphane dippf (**9a**). Cyclic triphosphenium ions containing a ferrocene backbone typically have a larger $^{1}J_{P\text{-}P}$ coupling constant compared to other cyclic triphosphenium ions and also the triplet is at higher frequency.[12] The $^{31}P\{^{1}H\}$ NMR data obtained for this cyclic triphosphenium ion were consistent with this (Table 2.3). Attempts to synthesise the hexachlorostannate salt proved to be unsuccessful. An orange precipitate formed upon addition of PCl_3, and no solution spectra could be obtained.

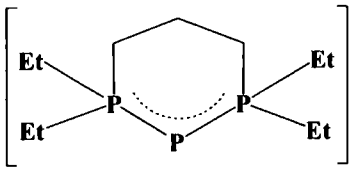
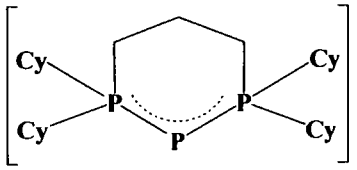
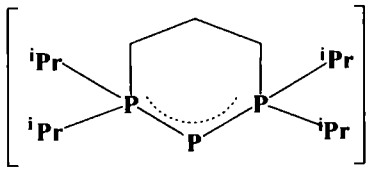
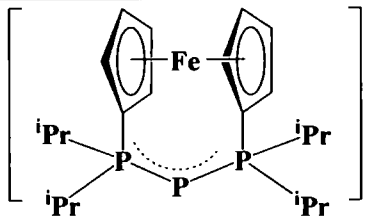
Cyclic triphosphenium ion		X=	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Reference
	**6a**	Cl^-	-254.3	30.7	417	12
	6b	$SnCl_6^{2-}$	-255.4	31.2	416	12
	6c	Br^-	-253.3	30.6	417	*
	6e	I^-	-252.1	30.6	418	*
	**7a**	Cl^-	-293.5	37.0	454	14
	7b	$SnCl_6^{2-}$	-292.9	36.6	456	14
	7c	Br^-	-297.7	36.7	450	*
	**8a**	Cl^-	-299.6	44.7	458	*
	8b	$SnCl_6^{2-}$	-299.4	44.8	457	*
	8c	Br^-	-299.7	44.8	458	*
	**9a**	Cl^-	-148.7	51.9	490	*

Table 2.3: $^{31}P\{^1H\}$ NMR data for six-membered ring cyclic triphosphenium ions (**6a-9a**) (* - previously unreported)

A new unsymmetrical cyclic triphosphenium ion was also synthesised from the diphosphane dpdtbpf, as various salts (Figure 2.2).

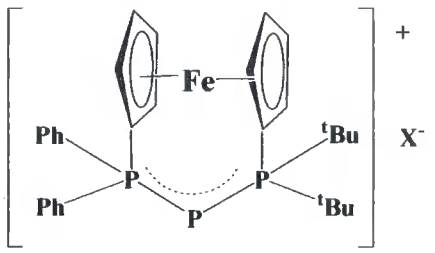


Figure 2.2:The unsymmetrical cyclic triphosphenium ion synthesised from dpdtbpf (**10a-c**)

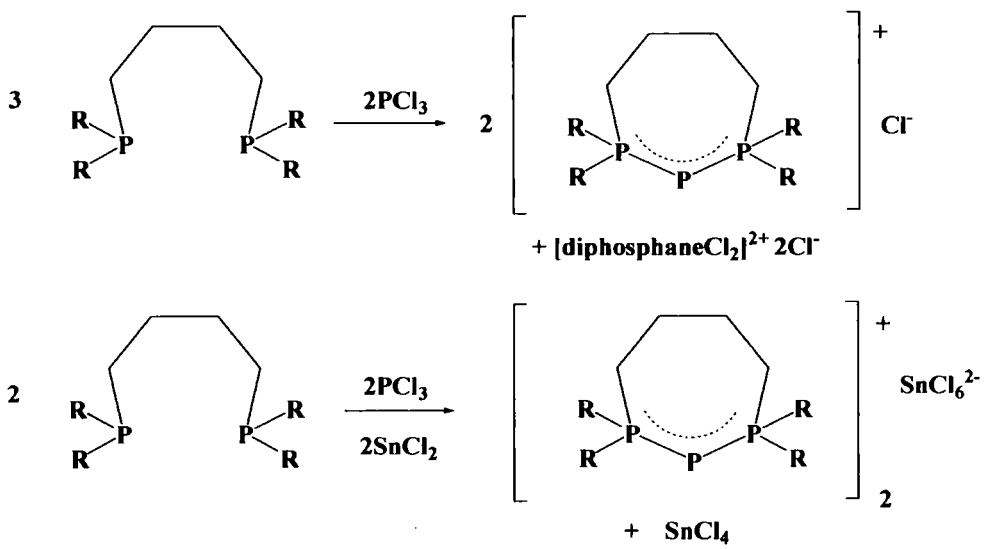
Instead of the unusual A_2B pattern we see that of ABX in the $^{31}P\{^1H\}$ NMR spectrum. The large $^1J_{P\text{-}P}$ values and shift of P_A are consistent with those previously reported for other cyclic triphosphenium ion containing a ferrocene backbone (Table 2.4).[12]

Compound No.	X=	δP_A, ppm	δP_B, ppm	δP_C, ppm	$^1J_{PA\text{-}PB}$, Hz	$^1J_{PA\text{-}PC}$, Hz	$^2J_{PB\text{-}PC}$, Hz
10a	Cl	-139.4	65.6	37.0	531	549	37
10b	$SnCl_6^{2-}$	-137.9	65.8	37.5	525	546	37
10c	$AlCl_4^-$	-139.3	65.5	37.2	529	548	37

Table 2.4: $^{31}P\{^1H\}$ NMR data for the six-membered ring cyclic triphosphenium ion synthesised from dpdtbpf (**10a-c**)

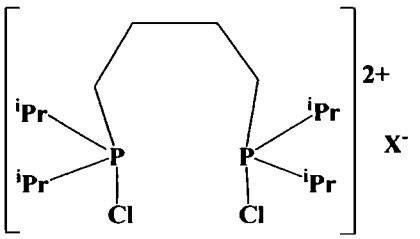
2.5 Synthesis of some seven-membered ring cyclic triphosphenium ions from dcypb, dppb and dippb

These heterocycles were synthesised both as a chloride salt and a hexachlorostannate salt (Scheme 2.5). The cyclic triphosphenium ions synthesised from dcypb and dppb, were obtained both as their chloride, **11a** and **12a**, and hexachlorostannate salts, **11b** and **12b**. The $^{31}P\{^{1}H\}$ NMR data for the chloride salts showed the expected doublet and triplet resonances with a large magnitude of $^{1}J_{P\text{-}P}$ (Table 2.5).[6, 12] The hexachlorostannate salts showed similar NMR parameters to the chloride. In the formation of the dcypb cyclic triphosphenium ion as its chloride salt, a singlet (107.1 ppm) was also observed in the $^{31}P\{^{1}H\}$ NMR spectrum and was assigned to $[dcypb.Cl_2]^{2+}2Cl^-$ (**11ax**).



Scheme 2.5: Synthesis of seven-membered ring cyclic triphosphenium ions (**11a-13b**)

The synthesis of the previously unreported dippb cyclic triphosphenium ion was also carried out to form both the chloride (**13a**) and hexachlorostannate (**13b**) salt. In each case a doublet and triplet resonance with a large value of $^{1}J_{P\text{-}P}$ were observed which were consistent with data reported for other cyclic triphosphenium ions (Table 2.5).[2-13] In the solution spectra of both the chloride and hexachlorostannate salt, an extra resonance was also visible (s, 116.5 ppm, **13ax**; s, 114.8 ppm, **13bx**) which was assigned to chlorinated dippb (Figure 2.3).



X = 2Cl⁻ **13ax**

X = $SnCl_6^{2-}$ **13bx**

Figure 2.3: By-product of the synthesis of the dippb cyclic triphosphenium ion

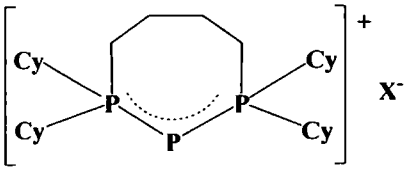
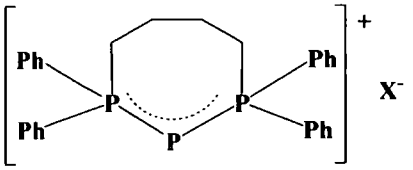
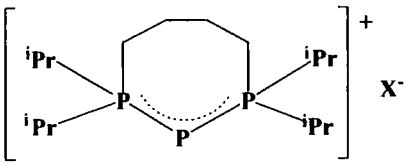
Cyclic triphosphenium ion		X=	δP_A, ppm	δP_B, ppm	$^1J_{P-P}$, Hz	Reference
	**11a**	Cl	-261.7	48.0	474	12
	11b	$SnCl_6^{2-}$	-260.8	48.1	476	12
	**12a**	Cl	211.1	34.3	454	6
	12b	$SnCl_6^{2-}$	-211.2	34.0	455	6
	**13a**	Cl	-264.8	55.9	474	-
	13b	$SnCl_6^{2-}$	-262.5	55.5	480	-

Table 2.5: $^{31}P\{^1H\}$ NMR data for seven membered cyclic triphosphenium ions (**11a – 13b**)

2.6 Conclusions

This chapter details the synthetic routes for the preparation of a family of cyclic triphosphenium ions. The synthesis of some known cyclic triphosphenium ions was carried out, along with the synthesis of some new heterocycles. The one pot synthesis gave the desired cyclic triphosphenium ions as the major product of the reactions, with only a small amount of [diphosphane.2Cl$^-$]$^{2+}$ X$^-$ in the case of depe (**2ax** and **2cx**), dppe (**4ax, 4bx** and **4dx**), depp (**6ax-cx** and **6ex**), dcypp (**7ax** and **7cx**), dippp (**8ax** and **8cx**), dcypb (**11 ax**) and dippb (**13ax-bx**). The cyclic triphosphenium ions themselves were readily characterised using $^{31}P\{^1H\}$ NMR spectroscopy, as they exhibit a doublet and triplet (at low frequency) with a large $^1J_{P\text{-}P}$.

This range of cyclic triphosphenium ions was prepared so that a thorough study into the reactivity and coordination of cyclic triphosphenium ions could be carried out. By having a variety of different ring sizes, with different backbones and with different substituents on the outer, four-coordinate P atoms, we could investigate the effect on the reactivity of these novel heterocycles and also their coordination to metal centres.

2.7 Experimental

All manipulations were carried out in a nitrogen-filled glove box or under an atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk and cannula techniques as these compounds are sensitive to both air and moisture. All NMR-scale reactions were conducted using Young's tap valve NMR tubes. The NMR solvent, $CDCl_3$, was dried over P_2O_5, distilled and degassed prior to use.

$^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 300, Mercury 400 or Inova 500 Fourier-transform spectrometer at 121.40, 161.91 or 202.3 MHz respectively. Chemical shifts were referenced to external aqueous 85 % H_3PO_4 (^{31}P), to residual protio impurities

in the deuterated solvent (^{1}H - $CDCl_3$, 7.27 (s)), or to the ^{13}C shift of the solvent (^{13}C - $CDCl_3$ 77.2 (d)). Chemical shifts are reported in ppm and coupling constants in Hz.

Example reactions:

Synthesis of the dppe cyclic triphosphenium ion

dppe (0.0430 g, 0.11 mmol) was dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.006 mL, 0.07 mmol) was then added and a $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after mixing.

Synthesis of the dppe cyclic triphosphenium ion using $SnCl_2$

dppe (0.0260 g, 0.07 mmol) and $SnCl_2$ (0.0133 g, 0.07 mmol) were dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.006 mL, 0.07 mmol) was then added and a $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after mixing.

Synthesis of the dppe cyclic triphosphenium ion using $AlCl_3$

dppe (0.0677 g, 0.17 mmol) and $AlCl_3$ (0.0227 g, 0.17 mmol) were dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.015 mL, 0.17 mmol) was then added and a $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after mixing.

General information:

For each cyclic triphosphenium ion synthesised any residual PCl_3 was removed *in vacuo*, although on occasion not all the PCl_3 was removed. Attempts to isolate the cyclic triphosphenium ions through crystallisation (by slow evaporation of solvent in an inert atmosphere or by layering with hexane or pentane) were unsuccessful. The cyclic triphosphenium ions were used without further purification in subsequent reactions.

Quantities of reagents used:

Diphosphane	Compound	Quantity of diphosphane used		Quantity of PX_3 used		Quantity of $SnCl_2$ used		Quantity of $AlCl_3$ used	
		g	mmol	mL	mmol	g	mmol	g	mmol
dcypm	**1a**	0.0248	0.06	0.010	0.11	-	-	-	-
dcypm	**1b**	0.0254	0.06	0.010	0.11	0.0198	0.10	-	-
depe	**2a**	0.0587	0.28	0.017	0.19	-	-	-	-
depe	**2b**	0.0263	0.13	0.011	0.13	0.0246	0.13	-	-
depe	**2c**	0.0745	0.36	0.025	0.26	-	-	-	-
dcype	**3a**	0.0060	0.01	0.010	0.11	-	-	-	-
dcype	**3b**	0.0400	0.10	0.008	0.10	0.0180	0.10	-	-
dppe	**4a**	0.0430	0.11	0.006	0.07	-	-	-	-
dppe	**4a**	0.0260	0.07	0.006	0.07	0.0133	0.07	-	-
dppe	**4d**	0.0677	0.17	0.015	0.17	-	-	0.0227	0.17
dmpe	**5a**	0.0133	0.09	0.005	0.06	-	-	-	-
depp	**6a**	0.0415	0.19	0.010	0.11	-	-	-	-
depp	**6b**	0.0093	0.04	0.003	0.04	0.0076	0.04	-	-
depp	**6c**	0.0444	0.20	0.010	0.11	-	-	-	-
depp	**6e**	0.0419	0.19	0.054	0.13	-	-	-	-
dcypp	**7a**	0.0250	0.05	0.005	0.05	-	-	-	-
dcypp	**7b**	0.0395	0.09	0.008	0.09	0.0170	0.09	-	-
dcypp	**7c**	0.0543	0.12	0.010	0.11	-	-	-	-
dippp	**8a**	0.0448	0.16	0.010	0.11	-	-	-	-
dippp	**8b**	0.0136	0.05	0.004	0.05	0.0100	0.05	-	-
dippp	**8c**	0.0396	0.14	0.010	0.11	-	-	-	-
dippf	**9a**	0.0508	0.12	0.010	0.11	-	-	-	-
dpdtbpf	**10a**	0.0361	0.08	0.010	0.11	-	-	-	-
dpdtbpf	**10b**	0.0140	0.03	0.003	0.03	0.0060	0.03	-	-

Quantities of reagents continued …

Diphosphane	Compound	Quantity of diphosphane used		Quantity of PX_3 used		Quantity of $SnCl_2$ used		Quantity of $AlCl_3$ used	
		g	mmol	mL	mmol	g	mmol	g	mmol
dpdtbpf	**10c**	0.0284	0.06	0.007	0.06	-	-	0.0085	0.06
dcypb	**11a**	0.0569	0.11	0.010	0.11	-	-	-	-
dcypb	**11b**	0.0329	0.07	0.006	0.07	0.0330	0.07	-	-
dppb	**12a**	0.1360	0.32	0.020	0.23	-	-	-	-
dppb	**12b**	0.0936	0.25	0.020	0.22	0.0938	0.49	-	-
dippb	**13a**	0.0286	0.10	0.010	0.11	-	-	-	-
dippb	**13b**	0.0235	0.08	0.007	0.08	0.0152	0.08	-	-

Additional analysis:

NMR for 2a:

^{1}H (399.9 MHz, $CDCl_3$): δ 0.99 (dt, $^3J_{P\text{-}H}$ = 20.0 Hz, ^2J = 8 Hz, 12H, $PCH_2C\underline{H}_3$); 2.02 (m, 8H, $PC\underline{H}_2CH_3$), 2.72 (m, $^3J_{P\text{-}H}$ = 13 Hz , 4H, -$P(C\underline{H}_2)_2P$)

NMR for 2b:

^{1}H (399.9 MHz, $CDCl_3$): δ 1.15 (dt, $^3J_{P\text{-}H}$ = 20.0 Hz, ^2J = 8 Hz, 12H, $PCH_2C\underline{H}_3$); 2.12 (m, 8H, $PC\underline{H}_2CH_3$), 2.83 (m, $^3J_{P\text{-}H}$ = 13 Hz , 4H, -$P(C\underline{H}_2)_2P$

^{13}C {^{1}H} (125.67 MHz, $CDCl_3$): δ 7.3 (s, $PCH_2\underline{C}H_3$), 21.9 (m, $^1J_{CP}$ = 53 Hz, $P(\underline{C}H_2)_2P$), 24.3 (m, $^1J_{CP}$ = 37 Hz, $P(\underline{C}H_2)_2P$)

NMR for 4a:

^{1}H (399.9 MHz, $CDCl_3$): δ 3.70 (d, $^2J_{P\text{-}H}$ = 16.4 Hz, 4H, P-$(C\underline{H}_2)_2$-P); 7.46 – 7.81 (*o-/m-/p-*Ph$\underline{H}$)

NMR for 4b:

^{1}H (299.9 MHz, $CDCl_3$): δ 3.70 (d, $^{2}J_{P\text{-}H}$ = 16.4 Hz, 4H, P-($C\underline{H}_2$)$_2$-P); 7.46 – 7.81 (*o*-/*m*-/*p*-Ph$\underline{H}$)

NMR for 4c:

^{1}H (399.9 MHz, $CDCl_3$): δ 3.33 (d, $^{2}J_{P\text{-}H}$ = 15 Hz, 4H, P-($C\underline{H}_2$)$_2$-P); 7.55 – 7.79 (20H, *o*-/*m*-/*p*-Ph$\underline{H}$)

NMR for 5a:

^{1}H (399.9 MHz, $CDCl_3$): δ 2.08 (m, $^{2}J_{P\text{-}H}$ = 13 Hz, 12H, P$C\underline{H}_3$); 3.23(d, $^{2}J_{P\text{-}H}$ = 13 Hz, 4H, P($C\underline{H}_2$)$_2$P)

^{13}C {^{1}H} (125.67 MHz, $CDCl_3$): δ 18.4 (d, $^{1}J_{C\text{-}P}$ = 57 Hz, P$\underline{C}H_3$), 27.9 (d, $^{1}J_{CP}$ = 45 Hz, P($\underline{C}H_2$)$_2$P)

NMR for 6b:

^{1}H (399.9 MHz, $CDCl_3$): δ 1.23 (m, $^{2}J_{P\text{-}H}$ = 16.4 Hz, 12H, P-CH_2-$C\underline{H}_3$), δ 1.23 (m, $^{2}J_{P\text{-}H}$ = 16.4 Hz, 8H, P-($C\underline{H}_2$-CH_2-$C\underline{H}_2$-P); δ 2.22 (m, 8H, P-$C\underline{H}_2$-CH_3), δ 2.22 (m, 8H, P-$C\underline{H}_2$-CH_3)

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Chapter 3:

Investigation into the Mechanism of Formation of Cyclic Triphosphenium Ions

3.1 Introduction

Since the first cyclic triphosphenium ion was reported back in 1982,[1] many different ring systems have been synthesised, varying in ring size, backbone and substituents on the two outer phosphorus atoms.[2-12] However, the mechanism of formation of these heterocycles had not yet been established.

Due to the formal conversion of the central phosphorus from P(III) to P(I), a redox step is necessary. It has been determined that a powerful reducing agent is not essential, as the cyclic triphosphenium ions can be synthesised from just a phosphorus trihalide and a diphosphane.[6-9,11-12] In this case the diphosphane itself acts as the reducing agent, which leads to the formation of the diphosphane tetrahalide, if the reagents are taken in the correct proportion.

For the synthesis of some cyclic triphosphenium ions containing ethyl substituents, a second doublet and triplet were sometimes observed in the $^{31}P\{^{1}H\}$ NMR spectra recorded

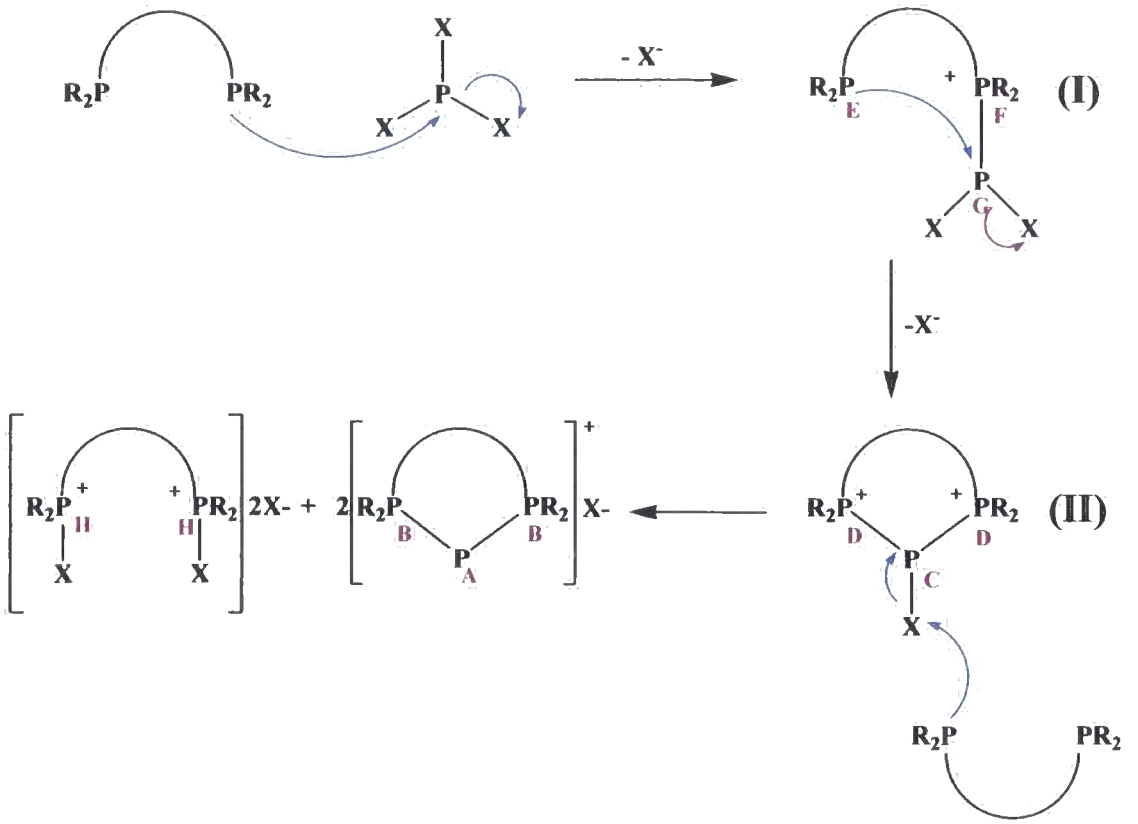
approximately 15 minutes after reactant mixing. However, as the reaction proceeded these peaks disappeared, suggesting that we were detecting an intermediate in the formation of the cyclic triphosphenium ions. This prompted us to undertake a more detailed study to investigate this further.

3.2 Detection of transient intermediates in the synthesis of the depp cyclic triphosphenium ion using PX_3 (X = Cl or Br)

A reaction between depp and PCl_3 at room temperature showed signals in the $^{31}P\{^1H\}$ NMR spectrum assignable to an acyclic intermediate and a cyclic intermediate, along with those corresponding to the cyclic triphosphenium ion (**6a**) 15 minutes after the addition of PCl_3. One doublet and triplet (30.7 ppm and –254.1 ppm, $^1J_{PP}$ = 417 Hz, respectively) correspond to the depp cyclic triphosphenium ion (**6a**).[13] The second doublet and triplet (43.0 ppm and -102.6 ppm $^1J_{P\text{-}P}$ = 351 Hz, respectively) were assigned to a cyclic intermediate (**6aII**) with a Cl still bound to the central phosphorus atom (Scheme 3.1).

Also evident were two doublets (57.2 ppm and -48.3 ppm, $^1J_{P\text{-}P}$ = 278 Hz) which were assigned to P_G and P_F in the acylic intermediate (**6aI**) and a singlet (17.7 ppm) corresponding to the 'free' end of the diphosphane, P_E (Scheme 3.1). The coupling constant for the doublets is typical of $^1J_{P\text{-}P}$ for this type of compound.[14]

The proposed mechanism for the formation of cyclic triphosphenium ions is shown in Scheme 3.1. The first step involves a reaction between the diphosphane and PX_3 to form an acyclic precursor (**I**). This is followed by cyclisation and the loss of a halide ion to afford a dication with one halogen atom on the central phosphorus (**II**). The final step involves the removal of the bound halogen by another equivalent of depp to form the cyclic triphosphenium ion and diphosphane tetrahalide (**6ax**).



Scheme 3.1: Proposed mechanism of formation of the cyclic triphosphenium ions

When carrying out the synthesis of the depp cyclic triphosphenium ion as its hexachlorostannate salt (**6b**), similar results were obtained with the only difference being a large shift change for P_H, which can be attributed to the change in counter-ion from $2Cl^-$ to $SnCl_6^{2-}$ or $2SnCl_5^-$ (Table 3.1). Other halogenophosphonium species have shown similar changes in chemical shift with differing counter-ions.[15,16]

In an attempt to trap the intermediates (**6aI** and **6aII**), the reaction was carried out at 0°C. However the $^{31}P\{^1H\}$ NMR spectrum recorded only five minutes after mixing gave similar results to those obtained from the room temperature reaction, except that the doublet and triplet corresponding to the cyclic triphosphenium ion were very weak (Table 3.1). The reaction was monitored as the solution warmed to room temperature, and a change in intensity of the signals was observed, as expected.

Compound Number	P atom	Room Temp.		Room Temp. + $SnCl_2$		0°C	
		δ, ppm	$^1J_{P-P}$, Hz	δ, ppm	$^1J_{P-P}$, Hz	δ, ppm	$^1J_{P-P}$, Hz
6aI	P_E	17.7 s	-	17.7 s	-	17.8 s	-
6aI	P_F	-48.3 d	278	-48.3 d	276	-48.3 d	276
6aI	P_G	57.2 d	278	57.4 d	278	57.5 d	277
6aII	P_C	-102.6 t	351	-103.5 t	352	-102.2 t	351
6aII	P_D	43.0 d	351	42.8d	352	42.9d	352
6a	P_A	-254.1 t	417	-252.3 t	419	-254.5 t	416
6a	P_B	30.7 d	417	30.5 d	418	31.1d	416
6x	P_H	109.0 s	-	79.6 s	-	109.0 s	-

Table 3.1: $^{31}P\{^1H\}$ NMR spectroscopic data for the depp-PCl_3 reaction

The same reaction was also carried out at -78°C, in a further attempt to trap the acylic intermediate (**6aI**). The spectrometer probe was pre-cooled to -60°C and $^{31}P\{^1H\}$ NMR spectra were recorded at 15 minute intervals. The reaction proceeded very slowly at -60°C so the temperature of the probe was also increased at intervals. Figure 3.1 shows a stackplot of the $^{31}P\{^1H\}$ NMR data obtained. The spectrum recorded 30 minutes after mixing showed only very weak signals corresponding to the cyclic triphosphenium ion, **6a**. The major components were the depp starting material and the cyclic intermediate, **6aII**. As both time and temperature increased, these signals became less intense and the doublet and triplet corresponding to the cyclic triphosphenium ion increased in intensity. After approximately 5 hours there were no signals corresponding to either the acylic or cyclic intermediates in the $^{31}P\{^1H\}$ NMR spectrum, only the doublet and triplet corresponding to the cyclic triphosphenium ion itself, the diphosphane tetrachloride, **6ax** (s, 109 ppm), and a peak corresponding to the diphosphane dioxide (impurity in starting material).

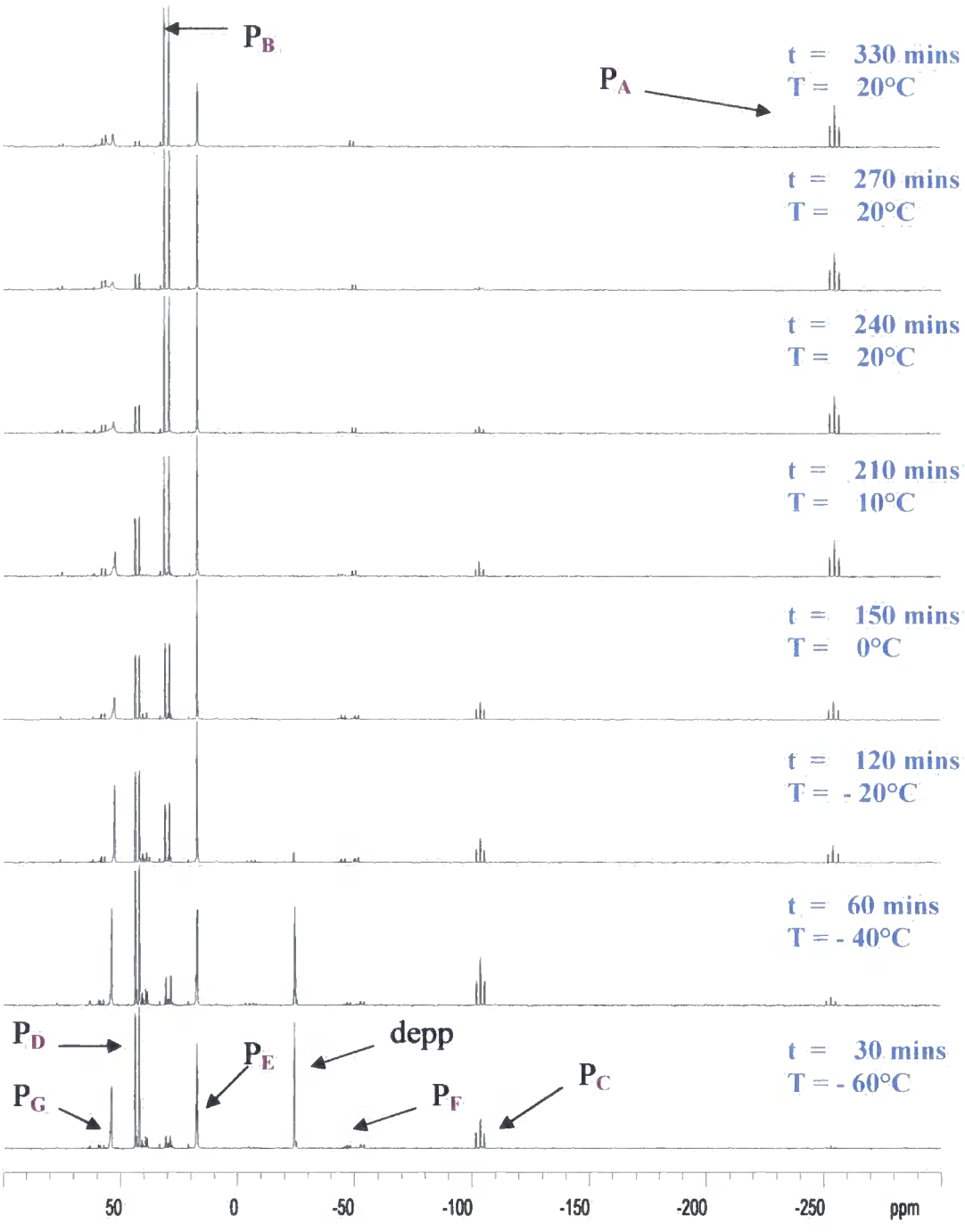


Figure 3.1: Stackplot of $^{31}P\{^{1}H\}$ NMR spectra for the reaction of depp and PCl_3. The addition of PCl_3 is taken as t = 0

To confirm the presence of a halogen on the central phosphorus atom, the reaction was carried out using PBr_3 instead of PCl_3. The cyclic intermediate would then contain a Br on the central phosphorus atom and hence cause a change in shift for the triplet corresponding to P_C the $^{31}P\{^1H\}$ NMR spectrum. Resonances corresponding to both the triphosphenium ion and its cyclic precursor were observed (Table 3.2). As expected, there was a significant change in shift for the triplet corresponding to P_C of the cyclic intermediate, to which the halogen is directly attached, when the halogen was changed from Cl to Br (-102.6 ppm to -85.1 ppm).

Compound Number	P atom	δ, ppm	$^1J_{P\text{-}P}$, Hz
6cII	P_C	-85.1 t	350
6cII	P_D	34.3 d	350
6c	P_A	-253.3 t	417
6c	P_B	30.6 d	417
6cx	P_H	94.9 s	-

Table 3.2: $^{31}P\{^1H\}$ NMR spectroscopic data for the depp-PBr_3 reaction

In an analogous reaction using PI_3 to synthesis the depp cyclic triphosphenium ion as its iodide salt (**6e**), the only peaks in the $^{31}P\{^1H\}$ NMR spectrum were those corresponding to the acylic intermediate (**6eI**), the depp cyclic triphosphenium ion (**6e**) and the diphosphane tetraiodide (**6ex**) (Table 3.3). There was no evidence of the cyclic precursor. The reaction was monitored using $^{31}P\{^1H\}$ NMR spectroscopy, and this showed that the resonances corresponding to the acylic intermediate (P_E, P_F and P_G) disappeared over time.

Since I^- is a better leaving group than Cl^-,[17] it can be removed much more quickly by the diphosphane. It is therefore conceivable that the cyclic intermediate would not be visible in the $^{31}P\{^1H\}$ NMR spectrum, for as soon as it forms, the I^- would be removed to leave just the depp cyclic triphosphenium ion as its iodide salt, **6e**.

Compound Number	P atom	δ, ppm	$^1J_{P-P}$, Hz
6eI	P_E	16.2 s	-
6eI	P_F	-47.9 d	278
6eI	P_G	57.2 d	278
6e	P_A	-252.1 t	418
6e	P_B	30.6 d	418
6ex	P_H	104.3 s	-

Table 3.3: $^{31}P\{^1H\}$ NMR spectroscopic data for the depp-PI_3 reactions

3.3 Detection of transient intermediates in the synthesis of the depe cyclic triphosphenium ion using PX_3 (X = Cl or Br)

It was proposed that the formation of the depe cyclic triphosphenium ion would also proceed *via* the same mechanism (Scheme 3.1). For the reaction between depe and PCl_3 at room temperature, signals corresponding to the cyclic precursor (**2aII**) were identified in the $^{31}P\{^1H\}$ NMR spectrum (Table 3.4). However signals corresponding to the acyclic intermediate were not observed. Also present were signals that could be assigned to the cyclic triphosphenium ion (**2a**) (t, -269.0 ppm, d, 81.5 ppm, $^1J_{P-P}$ = 441 Hz)[7] and the diphosphane tetrachloride (**2ax**) (109.9 ppm).

The reaction between depe and PCl_3 was also carried out at 0°C, but 30 minutes after the addition of PCl_3 the $^{31}P\{^1H\}$ NMR spectrum showed only peaks corresponding to the cyclic triphosphenium ion (**2a**), and none corresponding to either the acyclic or cyclic intermediate. Similarly, when carrying out the reaction in the presence of $SnCl_2$, the only product was the cyclic triphosphenium ion (**2c**) and there was no evidence of any intermediates in the $^{31}P\{^1H\}$ NMR spectrum.

The reaction between depe and PBr_3 at room temperature again showed the presence of the cyclic intermediate (**2cII**), cyclic triphosphenium ion (**2c**) and also the diphosphane

tetrabromide (**2cx**), and no signals corresponding to the acyclic intermediate were observed (Table 3.4). This could be due to the acyclic intermediates being in low concentration and/or the reaction proceeding too quickly.

Compound Number	P atom	X = Cl		X = Br	
		δ, ppm	$^1J_{P-P}$, Hz	δ, ppm	$^1J_{P-P}$, Hz
2cII	P_C	-96.2 t	369	-82.2 t	365
2cII	P_D	86.2 d	369	79.8 d	365
2c	P_A	-269.0 t	441	-268.8 t	441
2c	P_B	81.5 d	441	81.4 d	441
2cx	P_H	109.9 s	-	95.2 s	-

Table 3.4: $^{31}P\{^1H\}$ NMR spectroscopic data for the depe-PX_3 reactions

In the $^{31}P\{^1H\}$ NMR spectrum recorded for the reaction between depe and PBr_3, as expected, there was a significant change in shift for the triplet corresponding to P_C of the cyclic intermediate (**2cII**), compared with δP_C for the chloride analogue (**2dII**) (-96.2 ppm to -82.2 ppm).

3.4 Detection of transient intermediates in the synthesis of the dippp cyclic triphosphenium ion using PX_3 (X = Cl or Br)

Initially the reaction between dippp and PCl_3 was undertaken at room temperature. A $^{31}P\{^1H\}$ NMR spectrum was recorded as soon as possible after the mixing, and showed the presence of both the acyclic (**8aI**) and cyclic intermediates (**8aII**), although the signal intensities corresponding to the acyclic precursor were very low (Scheme 3.1).

This reaction was also carried out at 0°C to try and trap the intermediates. The $^{31}P\{^1H\}$ NMR spectrum showed much more intense signals corresponding to the acyclic precursor (**8aI**). $^{31}P\{^1H\}$ NMR spectra were recorded at intervals as the solution was allowed to

warm to room temperature. The initial $^{31}P\{^{1}H\}$ NMR spectrum showed mainly resonances corresponding to both the acyclic (**8aI**) and cyclic intermediates (**8aII**), but as time increased and the solution was allowed to warm up, these decreased in intensity and a new doublet and triplet appeared, corresponding to the cyclic triphosphenium ion (**8a**) (Figure 3.2). The NMR data are listed in Table 3.5.

Compound Number	P atom	Room Temperature		0°C	
		δ, ppm	$^{1}J_{P-P}$, Hz	δ, ppm	$^{1}J_{P-P}$, Hz
8aI	P_E	-6.4 s	-	-5.8 s	-
8aI	P_F	-26.7 d	303	-26.7 d	303
8aI	P_G	60.3 d	303	60.3 d	303
8aII	P_C	-81.0 t	394	-80.9 t	393
8aII	P_D	50.1 d	394	50.1 d	393
8a	P_A	-299.6 t	458	-299.9 t	458
8a	P_B	44.7 d	458	44.8 d	458
8ax	P_H	115.2 s	-	114.8 s	-

Table 3.5: $^{31}P\{^{1}H\}$ NMR spectroscopic data for the dippp-PCl_3 reactions

The reaction between dippp and PCl_3 in the presence of $SnCl_2$, showed no evidence of any intermediates in the $^{31}P\{^{1}H\}$ NMR spectrum.

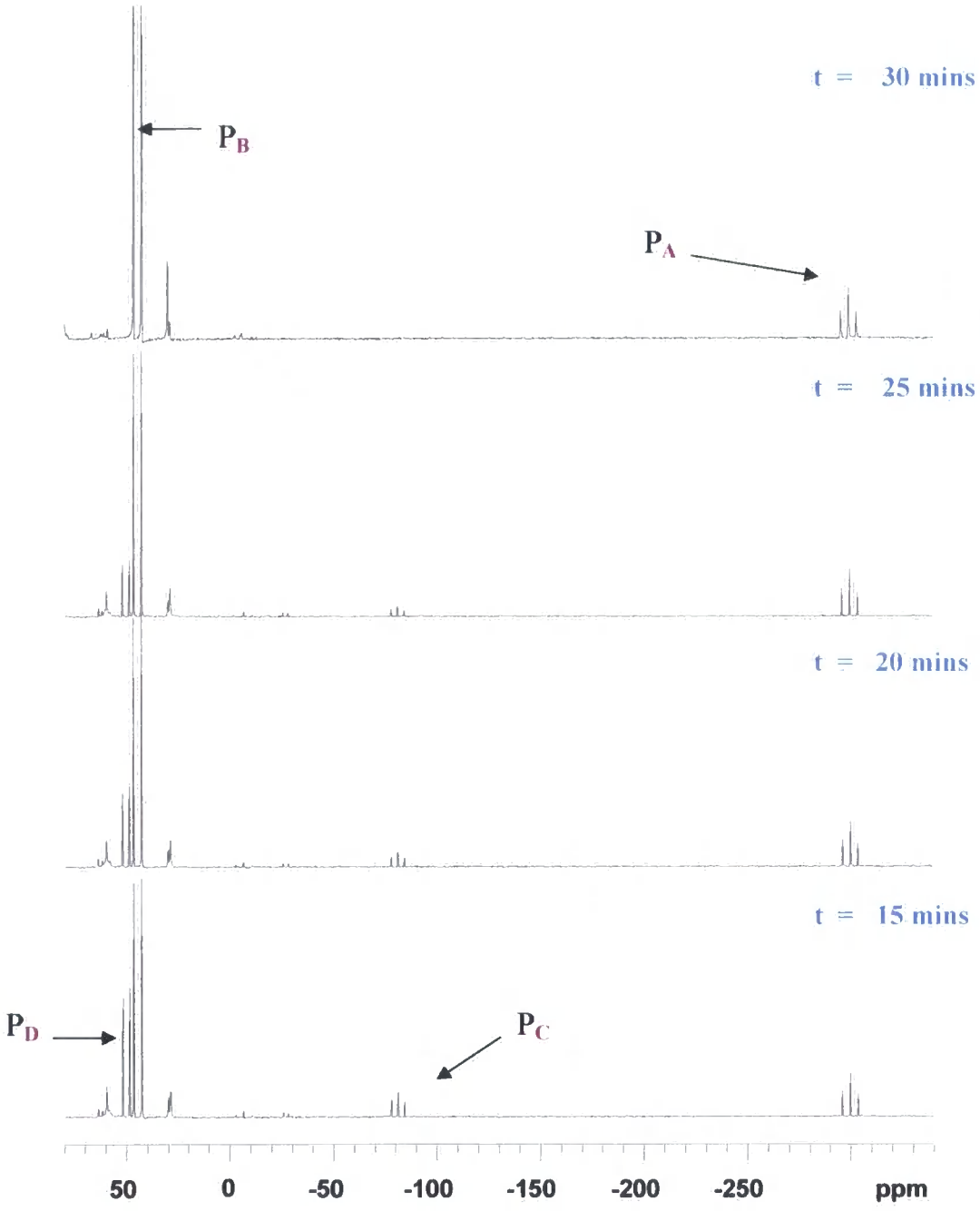


Figure 3.2: Stackplot of $^{31}P\{^{1}H\}$ NMR spectra for the reaction of dippp and PCl_3. Reaction carried out at 0°C. The addition of PCl_3 is taken as t = 0

3.5 Detection of transient intermediates in the synthesis of the dcypp cyclic triphosphenium ion using PX_3 (X = Cl or Br)

The reaction between dcypp and PCl_3 to synthesise the cyclic triphosphenium ion as a chloride salt was carried out at -78°C, again in the hope of observing the acyclic intermediate (Scheme 3.1). The spectrometer probe was pre-cooled to -60°C before the sample was prepared. After the initial spectrum had been recorded, the solution was allowed to warm up gradually and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 15 minute intervals with the results obtained being shown in Figure 3.3 and Table 3.6.

Compound Number	P atom	δ, ppm	$^{1}J_{P\text{-}P}$, Hz
7aI	P_E	-5.7 s	-
7aI	P_F	-33.8 d	301
7aI	P_G	48.7 d	298
7aII	P_C	-84.9 t	395
7aII	P_D	41.8 d	395
7a	P_A	-297.4 t	452
7a	P_B	36.5 d	453
7ax	P_H	104.3 s	-

Table 3.6: $^{31}P\{^{1}H\}$ NMR spectroscopic data for the dcypp-PCl_3 reaction

Figure 3.3: Stackplot of $^{31}P\{^{1}H\}$ NMR spectra for the reaction of dcypp and PCl_3. The addition of PCl_3 is taken as t = 0

The spectrum recorded at -60 °C, 20 minutes after mixing showed only weak signals corresponding to the cyclic triphosphenium ion (**7a**). The main component was the cyclic intermediate (**7aII**). As both time and temperature increased, these resonances became less intense and the doublet and triplet corresponding to the cyclic triphosphenium ion increased in intensity. After approximately 5 hours there were no resonances corresponding to either the acyclic, or cyclic intermediate in the $^{31}P\{^{1}H\}$ NMR spectrum. Only the doublet and triplet corresponding to the cyclic triphosphenium ion itself, the diphosphane tetrachloride (**7ax**) (s, 104.3 ppm) and a peak corresponding to the diphosphane dioxide were apparent (impurity present in the starting material).

The analogous reaction to form the dcypp cyclic triphosphenium ion as its bromide salt was also carried out at -78°C. This reaction proceeded much faster, with the intermediates not observed even in the first $^{31}P\{^{1}H\}$ NMR spectrum run at -50°C. The only apparent signals corresponded to the cyclic triphosphenium ion (**7c**) (t, -297.7 ppm, d, 36.7 ppm, $^{1}J_{P\text{-}P} = 450$ Hz) and the diphosphane tetrabromide (**7cx**) (s, 97.3 ppm).

3.6 Attempts to detect transient intermediates in the synthesis of the dppe, dcype, dippb and dcypb cyclic triphosphenium ions using PX_3 (X = Cl or Br)

Attempts to observe the intermediates in the synthesis of the dppe, dcype, dippb and dcypb cyclic triphosphenium ions were carried out at -78°C. For the dppe reaction, the $^{31}P\{^{1}H\}$ NMR spectrum showed no evidence of any intermediates, only peaks corresponding to the cyclic triphosphenium ion (**4a**) (t, -229.4 ppm, d, 65.0ppm, $^{1}J_{P\text{-}P} = 450$Hz).[6] The reaction appears to proceed too rapidly, even at low temperatures, for the intermediates to be observed.

In the reactions between dcype, dippb and dcypb with PCl_3, initial $^{31}P\{^{1}H\}$ NMR spectra showed that the reaction had almost gone to completion, even at -78°C. However, a small doublet resonance was observed, along with a broad resonance at low frequency in each spectrum (Table 3.7). The chemical shift and coupling constant consistent for the doublet

in each case, was consistent with those for observed for P_D in the depp, depe, dcypp and dippp systems. The broad resonance present in each spectrum is in the region where the triplet corresponding to P_C would be expected. However without resolving the broad resonances, these cannot be assigned conclusively to the cyclic intermediates in the formation of the cyclic triphosphenium ions in question.

diphosphane	PX_3, X=	$\delta P_{doublet}$, ppm	$^1J_{P-P}$, Hz	$\delta P_{broad\ signal}$, ppm
dcype	Cl	77.0	353	~ -70
dippb	Cl	68.9	414	~ -64
dcypb	Cl	62.4	447	~ -61
dcypb	Br	30.5	436	~ -103

Table 3.7: $^{31}P\{^1H\}$ NMR spectroscopic data for the dcype, dippb and dcypb-PCl_3 reactions at -78°C

3.7 Conclusions

Along with the expected acyclic initial product (**I**) from the reaction of PX_3 with a diphosphane, this ^{31}P NMR spectroscopic study has also shown that there is a second intermediate, a cyclic precursor (**II**), containing a halogen atom still bound to the central phosphorus atom (Scheme 3.1). The $^{31}P\{^1H\}$ NMR data clearly show that this is a halogen atom, as by changing the phosphorus trihalide from PCl_3 to PBr_3, we observed a significant change in the chemical shift of the triplet corresponding to the central phosphorus, as expected when changing from a P-Cl to P-Br.

When using PI_3 we only observed the acyclic intermediate and the cyclic triphosphenium ion in the $^{31}P\{^1H\}$ NMR spectrum. This is most probably due to the P-I bond being weaker than both P-Cl and P-Br, so that I^- can be lost more readily. This means that I^- can be

removed immediately after cyclisation to form the second intermediate, to leave the cyclic triphosphenium ion.

This study has also shown that the rate of reaction to form a cyclic triphosphenium ion follows the order $PI_3 > PBr_3 > PCl_3$. This can also be attributed to the relative P-X bond strengths, with P-I being the weakest and P-Cl being the strongest, meaning that I^- is a better leaving group than Br^- or Cl^-.

No intermediates in the formation of the cyclic triphosphenium ion were observed, even at low temperature, when using the diphosphane dppe. This behaviour must be due to electronic effects, as steric effects can be ruled out because intermediates were observed using the diphosphane dcypp which has cyclohexyl substituents that are as bulky as phenyl substituents. It is possible that phenyl substituents could help with the electron delocalisation recognised in cyclic triphosphenium ions and this provides the necessary driving force for rapid formation of the cyclic triphosphenium ion. It is also possible that the alkyl groups help to stabilise the phosphonium cations, so prolonging their lifetime in solution.

Although the transient intermediates have only been observed for the depp, depe, dippp and dcypp systems with PCl_3 and in some cases PBr_3, it is reasonable to propose that this same mechanism is followed in the formation of all cyclic triphosphenium ions using PCl_3, PBr_3 or PI_3 (Scheme 3.1).

3.8 Experimental

All manipulations were carried out in a nitrogen-filled glove box or under an atmosphere of dry nitrogen or *in vacuo,* using standard Schlenk and cannula techniques as these compounds are sensitive to both air and moisture. All NMR-scale reactions were conducted using Young's tap valve NMR tubes. The NMR solvent, $CDCl_3$, was dried over P_2O_5, distilled and degassed prior to use. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian

Unity 300, Mercury 400 or Inova 500 Fourier-transform spectrometers at 121.40, 161.91 or 202.3 MHz respectively. The chemical shifts are referenced to external 85% H_3PO_4.

Example reactions:

Synthesis of the depp cyclic triphosphenium ion at room temperature

depp (0.0415 g; 0.19 mmol) was dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.01 mL, 0.11 mmol) was then added and a $^{31}P\{^1H\}$ NMR spectrum recorded as quickly as possible after mixing.

Synthesis of the depp cyclic triphosphenium ion using $SnCl_2$

depp (0.0230 g, 0.10 mmol) and $SnCl_2$ (0.0197 g, 0.10 mmol) were dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.01mL, 0.11 mmol) was then added and a $^{31}P\{^1H\}$ NMR spectrum recorded as quickly as possible after mixing.

Synthesis of the depp cyclic triphosphenium ion at 0°C

depp (0.0230 g, 0.10 mmol) was dissolved in 0.5 mL $CDCl_3$. A solution of PCl_3 (0.01 mL, 0.11 mmol) in 0.5 mL $CDCl_3$ was also prepared and both solutions were cooled in a Dewer containing crushed ice for 15 minutes. The two solutions were mixed and then transported to the spectrometer in the ice bath. A $^{31}P\{^1H\}$ NMR spectrum was recorded as quickly as possible after mixing.

Synthesis of the depp cyclic triphosphenium ion at -78°C

depp (0.0206 g, 0.09 mmol) was dissolved in 0.5 mL $CDCl_3$. A solution of PCl_3 (0.005 mL, 0.055 mmol) in 0.5 mL $CDCl_3$ was also prepared and both solution were cooled in a Dewer containing an acetone/solid carbon dioxide slush bath for 15 minutes. The two solutions were mixed and then transported to the spectrometer in the acetone/solid carbon dioxide slush bath. The spectrometer probe was pre-cooled to -60°C so that $^{31}P\{^1H\}$ NMR spectra could be recorded as quickly as possible after mixing.

Quantities of reagents used:

Diphosphane			PX_3			Mixing Temp./ °C
Compound	**g**	**mmol**	**X**	**mL**	**mmol**	
depp	0.0415	0.19	Cl	0.010	0.11	RT
depp[a]	0.0230	0.10	Cl	0.010	0.11	RT
depp	0.0188	0.09	Cl	0.005	0.06	0°C
depp	0.0206	0.09	Cl	0.005	0.06	-78°C
depp	0.0444	0.20	Br	0.010	0.11	RT
depp	0.0419	0.19	I	0.054	0.13	RT
depe	0.1132	0.55	Cl	0.030	0.34	RT
depe	0.0365	0.18	Cl	0.010	0.11	0°C
depe	0.0745	0.36	Br	0.025	0.26	RT
dippp	0.0448	0.16	Cl	0.010	0.11	RT
dippp	0.0397	0.14	Cl	0.010	0.11	0°C
dippp	0.0396	0.14	Br	0.010	0.11	RT
dcypp	0.0451	0.10	Cl	0.010	0.11	RT
dcypp	0.0543	0.12	Cl	0.010	0.11	-78°C
dcypp	0.0543	0.12	Br	0.010	0.11	-78°C
dppe	0.0236	0.06	Cl	0.004	0.04	-78°C
dcype	0.0310	0.07	Cl	0.010	0.11	-78°C
dippb	0.0605	0.21	Cl	0.010	0.11	-78°C
dippb	0.0396	0.14	Br	0.010	0.11	-78°C
dcypb	0.0569	0.13	Cl	0.010	0.11	-78°C
dcypb	0.0797	0.18	Br	0.010	0.11	-78°C

[a] 0.0197 g (0.10 mmol) of $SnCl_2$ was also added

3.9 References

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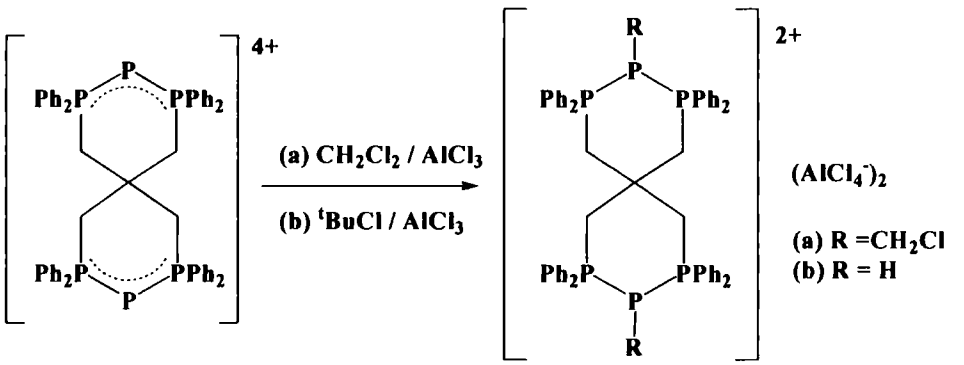
Chapter 4:

Synthesis and Characterisation of P-Alkyl and P-Aryl Derivatives of Cyclic Triphosphenium Ions

4.1 Introduction

Since the formal oxidation state of the central P atom of cyclic triphosphenium ions is P(I), oxidation reactions would be expected to take place at this centre. Indeed, Schmidpeter *et al.* demonstrated in 1985 that oxidation reactions at this centre could take place (Scheme 4.1).[1]



Scheme 4.1: First oxidation reactions carried out on a cyclic triphosphenium ion

Since then the formation of P-protonated derivatives using two different methods has been reported,[1-4] along with direct methylation of the central phosphorus atom using methyl triflate.[5, 6] Attempts to synthesise ethyl derivatives using this direct method proved to be unsuccessful when the substituents on the outer P atoms were phenyl.[5] However with ethyl groups on these P atoms, direct ethylation using ethyl triflate was possible for the depe and depp systems.[7]

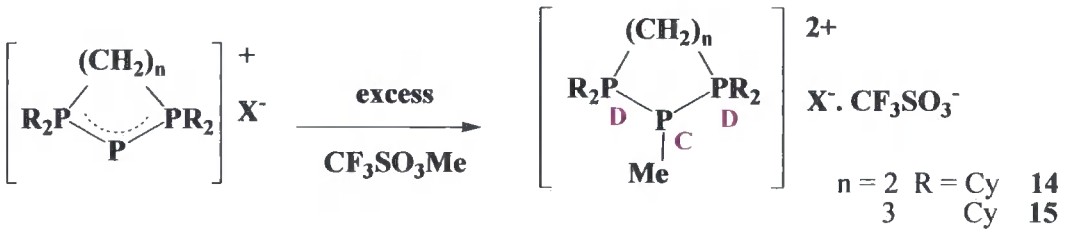
Schmidpeter *et al.* also described the synthesis of two other alkyl derivatives derived from the diphosphane dppe.[3] They involved the reaction of the diphosphane with a dichlorophosphane in the presence of $AlCl_3$ (Scheme 1.11). The products were readily characterised using $^{31}P\{^1H\}$ NMR spectroscopy. The alkyl derivatives show a shift to higher frequency for the triplet corresponding to P_C, and a marked reduction in the magnitude of $^1J_{P\text{-}P}$ compared to that of the equivalent cyclic triphosphenium ion.

This chapter details the synthesis of a number of P_C-alkyl and P_C-aryl derivatives by two different methods: a direct route which involves the synthesis of the cyclic triphosphenium ion first, followed by a reaction of the ring with an alkyl triflate; or an indirect method, following Schmidpeter's route, by which a diphosphane is reacted with an equivalent of a dichloroalkylphosphane or a dichloroarylphosphane to form the derivative in one step.

4.2 Synthesis of P_C-alkyl and P_C-aryl derivatives – A direct method

4.2.1 Synthesis of P_C-methyl derivatives

The synthesis of some new methylated cyclic triphosphenium ions was attempted by reacting excess methyl triflate with some cyclic triphosphenium ions (Scheme 4.2).



Scheme 4.2: Direct methylation of cyclic triphosphenium ions

The $^{31}P\{^1H\}$ NMR spectra of compounds **14** and **15** each showed, as expected, a doublet and triplet resonance. In both cases, there was a large shift to higher frequency for the signal arising from the central P atom, and also a marked reduction in the magnitude of $^1J_{P\text{-}P}$, compared to the corresponding values for the parent cyclic triphosphenium ions. The $^{31}P\{^1H\}$ NMR data are shown in Table 4.1. Included are the shifts and coupling constants of the precursor triphosphenium ions for comparison.

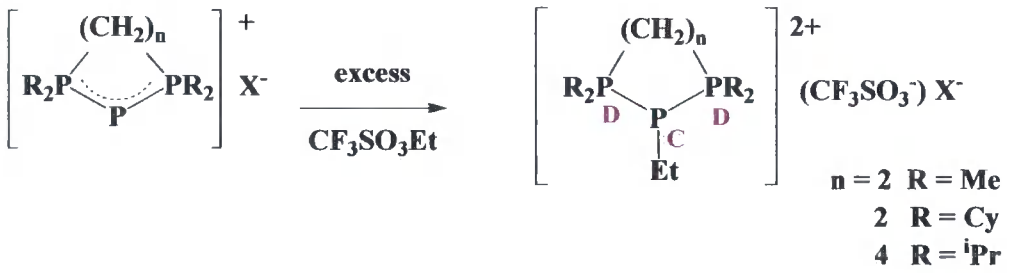
Diphosphane	Compound (CTI)	δP_B, ppm	δP_A, ppm	$^1J_{P\text{-}P}$, Hz	Compound (P-Me)	δP_D, ppm	δP_C, ppm	$^1J_{P\text{-}P}$, Hz
dcype	**3a**	87.3	–289.3	457	**14**	65.1	–96.1	301
dcypp	**7a**	36.2	–293.0	458	**15**	27.0	–109.5	281

Table 4.1: $^{31}P\{^1H\}$ NMR data for cyclic triphosphenium ions **3a** and **7a** and their P-methyl derivatives **(14** and **15)**

The large shift to higher frequency of the triplet corresponding to P_C can be attributed to the change in oxidation state of the P atom from P(I) to P(III). The loss of π-bonding as the delocalisation is removed upon methylation results in the reduction in the magnitude of $^1J_{P\text{-}P}$.

4.2.2 Synthesis of P_C-ethyl derivatives

Attempts to form P_C-ethyl derivatives of cyclic triphosphenium ions using excess ethyl triflate had been carried out on some cyclic triphosphenium ions. However when the cyclic triphosphenium ion had large substituents on the outer P atoms, the reaction was unsuccessful.[5] Direct ethylation of cyclic triphosphenium ions with ethyl substituents had been a success (Table 1.17)[7, 8] Further reactions were attempted using excess ethyl triflate for methyl, *iso*-propyl and *cyclo*-hexyl substituents (Scheme 4.3).



Scheme 4.3: Attempted direct ethylation of some cyclic triphosphenium ions

Attempted reactions to synthesise P-ethyl derivatives from dcype and dippb cyclic triphosphenium ions were unsuccessful, even after the addition of four equivalents of ethyl triflate. This suggests that there is considerable steric hindrance to formation of the ethyl derivatives. It is expected that the cyclic triphosphenium ion derived from dmpe should form the ethylated derivative upon reaction with excess ethyl triflate, as the substituents on the four-coordinate phosphorus atoms are methyl. However, the products of the reaction proved to be insoluble and hence no solution-state spectra could be obtained.

4.2.3 Attempted synthesis of P_C-phenyl derivatives

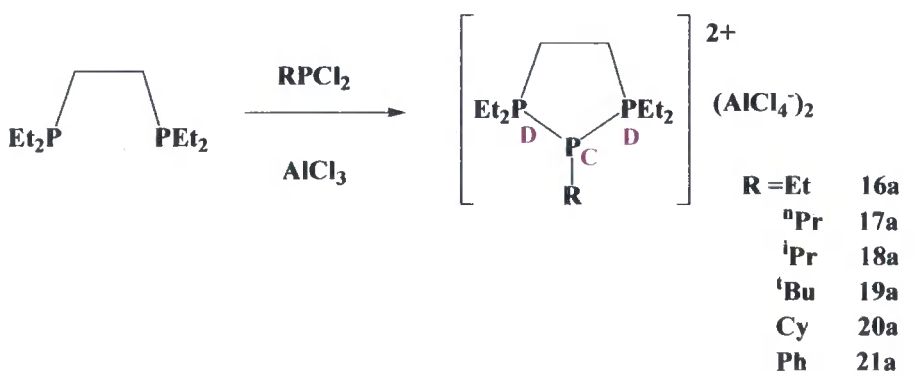
Following on from the successful reactions to form P_C-methyl, and some P_C-ethyl, derivatives of cyclic triphosphenium ions, reactions using phenyl triflate were carried out.

The reaction of excess phenyl triflate with both the depe cyclic triphosphenium ion (**2a**) and the dippb cyclic triphosphenium ion (**13a**) did not lead to formation of the P_C-phenyl dication. For each reaction, the $^{31}P\{^1H\}$ NMR spectra only showed resonances corresponding to the cyclic triphosphenium ion.

4.3 Synthesis of P_C-alkyl and P_C-aryl derivatives – An indirect method

4.3.1 Derivatives of the depe cyclic triphosphenium ion

The syntheses of some new P_C-alkyl and P_C-aryl cyclic triphosphenium ions were attempted by reacting depe with various dichlorophosphanes and $AlCl_3$ (**16a-21a**) (Scheme 4.4).



Scheme 4.4: Synthesis of alkyl and aryl derivatives of the depe cyclic triphosphenium ion by an indirect method

The $^{31}P\{^{1}H\}$ NMR spectrum of compound **16a** showed, as expected, a doublet and triplet resonance (Table 4.2). There was a large shift to higher frequency for the central P atom, and also a marked reduction in the magnitude of $^{1}J_{P\text{-}P}$, compared to those of the cyclic triphosphenium ion.[9, 10] These NMR data are in good agreement with those obtained for the product of direct ethylation of the depe cyclic triphosphenium ion using ethyl triflate.[7, 8]

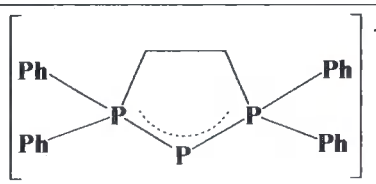
Compound	Compound number	δP_D, ppm	δP_C, ppm	$^{1}J_{P\text{-}P}$, Hz
	**2a**	81.7	–269.2	441
Ethylated using ethyl triflate	**N/A**	66.1	–89.8	291
Ethyl derivative using $EtPCl_2$	**16a**	66.0	–92.7	293

Table 4.2: $^{31}P\{^{1}H\}$ NMR data for the depe cyclic triphosphenium ion and ethyl derivatives

Further reactions were carried out using chlorophosphanes with ^{n}Pr, ^{i}Pr, ^{t}Bu, Cy and Ph groups. It was hoped that by using this method, derivatives containing larger substituents on the central phosphorus atom could be synthesised, similar to those previously reported by Schmidpeter.[3]

The $^{31}P\{^{1}H\}$ NMR spectra of each compound (**17a - 21a**) showed, as expected, a doublet and triplet resonance (Table 4.3). For each derivative in this series there is a large shift to higher frequency of the triplet corresponding to the central phosphorus atom, P_C compared to P_A of the cyclic triphosphenium ion. This suggests that for P-alkylated derivatives the central P is effectively deshielded compared with the P(I) centre in cyclic

triphosphenium ions. Also noteworthy is the marked reduction in the magnitude of $^{1}J_{P\text{-}P}$ compared with the values determined for the parent cyclic triphosphenium ion **2a** probably due to the increased P-P distance upon loss of delocalisation. There is a much smaller shift to lower frequency for the doublet corresponding to the outer P atoms for the alkyl/aryl derivatives, compared to that of the depe cyclic triphosphenium ion, **2a**. Although the $^{1}J_{P\text{-}P}$ values are very similar for R = Et or ^{n}Pr, on going from ^{n}Pr through to ^{t}Bu substituents there is a significant increase.

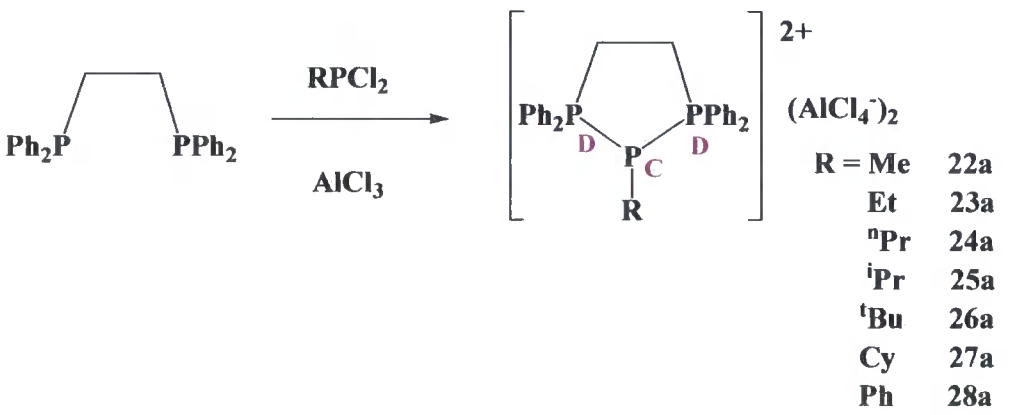
Substituent	**Compound Number**	**δP_D, ppm**	**δP_C, ppm**	**$^{1}J_{P\text{-}P}$, Hz**
None (CTI)	**2a**	81.7	–269.2	441
Et	**16a**	66.0	–92.7	293
^{n}Pr	**17a**	62.2	–95.1	295
^{i}Pr	**18a**	67.3	–66.6	311
^{t}Bu	**19a**	66.8	–33.6	338
Cy	**20a**	67.0	–71.9	309
Ph	**21a**	60.2	–94.2	280

Table 4.3: ^{31}P {^{1}H} NMR data for some P_C-alkyl and P_C-aryl derivatives of depe

Attempts to synthesise the P_C-methylated derivative *via* this route were unsuccessful. Indeed, upon addition of $MePCl_2$ to a solution of the cyclic triphosphenium ion, the solution turned cloudy and eventually separated out into two layers, one being oily. The $^{31}P\{^{1}H\}$ NMR spectrum showed no evidence to support the formation of the P-methylated derivative.

4.3.2 Derivatives of the dppe cyclic triphosphenium ion

Previous attempts to form a P_C-ethylated derivative of the dppe cyclic triphosphenium ion had been unsuccessful when using ethyl triflate. Schmidpeter had reported the synthesis of P_C-chloromethyl and P_C-^{t}Bu derivatives of the dppe cyclic triphosphenium ion.[3] Using this method it was hoped to synthesise a series of P_C-alkyl and P_C-aryl derivatives of the dppe cyclic triphosphenium ion, which would be unattainable using the direct method (Scheme 4.5). The P_C-ethyl P_C-^{t}Bu and P_C-phenyl derivatives were also synthesised as their chlorostannate salts (**23b, 26b** and **28b**) using $SnCl_2$ instead of $AlCl_3$.



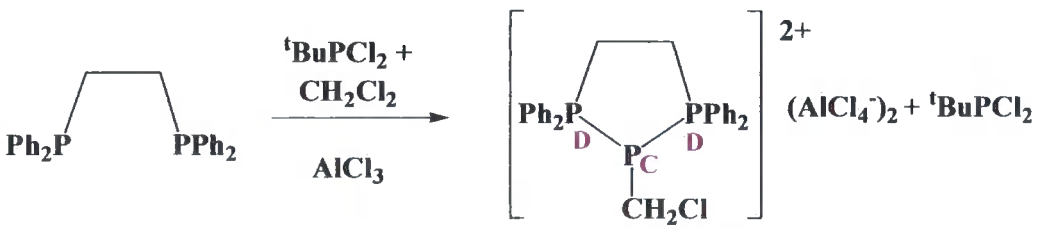
Scheme 4.5: Synthesis of alkyl and aryl derivatives of the dppe cyclic triphosphenium ion by an indirect method

The $^{31}P\{^1H\}$ NMR spectra of the P_C-methylated derivative (**22a**) showed a doublet and triplet resonance, as expected (Table 4.4). These data are in good agreement with those reported for the heterocycle obtained from direct methylation of the dppe cyclic triphosphenium ion (δP_C -91.3 ppm, δP_D 54.8 ppm, $^1J_{P\text{-}P}$ 284 Hz),[5] considering the difference in counter-ion.

The complete family of such derivatives was synthesised in solution for R= Me (**22a**), Et (**23a** and **23b**), ^{n}Pr (**24a**), ^{i}Pr (**25a**), ^{t}Bu (**26a** and **26b**), Cy (**27a** and **27c**) and Ph (**28a**

and **28b**) (Table 4.4). Similar to the depe series, the $^{1}J_{P\text{-}P}$ values increase along the series with a significant increase for ^{n}Pr to ^{i}Pr to ^{t}Bu substituents .

Schmidpeter *et al.* reported δP_D 52 ppm, δP_C -79 ppm, $^{1}J_{P\text{-}P}$ 283 Hz, for **26a**.[3] The $^{31}P\{^{1}H\}$ NMR data obtained here from an equivalent reaction gave very different results which are much more consistent with the results for the depe series (Table 4.4). It is possible that, under the experimental conditions they used, Schmidpeter *et al.* obtained the chloromethyl derivative (also described in the same paper (δP_D 52.0 ppm, δP_C -78.0 ppm, $^{1}J_{P\text{-}P}$ 282 Hz))[3] in preference to the ^{t}Bu derivative (Scheme 4.6).



Scheme 4.6: Proposed reaction pathway for the formation of the P_C-chloromethyl derivative of the dppe cyclic triphosphenium ion

For the P_C-*cyclo*-hexyl derivative of the dppe cyclic triphosphenium ion from the reaction using $AlCl_3$, two sets of doublet and triplet resonances were observed. This can be explained by having a mixture of Cl^- and $AlCl_4^-$ counter-ions. Adding more $AlCl_3$ to the reaction mixture caused an increase in relative intensity for the signals at 48.9 and -75.7 ppm, allowing these signals to be assigned to the bis-$AlCl_4^-$ salt (**27a**), with the other resonances being attributed to the mixed counter-ion species (**27c**).

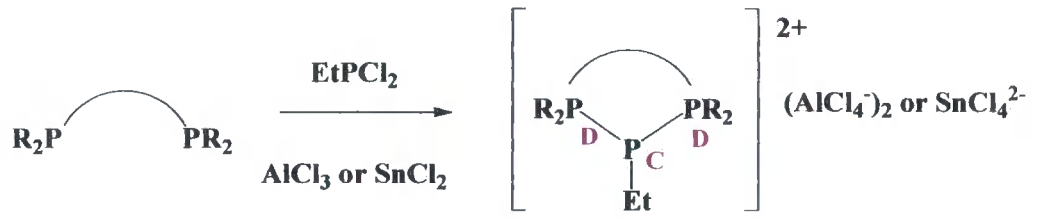
The reaction between dppe and $^{i}PrPCl_2$ was also carried out in the presence of $SnCl_2$. Unfortunately, the $^{31}P\{^{1}H\}$ NMR solution spectra could not be resolved, and showed just broad signals at 50 ppm and -70ppm, although, crystals suitable for X-ray diffraction studies were obtained (see Section 4.4).

Substituent	Compound Number	δP_D, ppm	δP_C, ppm	$^1J_{P-P}$, Hz
None (CTI)	**4a**	65.0	-230.0	450
Me	**22a**	53.2	-96.9	279
Et	**23a**	53.4	–93.0	287
Et	**23b**	53.6	-96.2	299
^{n}Pr	**24a**	53.8	–95.1	288
^{i}Pr	**25a**	49.0	–71.3	304
^{t}Bu	**26a**	49.5	–54.0	332
^{t}Bu	**26b**	50.2	-54.2	336
Cy	**27a**	48.9	-75.7	308
Cy	**27c**	50.4	–79.1	311
Ph	**28a**	53.1	–76.9	280
Ph	**28b**	52.8	-79.2	293

Table 4.4: $^{31}P\{^1H\}$ NMR data for some alkyl and aryl derivatives of dppe

4.3.3 P_C-ethyl derivatives of other cyclic triphosphenium ions

Ethyl derivatives of a number of other cyclic triphosphenium ions were also synthesised using the same method (Scheme 4.7). The syntheses were carried out to form either the tetrachloroaluminate or chlorostannate salts, or in the case of the dcypm, depp and dppben systems, both. The $^{31}P\{^1H\}$ NMR data are in good agreement with those obtained for the ethyl derivatives of dppe and depe synthesised using this method, and also previously reported data for other protonated and alkylated derivatives (Table 4.5).[1-6]



Scheme 4.7: General synthesis of P-ethyl derivatives of cyclic triphosphenium ion using $AlCl_3$ or $SnCl_2$

For the P_C-ethylated derivative of the dcypm cyclic triphosphenium ion, the $^1J_{P\text{-}P}$ value is considerably smaller than for any other ethyl derivative. However, this is not surprising since the parent cyclic triphosphenium ion has the smallest $^1J_{P\text{-}P}$ values reported for these systems, 331 Hz.[6] The $^{31}P\{^1H\}$ NMR data for the product of direct methylation of this cyclic triphosphenium ion also exhibited a small $^1J_{P\text{-}P}$ value, 195 Hz.[6] The reactions to form both the tetrachloroaluminate and chlorostannate salt gave rise to another product, a tetraphosphonium ion. This will be discussed in more detail in Chapter 5. A small amount of the dcypm cyclic triphosphenium ion was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture. This formed due to a small amount of PCl_3 impurity present in the $EtPCl_2$.

For the dppben and depp systems, the P_C-ethyl derivatives were synthesised using both $AlCl_3$ (**32a** and **33a**) and $SnCl_2$ (**32b** and **33b**). The $^{31}P\{^1H\}$ NMR data for the two salts show a difference in shift for the triplet resonance corresponding to the central P atom compared to P_A of the parent cyclic triphosphenium ion, and also in the magnitude of the $^1J_{P\text{-}P}$ value (Table 4.5). This can be attributed to the difference in counter-ion.[11, 12]

Diphosphane	Compound	δP_D, ppm	δP_C, ppm	$^1J_{P-P}$, Hz
dcypm	**29a**	40.4	–59.7	156
dcypm *	**29b**	39.5	-62.8	157
dcype *	**30b**	57.0	–85.2	319
dppE	**31a**	58.9	–93.2	307
dppben	**32a**	44.8	–66.7	286
dppben *	**32b**	45.1	–72.2	300
depp	**33a**	28.9	–85.8	301
depp *	**33b**	29.3	-81.9	303
dcypp	**34a**	28.7	–92.4	303
dcypb *	**35b**	32.1	–52.6	305
biphep*	**36b**	12.8	–14.2	322

Table 4.5: $^{31}P\{^1H\}$ NMR data for some ethyl derivatives of cyclic triphosphenium ions
* $SnCl_2$ was added instead of $AlCl_3$

4.3.4 Other P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions

The synthesis of P_C-methyl, n-propyl, iso-propyl and phenyl derivatives was also carried out using $MePCl_2$, $^nPrPCl_2$ $^iPrPCl_2$ and $PhPCl_2$ instead of $EtPCl_2$ (Scheme 4.7).

The $^{31}P\{^{1}H\}$ NMR data for the P_C-methyl derivative of the dppE ring (**37a**) are in good agreement with those reported for the corresponding product obtained from direct methylation of the parent cyclic triphosphenium ion (δP_A = -96.5 ppm, δP_B = 57.7 ppm, $^{1}J_{P\text{-}P}$ = 311 Hz),[5] when taking into account the change in counter-ion (Table 4.6). Attempts to synthesise other P-methylated derivatives of cyclic triphosphenium ions gave either a white precipitate or an oily solution and $^{31}P\{^{1}H\}$ NMR solution spectra could not be obtained.

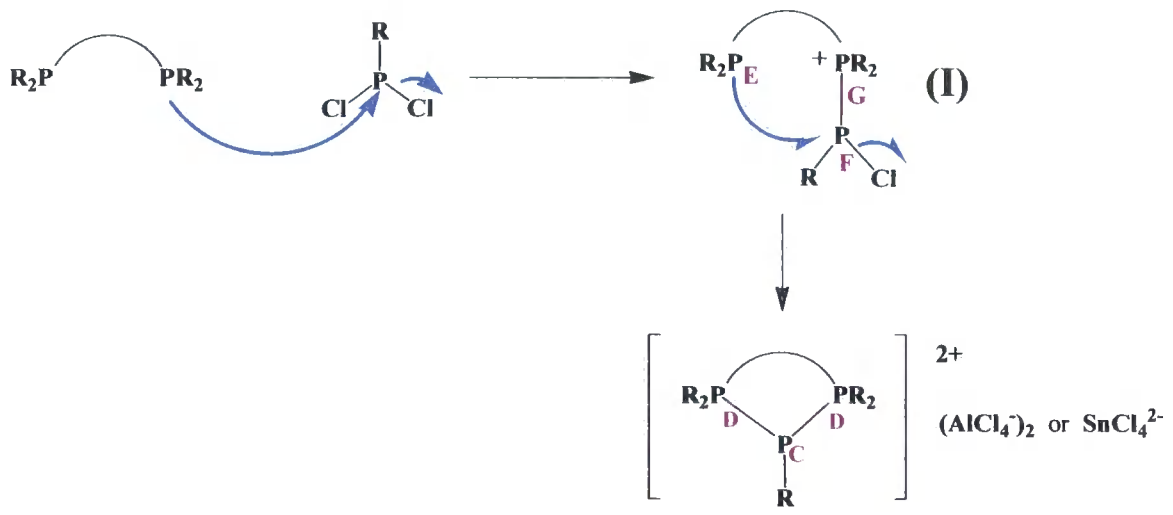
The iso-propyl derivatives of the dcypm cyclic triphosphenium ion were synthesised using both $AlCl_3$ and $SnCl_2$ (**41a** and **41b**). However, the reactions were not very clean and resulted in a 50:50 mixture of the desired product and a tetraphosphonium ion (which will be discussed in greater detail in Chapter 5). A mixture of the alkylated product and a tetraphosphonium ion was also observed in the reaction to form a P_C-^{n}propyl derivative of the dcypm cyclic triphosphenium ion.

Diphosphane	Compound	R'=	δP_D, ppm	δP_C, ppm	$^{1}J_{P\text{-}P}$, Hz
dppE	**37a**	Me	59.8	–97.0	301
depp	**38a**	^{n}Pr	30.0	–89.1	306
dippp	**39a**	^{n}Pr	37.2	–92.8	288
dcypm	**40b**	^{n}Pr	41.4	-64.0	159
dcypm	**41a**	^{i}Pr	38.8	–29.1	152
dcypm*	**41b**	^{i}Pr	38.8	–28.9	150
dmpe	**42a**	Ph	46.6	–76.4	290
depp	**43a**	Ph	27.8	–83.7	295

Table 4.6: $^{31}P\{^{1}H\}$ NMR data for some alkyl and aryl derivatives of cyclic triphosphenium ions (*$SnCl_2$ was added instead of $AlCl_3$)

4.3.5 Mechanism of formation of P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions

The mechanism of formation of P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions necessarily involves the addition of the chlorophosphane to one of the P atoms of the diphosphane to form a P-P bond and the loss of a halogen, which would be accepted by $AlCl_3$ or $SnCl_2$, to form a tetrachloroaluminate or chlorostannate anion respectively (Scheme 4.8). Cyclisation would then occur, with loss of the second halogen (in the presence of $AlCl_3$ or $SnCl_2$) to yield the product. One noteworthy point is that the acyclic intermediate is the same as the first intermediate in the formation of the cyclic tetraphosphonium ions, which will be discussed in greater detail in Chapter 5.



Scheme 4.8: General mechanism of formation for aryl and alkyl derivatives of some cyclic triphosphenium ion using $AlCl_3$ or $SnCl_2$

In some systems, the formation of the alkyl derivative occurred relatively slowly, which allowed detection of the acyclic intermediate. By $^{31}P\{^1H\}$ NMR spectroscopy, this acyclic intermediate is observed to give rise to two doublet resonances corresponding to P_F and P_G, which have a large $^1J_{P\text{-}P}$ value, and a singlet corresponding to the 'free' end, P_E.

Low intensity signals were observed in a $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between depp and $EtPCl_2$ in the presence of $AlCl_3$, which could be assigned to P_E, P_F and P_G of the acyclic intermediate (**33aI**) (Table 4.7). This acyclic intermediate was only present as a minor component of the reaction mixture. The shift of P_F suggests there is only one Cl bonded to the P atom, as the shift is more consistent with other phosphanes containing one chlorine atom than ones with two chlorines (Table 4.8).[13-17]

Similar signals were observed for the reactions of depp with $^{i}PrPCl_2$ and with $^{t}BuPCl_2$, of dcypp with $^{n}PrPCl_2$, and of dippp with $^{t}BuPCl_2$ (Table 4.7). However, cyclisation did not occur in these four reactions. It seems probable that, due to the bulky substituents on either the diphosphane and/or the chlorophosphane, cyclisation to form the alkyl derivative is unfavourable.

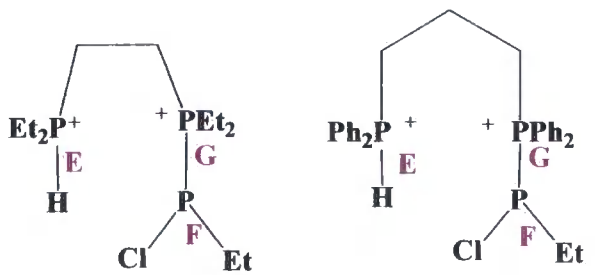
Diphosphane	**Compound**	**R' =**	**δP_E, ppm**	**δP_F, ppm**	**δP_G, ppm**	**$^{1}J_{P\text{-}P}$, Hz**	**$^{1}J_{P\text{-}H}$, Hz**
dppp	**44aI**	Me	10.2	60.0	28.7	324	NR
depe	**16aI**	Et	37.6	71.8	22.4	345	470
depp	**33aI**	Et	17.4	57.2	–48.1	278	NR
dppp	**45I**	Et	9.9	68.7	26.7	329	494
dcypp	**46I**	^{n}Pr	11.7	50.4	–28.8	309	NR
depp	**47I**	^{i}Pr	18.2	57.3	–48.3	278	NR
depp	**48I**	^{t}Bu	17.5	57.2	–48.2	279	NR
dippp	**49I**	^{t}Bu	33.3	60.1	–26.4	309	NR

Table 4.7: $^{31}P\{^{1}H\}$ NMR data for the acyclic intermediate in the mechanism of formation of alkyl derivatives (NR – not recorded)

Compound	δP, ppm	Reference
Cl_2PPh	166	13, 14
Cl_2PPr	201	13, 15
Cl_2PBu	195	13, 16
$ClP(^tBu)Ph$	84	13, 17
$ClPPh_2$	82	13, 14

Table 4.8: $^{31}P\{^1H\}$ NMR data for some –PRCl and $–PCl_2$ compounds

For the reactions of dppp with $MePCl_2$ and $EtPCl_2$, and depe with $EtPCl_2$, resonances were observed in the $^{31}P\{^1H\}$ NMR spectra that were assigned to acyclic intermediates in the formation of the P-alkyl derivatives (Table 4.7). For the depe reaction, $^3J_{PF\text{-}PG}$ was measured as 45 Hz. In each of these reactions, the resonance corresponding to P_G was at much higher frequency compared to those described previously. $^{31}P\{^1H\}$ NMR spectra were recorded for the depe and dppp with $EtPCl_2$ reactions. In these spectra, P_E became a doublet with $^1J_{P\text{-}H}$ values of 470 Hz and 494 Hz respectively, suggesting protonation of P_E had occurred (Figure 4.1). The values obtained for $^1J_{P\text{-}H}$ in **16aI** and **33aI**, and the chemical shifts, are comparable to those in other R_3P^+-H systems (Table 4.9).[13, 18-20]



16aI **33aI**

Figure 4.1: Suggested structures for compounds **16aI** and **33aI**

Compound	δP, ppm	$^{1}J_{P-H}$, Hz	Reference
Et_3P^+H (FSO_3^-)[13, 18]	22.5	471	13, 18
Me_3P^+H (Cl^-)	-2.8	495	13, 19
Et_2PhP^+H (HBr_2^-)	18.3	490	13, 20
Bu_3P^+H (FSO_3^-)[13, 18]	13.7	470	13, 18
Ph_3P^+H (FSO_3^-)	6.8	510	13, 18
$EtPh_2P^+H$ (HBr_2^-)	8.3	515	13, 20
$BuPh_2P^+H$ (HBr_2^-)	2.1	520	13, 20
$^{i}PrPh_2P^+H$ (HBr_2^-)	14.0	510	13, 20

Table 4.9: ^{31}P NMR data for some R_3P^+-H compounds

$AlCl_3$ readily picks up water on the surface, so protonation is not impossible. When using $SnCl_2$, this side reaction is less probable. It is likely that when protonation of the acyclic intermediate occurs, no further reaction, *i.e.* cyclisation, can take place. Protonation is also more likely to occur when the reaction is slower *e.g.* when there are bulky substituents on either the diphosphane or the chlorophosphane.

4.4 Molecular structures of some P-alkyl derivatives of cyclic triphosphenium ions

Crystals suitable for study by X-ray diffraction of seven P_C–alkyl derivatives of cyclic triphosphenium ions were isolated (**16c**, **17c**, **23a**, **25b**, **34d**, **36b** and **40a**) and the resulting structures are shown in Figures 4.2-4.8. Selected bond lengths and angles are shown in Table 4.10. However, due to the air-sensitive nature of **40a**, the quality of the data obtained is such that chemical connectivity can be confirmed but no reliable information regarding the bond lengths and/or angles can be obtained. In addition the structure shows significant disorder (ca. 30% occupancy) in the central P atom and one $AlCl_4^-$ counter-ion.

In each of the structures the ring containing the three P atoms is non-planar as expected. The P-P bond lengths in each of these derivatives are typical values for normal P-P single bonds (*e.g.* 2.218(2) -2.235(2) Å in the tetraphosphonium ion derived from biphep[21] and 2.217(1) Å in Ph_2P-PPh_2[22]). These P-P bond lengths are significantly longer than those observed in cyclic triphosphenium ions (2.1132(8) – 2.1326(14) Å)[9, 23-28] which confirms the lack of any P-P multiple bond character consistent with no charge delocalisation for an alkyl derivative, as inferred from the NMR data.

The P-P-P bond angles in the dppe P-alkyl derivatives (**23a** and **25b**) are consistent with those reported for the parent cyclic triphosphenium ion, **4**.[29,25, 27] For the five membered ring P-alkylated derivatives, **16c**, **17c**, **23a**, and **25b**, the P-P-P bond angles are very similar [90.3(3) (**16c**), 90.06(3) (**17c**), 89.16(11) (**23a**) and 89.16(11)° (**25b**)]. Bond angles close to 90° suggest that the main contribution to the P-P bonding is from P-orbitals. As expected, the P-P-P bond angles for **34d** and **36b** are larger than those for **16c**, **17c**, **23a**, and **25b**, due to the increase in ring size. In all six structures (**16c**, **17c**, **23a**, **25b**, **34d** and **36b**) the P-P-P bond angle is much smaller than the P-P_A-C angle, which again suggests that there is a large P-orbital contribution to P-P bonding in these P-alkyl derivatives. This is also observed for tetraphosphonium ions[21] and some other compounds containing four adjacent P atoms.[30-32]

	Bond Length /Å			**Bond Angle / °**
	P(1)–P(2)	**P(1)–P(3)**	**P(2)–C(1)**	**P(2)–P(1)–P(3)**
16c	2.2327(9)	2.2108(9)	1.864(3)	90.3(3)
17c	2.2302(8)	2.2105(8)	1.867(2)	90.06(3)
23a	2.225(3)	2.202(3)	1.781(8)	89.16(11)
25b	2.231(3)	2.220(3)	1.880(8)	86.09(11)
34d	2.199(2)	2.202(2)	1.807(6)	102.95(8)
36b	2.214(3)	2.197(4)	1.867(9)	96.59(13)

Table 4.10: Selected bond lengths and angles for isolated P-alkyl derivatives (**16c**, **17c**, **23a**, **25b**, **34d**, and **36b**)

16c and **17a** have mixed counter-ions, one $AlCl_4^-$ and one Cl^-. This mixture of Cl^- and $AlCl_4^-$ counter-ions was observed in the $^{31}P\{^1H\}$ NMR spectrum for the P_C-*cyclo*-hexyl derivative of the dppe cyclic triphosphenium ion from the reaction using $AlCl_3$. Two sets of doublet and triplet resonances were attributed to having a mixture of Cl^- and $AlCl_4^-$ counter-ions.

A more unusual counter-ion was observed in **34d**, $[Al_4O_2Cl_{10}]^{2-}$, although there are several reported examples of this anion in the literature.[33-39] The bond lengths and angles in the anion are consistent with those previously reported.[33, 37-39]

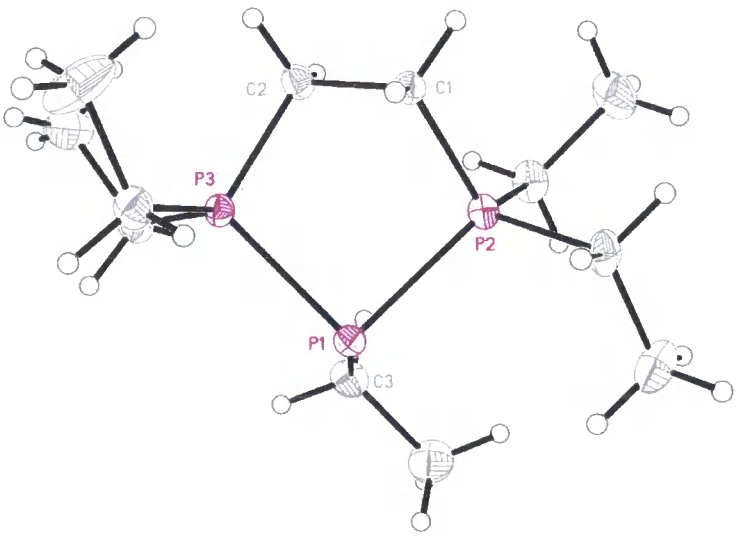


Figure 4.2: The molecular structure of the dication **16c**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

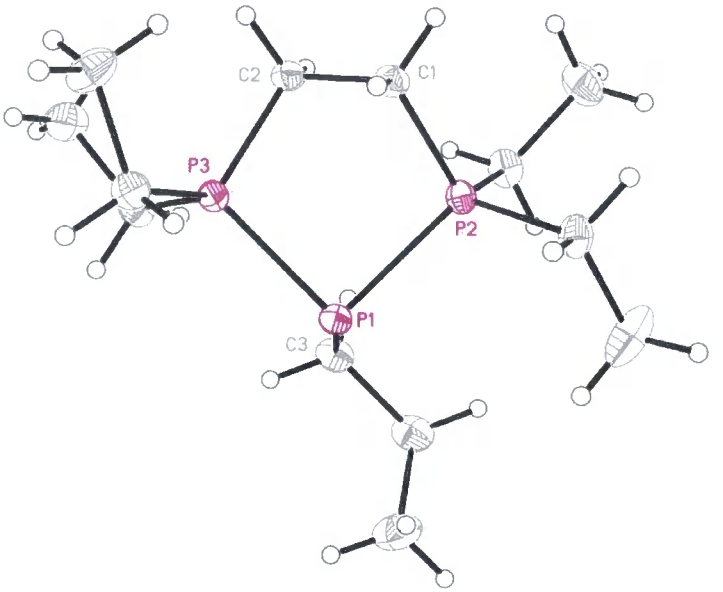


Figure 4.3: The molecular structure of the dication **17c**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

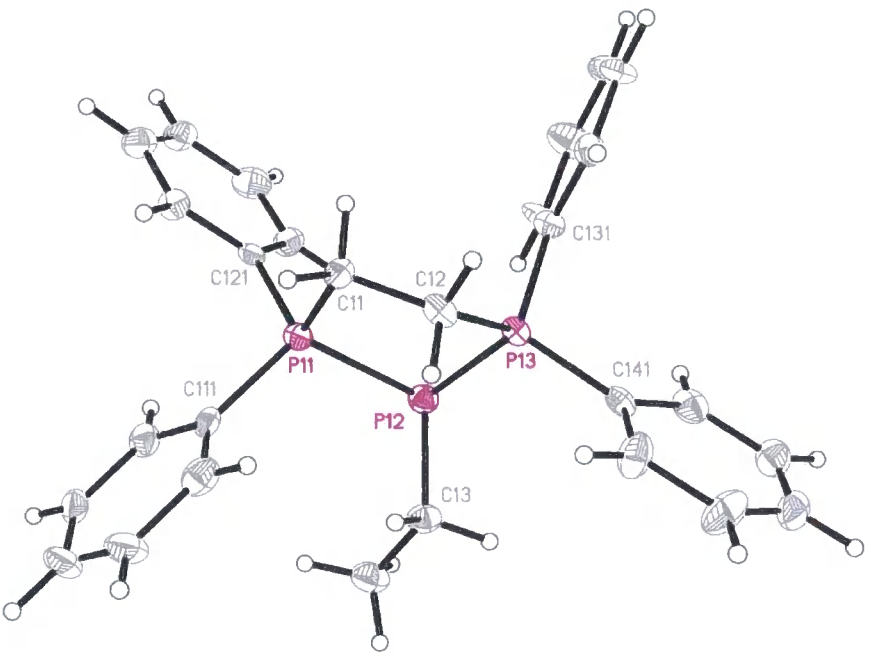


Figure 4.4: The molecular structure of the dication **23a** (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

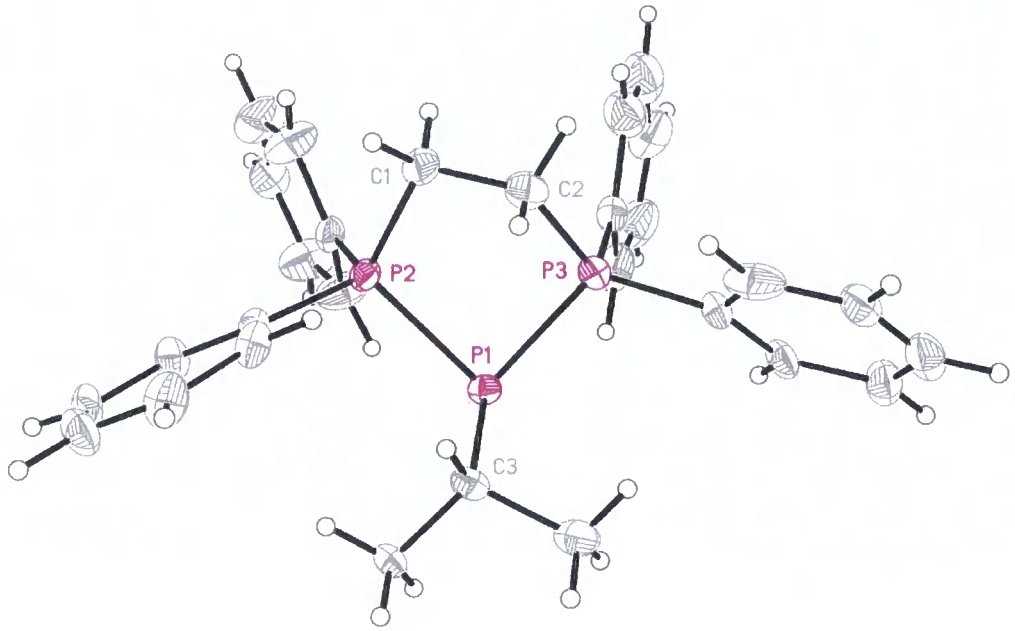


Figure 4.5: The molecular structure of the dication **25b**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

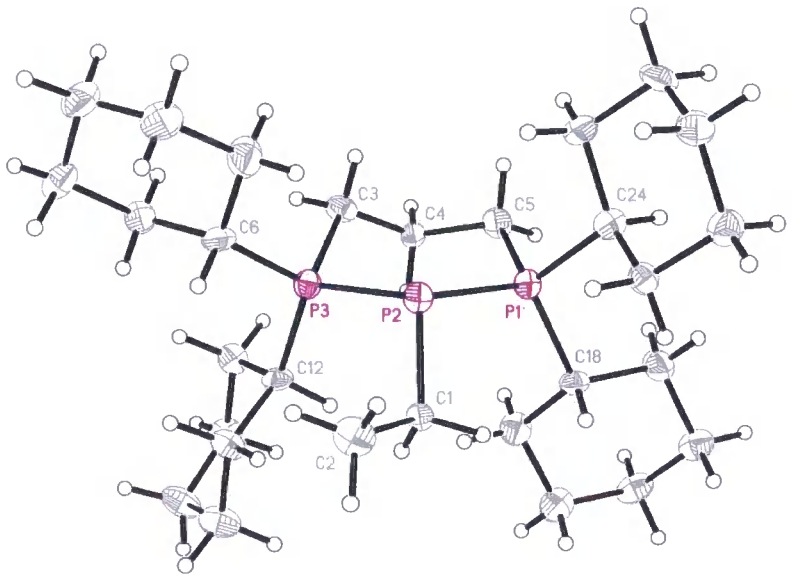


Figure 4.6: The molecular structure of the dication **34d**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

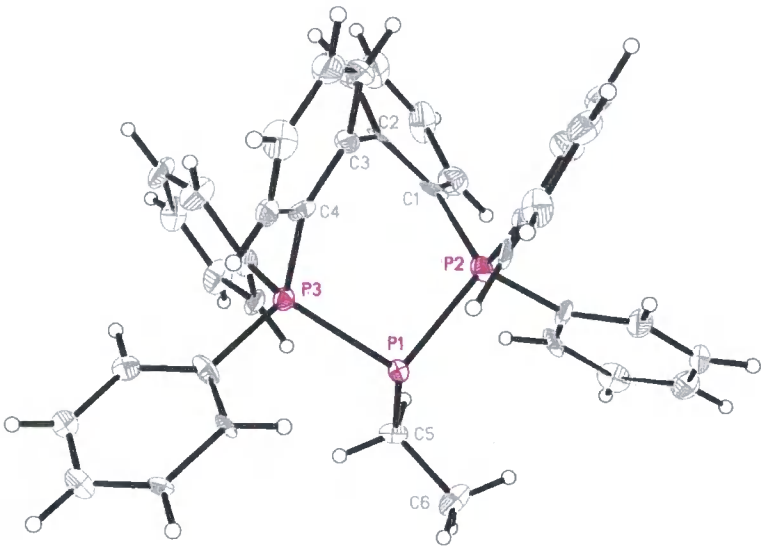


Figure 4.7: The molecular structure of the dication **36b**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50 % probability.

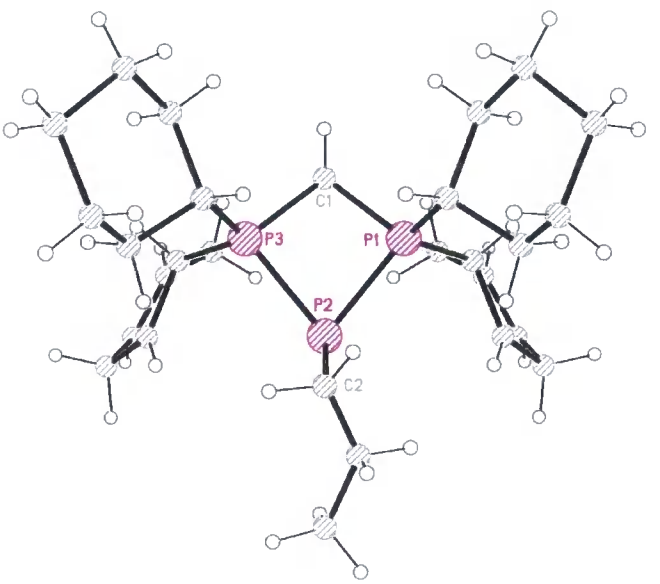
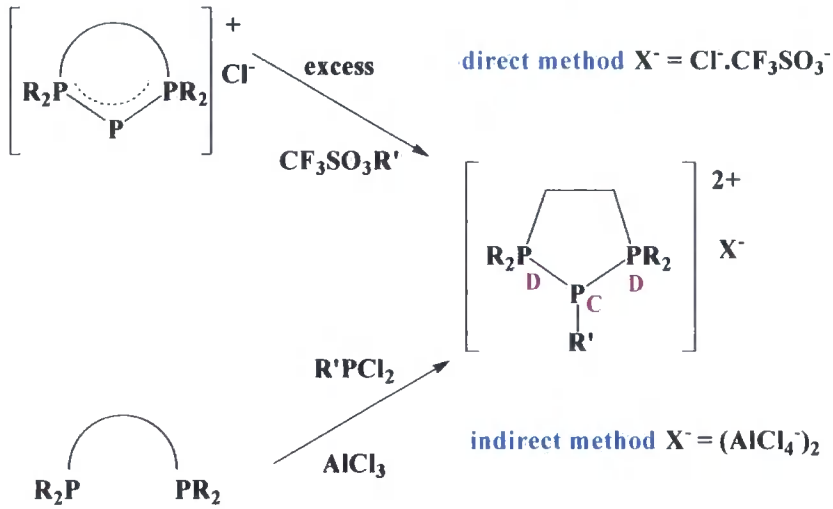


Figure 4.8: The molecular structure of the dication **40a**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity).

4.5 Conclusions

This chapter outlines the synthesis of some P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions using a direct and/or indirect method (Scheme 4.9). They have been readily characterised using $^{31}P\{^1H\}$ NMR spectroscopy as they show a doublet and triplet resonance, with the triplet at higher frequency compared to that of the parent cyclic triphosphenium ion. This suggests that for P-alkylated derivatives the central P is effectively deshielded compared with the P(I) centre in cyclic triphosphenium ions. In all cases $^1J_{P\text{-}P}$ is decreased, compared with those for the parent cyclic triphosphenium ion probably due to the increased P-P distance upon loss of delocalization. The presence of single P-P bonds has been confirmed by X-ray crystallographic studies carried out on seven of the derivatives.



Scheme 4.9: Synthesis of P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ion by direct and indirect methods

The direct method involves the reaction of a cyclic triphosphenium ion with an excess of an alkyl triflate. The results of these reactions show that in order for direct alkylation to take place, the attacking reagent (alkyl triflate) must contain a small organic substituent

e.g. methyl. If the cyclic triphosphenium ion itself contains ethyl groups on the outer P atoms, then direct ethylation is possible.

Using the indirect method of forming alkyl or aryl derivatives, a larger family of derivatives has been successfully synthesised, including two series for the depe and dppe systems. For the derivatives of the depe and dppe systems the $^{1}J_{P\text{-}P}$ values are very similar for R' = Et or ^{n}Pr. However, going from ^{n}Pr through to ^{t}Bu substituents there is a significant increase in this value.

Sterics play a significant role in the formation of P_C-alkyl and P_C-aryl derivatives of cyclic triphosphenium ions. Direct alkylation reactions are limited due to steric constraints. Sterics are also very important in the formation of alkyl or aryl derivatives using the indirect approach.

The mechanism of formation of the derivatives using the indirect method necessarily involves the addition of the chlorophosphane to one of the P atoms of the diphosphane to form a P-P bond, and the loss of a halogen, to form an acyclic intermediate. Cyclisation could then occur, sterics permitting, with loss of the second halogen to afford the alkyl/aryl derivative. In several reactions the acyclic intermediate was observed in the $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after the addition of the chlorophosphane. When the diphosphane and/or the chlorophosphane contained bulky groups often cyclisation did not occur.

4.6 Experimental

Example reaction of direct alkylation:

Under a nitrogen atmosphere and at room temperature dcype (0.0211 g, 0.05 mmol) was dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.04 mL, 0.03 mmol) was then added, and a $^{31}P\{^1H\}$ NMR spectrum recorded soon after mixing to check that the cyclic triphosphenium ion had formed. An excess of methyl triflate (0.02 mL, 0.18 mmols) was added, and a $^{31}P\{^1H\}$ NMR spectrum recorded.

Quantities of reagents used:

Diphosphane	CF_3SO_3R R=	Compound	Quantity of diphosphane used		Quantity of PCl_3 used		Quantity of CF_3SO_3R used	
			mL	mmol	mL	mmol	mL	mmol
dcype	Me	**14**	0.0211	0.05	0.004	0.03	0.020	0.18
dcypp	Me	**15**	0.0696	0.16	0.010	0.11	0.017	0.15
dcype	Et	-	0.0042	0.01	0.001	0.01	0.005	0.04
dippb	Et	-	0.0145	0.05	0.060	0.05	0.030	0.20
dmpe	Et	-	0.0135	0.09	0.090	0.08	0.010	0.08
depe	Ph	-	0.0243	0.12	0.010	0.11	0.080	0.48

Example reaction of indirect alkylation:

Using $AlCl_3$:

$MePCl_2$ (0.01 mL, 0.11 mmol) was added, *via* syringe, to a solution of dppe (0.0282 g, 0.07 mmol), and $AlCl_3$ (0.0193 g, 0.14 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Using $SnCl_2$:

$EtPCl_2$ (0.03 mL, 0.28 mmol) was added *via* syringe to a solution of dcypm (0.0497 g, 0.12 mmol), and $SnCl_2$ (0.0455 g, 0.24 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Quantities of reagents used:

Diphosphane	R'=	Compound	Quantity of diphosphane used		Quantity of $R'PCl_2$ used		Quantity of $AlCl_3$ used	
			g	mmol	mL	mmol	g	mmol
depe	Me	-	0.0406	0.20	0.020	0.22	0.0555	0.42
depe	Et	**16a/16aI**	0.0082	0.04	0.004	0.04	0.0162	0.11
depe	n-Pr	**17a**	0.0347	0.17	0.022	0.17	0.0453	0.34
depe	i-Pr	**18a**	0.0407	0.20	0.025	0.20	0.0533	0.40
depe	^{t}Bu	**19a**	0.0215	0.10	0.016	0.10	0.0267	0.20
depe	Cy	**20a**	0.0255	0.12	0.018	0.12	0.0322	0.24
depe	Ph	**21a**	0.4037	0.44	0.270	0.44	0.5220	0.87
dppe	Me	**22**	0.0282	0.07	0.010	0.11	0.0193	0.14
dppe	Et	**23a**	0.1372	0.34	0.070	0.68	0.0906	0.68
dppe	^{n}Pr	**24a**	0.1215	0.30	0.040	0.30	0.0800	0.60
dppe	^{i}Pr	**25a**	0.0826	0.21	0.025	0.20	0.0600	0.45
dppe	^{t}Bu	**26a**	0.0598	0.15	0.024	0.15	0.0400	0.30
dppe *	^{t}Bu	**26b**	0.0657	0.17	0.053	0.33	0.0449	0.34
dppe	Cy	**27a/27c**	0.0438	0.11	0.017	0.11	0.0304	0.23
dppe	Ph	**28a**	0.0598	0.15	0.090	0.15	0.0569	0.30
dppe *	Ph	**28b**	0.3306	0.83	0.230	1.69	0.3204	1.69
dcypm	Et	**29a**	0.0330	0.08	0.010	0.10	0.0220	0.16
dcypm *	Et	**29b**	0.0497	0.12	0.030	0.28	0.0455	0.24
dcype *	Et	**30b**	0.0273	0.06	0.020	0.19	0.0280	0.12
dppE	Et	**31b**	0.0638	0.16	0.020	0.19	0.0421	0.32
dppben	Et	**32a**	0.0827	0.18	0.020	0.19	0.0481	0.36
dppben *	Et	**32b**	0.1004	0.23	0.050	0.48	0.1023	0.54
depp	Et	**33a/33aI**	0.0417	0.13	0.020	0.19	0.0349	0.27
depp *	Et	**33b**	0.0228	0.07	0.020	0.19	0.0265	0.14

Quantities of reagents used (continued):

Diphosphane	R'=	Compound	Quantity of diphosphane used		Quantity of $R'PCl_2$ used		Quantity of $AlCl_3$ used	
			g	mmol	mL	mmol	g	mmol
dcypp	Et	**34a**	0.0286	0.07	0.010	0.10	0.0187	0.14
dcypb *	Et	**35b**	0.0226	0.05	0.010	0.10	0.0500	0.26
biphep*	Et	**36b**	0.0301	0.08	0.010	0.10	0.0301	0.16
dppE	Me	**37**	0.0223	0.06	0.005	0.06	0.0182	0.13
depp	^{n}Pr	**38a**	0.0098	0.04	0.005	0.04	0.0107	0.08
dippp	^{n}Pr	**39a**	0.0130	0.05	0.006	0.05	0.0133	0.10
dcypm	^{n}Pr	**40b**	0.0394	0.10	0.013	0.10	0.0267	0.20
dcypm	^{i}Pr	**41a**	0.0369	0.09	0.011	0.09	0.0240	0.18
dcypm *	^{i}Pr	**41b**	0.0319	0.08	0.020	0.16	0.0303	0.23
dmpe	Ph	**42a**	0.0460	0.30	0.180	0.29	0.0816	0.61
depp	Ph	**43a**	0.0359	0.11	0.150	0.11	0.0293	0.23
dppp	Me	**44I**	0.0382	0.09	0.020	0.22	0.0280	0.21
dppp	Et	**45I**	0.3189	0.72	0.080	0.77	0.1932	1.45
dcypp	^{n}Pr	**46I**	0.0438	0.11	0.017	0.11	0.0304	0.23
depp	^{i}Pr	**47I**	0.0105	0.05	0.007	0.05	0.0133	0.10
depp	^{t}Bu	**48I**	0.0129	0.06	0.010	0.06	0.0163	0.12
dippp	^{t}Bu	**49I**	0.0173	0.06	0.010	0.06	0.0162	0.12

*$SnCl_2$ was added instead of $AlCl_3$

Isolation of compounds:

For compounds **16c**, **17c**, **23a**, **25b**, **34d**, **36b** and **40a** crystals suitable for analysis by X-ray diffraction were obtained through evaporation of solvent in an inert atmosphere. It is notable that these compounds, as with the others described in this chapter are sensitive to both air and moisture.

Elemental analysis

Compound 23a:
Calculated: %C 42.25 %H 3.67 %N 0.00
Found: %C 42.81 %H 3.79 %N 0.00

Compound 25b:
Calculated: %C 35.71 %H 3.19 %N 0.00
Found: %C 35.66 %H 3.22 %N 0.00

Compound 36b:
Calculated: %C 49.93 %H 3.64 %N 0.00
Found: %C 49.79 %H 3.72 %N 0.00

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Chapter 5:

Synthesis and Characterisation of Some Cyclic Tetraphosphonium Ions

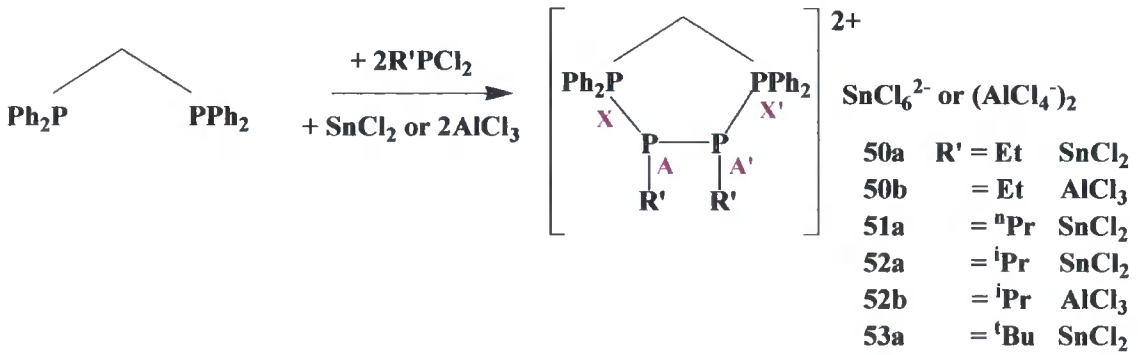
5.1 Introduction

In 1985, Schmidpeter *et al.* demonstrated that alkyl derivatives of cyclic triphosphenium ions could be synthesised in an (n + 1) cycloaddition reaction (Scheme 1.11)[1] Continued work in this area led to the synthesis of some cyclic tetraphosphonium ions containing four adjacent phosphorus atoms linked by a hydrocarbon backbone.[2, 3] These heterocycles were synthesised in a reaction between a diphosphane and $EtPCl_2$ in a novel (n + 1 + 1) cycloaddition reaction, where $SnCl_2$ was required for formation of the tetraphosphonium ion to occur (Scheme 1.21).[2, 3]Although there are several examples of cycles containing four adjacent phosphorus atoms,[4-10] these are the first examples of heterocyclic diphosphonium cations containing four adjacent phosphorus atoms linked by a hydrocarbon backbone.

This chapter outlines the synthesis and characterisation of a series of cyclic tetraphosphonium ions, with and without $SnCl_2$, and also further investigations into the mechanism of formation of these novel heterocycles.

5.2 Synthesis of tetraphosphonium ions from dppm

Attempts to synthesise cyclic triphosphenium ions using dppm had been unsuccessful,[11] possibly because the product would be a four-membered ring, which would be strained and unstable. It was hoped that carrying out the (n + 1 + 1) cycloaddition to afford cyclic tetraphosphonium ions would be more successful, given that the products would be five-membered heterocycles, which are known to be more stable (Scheme 5.1).



Scheme 5.1: Synthetic route to cyclic tetraphosphonium ions derived from dppm

The reaction between dppm and $EtPCl_2$, in the presence of $SnCl_2$, to afford the dppm (R'=Et) tetraphosphonium ion, **50a**, was successful. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed two identical multiplet resonances at 57.5 ppm and -40.8 ppm, as expected for an AA'XX' species (Figure 5.1). The NMR data were analysed as described by Günther[12] (see Appendix 2 for full details of the analysis carried out), with the resulting coupling constants being shown in Table 5.1. Notably, the coupling constants calculated for this compound are similar to those reported for other tetraphosphonium ions (Table 5.2).[2, 3]

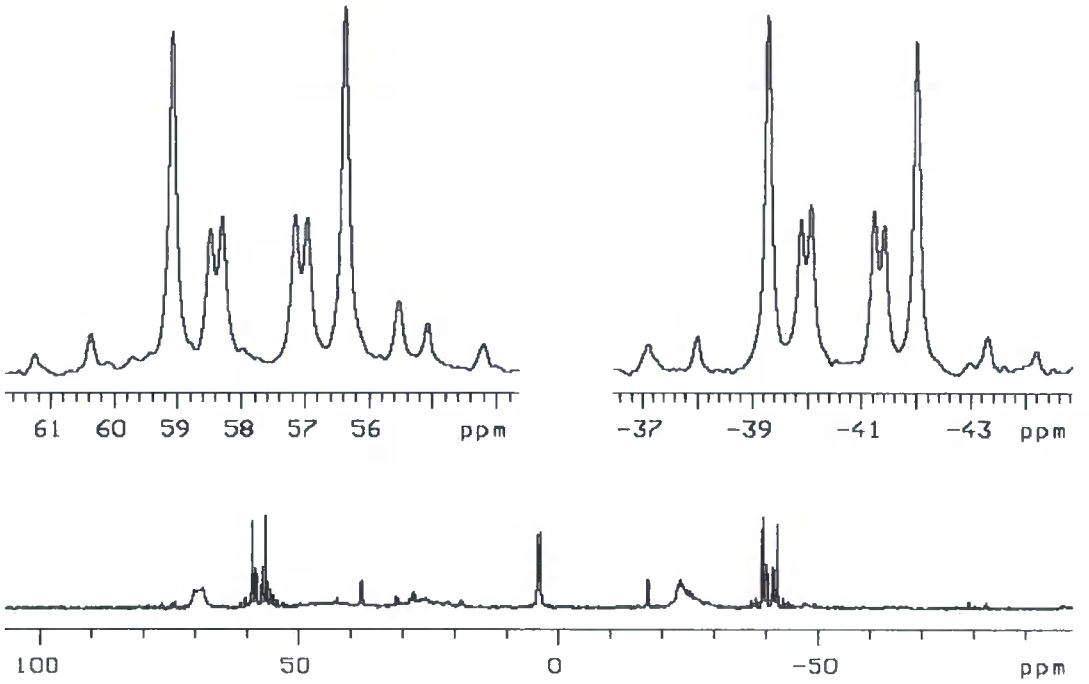


Figure 5.1: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture in the formation of the dppm (R'=Et) cyclic tetraphosphonium ion, **50a**

Compound Number	$R'PCl_2$, R' =	$SnCl_2$ or $AlCl_3$	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
50a	Et	$SnCl_2$	-40.8	57.5	357	-30	175	74
50b	Et	$AlCl_3$	-41.9	55.3	384	-56	280	58
51a	^{n}Pr	$SnCl_2$	-48.7	58.1	-	-	-	-
52a	^{i}Pr	$SnCl_2$	-26.2	51.7	-	-	-	-
52b	^{i}Pr	$AlCl_3$	~ -31	~ 40	-	-	-	-
53a	^{t}Bu	$SnCl_2$	4.2	44.7	339	-9	287	15

Table 5.1: $^{31}P\{^{1}H\}$ NMR data for various dppm cyclic tetraphosphonium ions

Diphosphane	$R'PCl_2$, R' =	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
dppb	Et	-64.7	29.4	289.2	-95.1	263.1	64.0
biphep	Et	-55.9	30.1	321.0	-77.2	121.7	12.5
dppdmx	Et	-41.9	28.5	309.5	-86.5	202.4	123.8
dppe	Et	-73.6	27.3	297.5	-48.1	87.5	2.7

Table 5.2: $^{31}P\{^1H\}$ NMR literature data for other cyclic tetraphosphonium ions [2, 3]

An analogous reaction to afford the dppm (R'=Et) tetraphosphonium ion as its tetrachloroaluminate salt, **50b,** was carried out using $AlCl_3$ instead of $SnCl_2$. The reaction proceeded very slowly. Initial $^{31}P\{^1H\}$ NMR spectra showed three doublets of doublets which were attributed to the formation of an acyclic intermediate, **50bI** (Figure 5.2, Table 5.3).

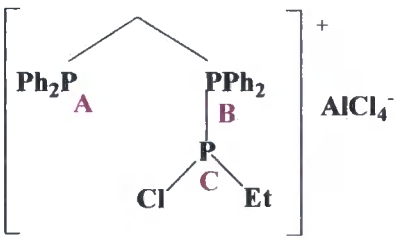


Figure 5.2: The acyclic intermediate **50bI** in the formation of **50b**

δP (ppm)	$^1J_{P\text{-}P}$, Hz	$^2J_{P\text{-}P}$, Hz	$^3J_{P\text{-}P}$, Hz	Assignment
68.6	329	-	87	P_C
26.6	329	66	-	P_B
-27.8	-	66	87	P_A

Table 5.3: $^{31}P\{^1H\}$ NMR data for the acyclic intermediate **50bI** in the formation of **50b**

Upon standing for one week the cyclic tetraphosphonium ion (**50b**) formed, with the $^{31}P\{^{1}H\}$ NMR spectrum showing two identical multiplet resonances at 55.3 ppm and -41.9 ppm. Coupling constants were calculated and were consistent with those previously reported for other tetraphosphonium ions (Table 5.1).

Reaction between $^{n}PrPCl_2$ and $^{i}PrPCl_2$ with dppm in the presence of $SnCl_2$, showed two multiplet resonances corresponding to the tetraphosphonium ions **51a** and **52a** in a $^{31}P\{^{1}H\}$ NMR spectrum taken of the reaction solution (Table 5.1). Precipitation of unidentified products in both reactions, however, led to a poor quality spectrum being obtained, so the coupling constants could not be calculated.

In an analogous reaction between dppm and $^{i}PrPCl_2$ with $AlCl_3$, a $^{31}P\{^{1}H\}$ NMR spectrum run soon after the addition of the chlorophosphane showed evidence of an acyclic intermediate, **52bI** (Figure 5.3, Table 5.4).

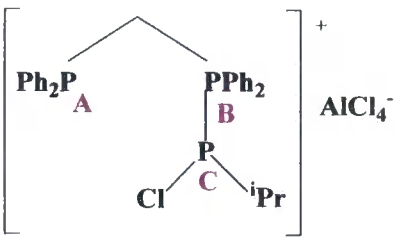


Figure 5.3: The acyclic intermediate **52bI** in the formation of **52b**

δP, ppm	$^{1}J_{P\text{-}P}$, Hz	$^{2}J_{P\text{-}P}$, Hz	$^{3}J_{P\text{-}P}$, Hz	Assignment
79.4	345	-	65	P_C
25.2	345	69	-	P_B
-28.2	-	67	67	P_A

Table 5.4: $^{31}P\{^{1}H\}$ NMR data for the acyclic intermediate **52bI** in the formation of **52b**

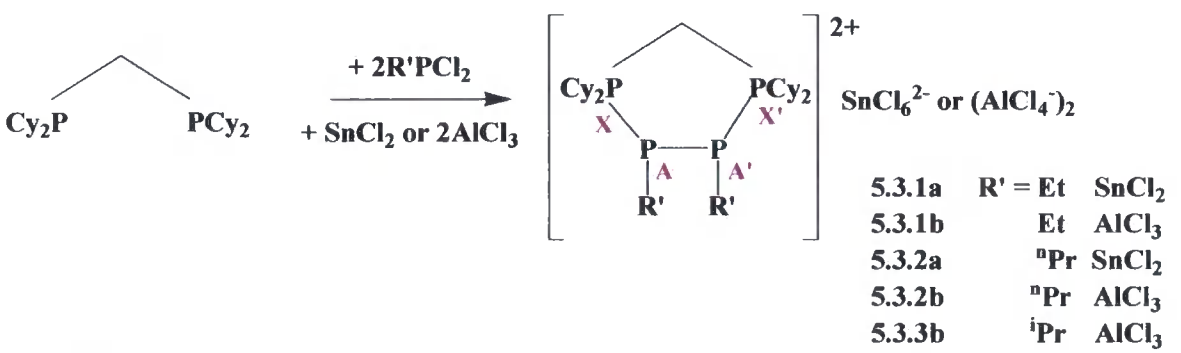
This reaction also proceeded very slowly. One week after the addition of the chlorophosphane two multiplets (δP 40.2 and -31.8 ppm) were visible as the minor

component in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture. However the signals were very weak, and coupling constants could not be calculated.

A reaction between dppm and $^{t}BuPCl_2$ in the presence of $SnCl_2$ proceeded even slower than when using other chlorophosphanes, probably due to the greater steric bulk of the ^{t}Bu groups. The initial $^{31}P\{^{1}H\}$ NMR spectrum showed only resonances corresponding to the starting materials ($^{t}BuPCl_2$ 200.2ppm, dppm -19.4 ppm). After two days new weak signals were observed in the $^{31}P\{^{1}H\}$ NMR spectrum. Heating the reaction mixture led to a noticeable enhancement in the rate of reaction, with new resonances becoming visible in the $^{31}P\{^{1}H\}$ NMR spectrum. These multiplet resonances at 44.7 ppm and 4.2 ppm corresponded to the dppm (R'=^{t}Bu) tetraphosphonium ion, **53a**. Coupling constants were again calculated and were consistent with those reported for similar systems (Table 5.1).

5.3 Synthesis of tetraphosphonium ions from dcypm

Cyclic triphosphenium ions, and their alkyl or aryl derivatives, can be synthesised from the diphosphane dcypm.[13, 14] Synthesis of a tetraphosphonium ion using this diphosphane would afford a five-membered heterocycle (Scheme 5.2).



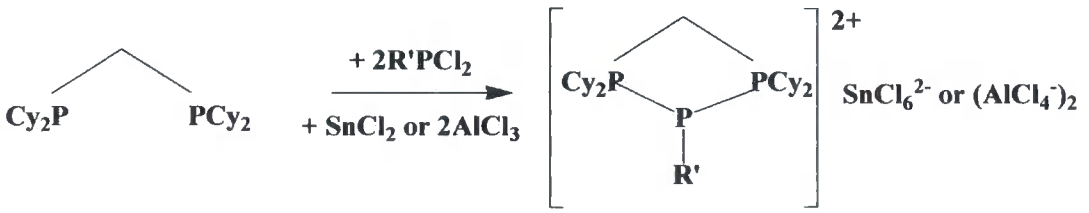
5.3.1a	**R' = Et**	**$SnCl_2$**
5.3.1b	**Et**	**$AlCl_3$**
5.3.2a	**^{n}Pr**	**$SnCl_2$**
5.3.2b	**^{n}Pr**	**$AlCl_3$**
5.3.3b	**^{i}Pr**	**$AlCl_3$**

Scheme 5.2: Synthetic route for cyclic tetraphosphonium ions derived from dcypm

A reaction between dcypm and $EtPCl_2$ in the presence of $SnCl_2$, gave a mixture of products. Two identical multiplets, as expected for an AA'XX' species were visible,

corresponding to the cyclic tetraphosphonium ion **54a** (-51.6 ppm and 54.4 ppm). The calculated coupling constants for this ring were consistent with those for other tetraphosphonium ions (Table 5.5).[2, 3]

In addition to the tetraphosphonium ion, the major product was the P-ethylated derivative (**29b**) (δP_A = -62.8 ppm (t), δP_B = 39.5 ppm(d), $^1J_{P\text{-}P}$ = 157 Hz) (Scheme 5.3).[14] A doublet and triplet corresponding to the dcypm cyclic triphosphenium ion (**1b**) were also apparent (δP_A = -215.2 ppm (t), δP_B = 45.0 ppm (d), $^1J_{P\text{-}P}$ = 333 Hz).[13, 15]



Scheme 5.3: Formation of P-alkylated by-products in the formation of the tetraphosphonium ions

An analogous reaction between dcypm and $EtPCl_2$ in the presence of $AlCl_3$ was also carried out. Similar to the reaction involving $SnCl_2$, the tetraphosphonium ion was not the only product of the reaction. The major product was again the P-ethyl derivative (**29a**) (δP_A = -59.7 ppm (t), δP_B = 40.4 ppm(d), $^1J_{P\text{-}P}$ = 156 Hz) (Scheme 5.3)[14] There was also a small amount of the cyclic triphosphenium ion (**1a**) present in the reaction mixture (δP_A = -215.2 ppm (t), δP_B = 45.4 ppm(d), $^1J_{PP}$ = 333 Hz).[13, 15] The tetraphosphonium ion (**54b**) gave rise to the expected two identical multiplets in the $^{31}P\{^1H\}$ NMR spectrum at -51.9 ppm and 54.4 ppm.

Compound Number	$R'PCl_2$, R' =	$SnCl_2$ or $AlCl_3$	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
54a	Et	$SnCl_2$	-51.6	54.4	290	-36	203	36
54b	Et	$AlCl_3$	-51.9	54.4	288	-36	202	34
55a	^{n}Pr	$SnCl_2$	-49.2	54.0	241	-49	241	8
55b	^{n}Pr	$AlCl_3$	-48.5	57.2	-	-	-	-
56b	^{i}Pr	$AlCl_3$	-37.9	51.8	306	-41	306	46

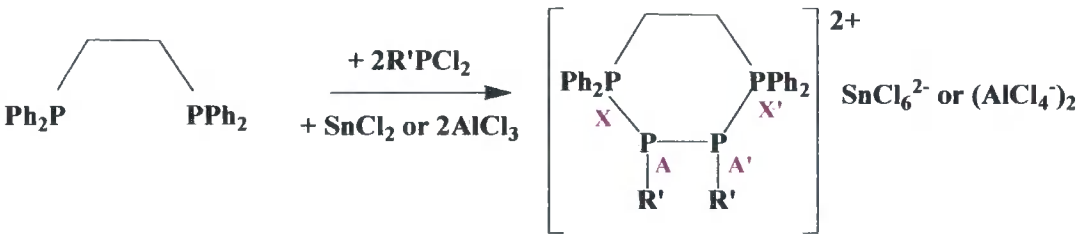
Table 5.5: $^{31}P\{^1H\}$ NMR data for dcypm derived cyclic tetraphosphonium ions

Tetraphosphonium ions were also synthesised from dcypm with $^nPrPCl_2$, as both the hexachlorostannate and tetrachloroaluminate salts (**55a** and **55b**). The reaction to synthesise the dcypm tetraphosphonium using $SnCl_2$ afforded the hexachlorostannate salt, **55a**, as the only product of the reaction (Scheme 5.2). However, the analogous reaction using $AlCl_3$ afforded both the tetraphosphonium ion as its tetrachloroaluminate salt (**55b**) and the P_C-^{n}propyl derivative of the cyclic triphosphenium ion, **40b**, although coupling constants were not calculated as all the peaks were not resolved.

Surprisingly, reactions between dcypm and $^iPrPCl_2$ with $SnCl_2$ showed no evidence of tetraphosphonium ion formation, only the synthesis of the P-^{i}Pr derivative, **41b** (δP_A = -29.1 ppm (t), δP_B = 38.8 ppm (d), $^1J_{P\text{-}P}$ = 152 Hz).[14] A similar reaction carried out using $AlCl_3$, however, gave a mixture of products. Identical multiplets, consistent with an AA'XX' species, **56b**, were observed in the $^{31}P\{^1H\}$ NMR spectrum at 51.8 ppm and -37.9 ppm, and corresponding coupling constants could be calculated from the data obtained (Table 5.5). The other major product was the P-^{i}Pr derivative, **41a** (δP_A = -29.0 ppm (t), δP_B = 38.8 ppm (d), $^1J_{P\text{-}P}$ = 152 Hz) (Scheme 5.3).[14]

5.4 Synthesis of tetraphosphonium ions from dppe

Synthesis of tetraphosphonium ions from dppe would afford six-membered heterocycles which are known to be stable (Scheme 5.4).[15-20]



Scheme 5.4: Synthetic route for cyclic tetraphosphonium ions derived from dppe

An attempt to synthesise a dppe based cyclic tetraphosphonium ion with ethyl groups on the central P atoms using $AlCl_3$ was unsuccessful. A $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture showed no evidence to support tetraphosphonium ion formation, only a doublet and triplet corresponding to the P-ethylated derivative, **23b** (δP_A = -92.8 ppm (t), δP_B = 53.5 ppm (d), $^1J_{P\text{-}P}$ = 287 Hz).[14]

In contrast a cyclic tetraphosphonium ion was successfully synthesised from dppe and $PhPCl_2$ as its hexachlorostannate salt. Two products were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, the desired cyclic tetraphosphonium ion (**57a**) and the P_C-Phenyl 3P derivative of the cyclic triphosphenium ion, **28b** (δP_A = -80.0 ppm (t), δP_B = 52.8 ppm (d), $^1J_{P\text{-}P}$ = 293 Hz).[14] Two identical multiplets corresponding to the cyclic tetraphosphonium ion (δP_A = -73.6ppm, δP_X =27.3 ppm) were apparent. Using the data obtained from the $^{31}P\{^1H\}$ NMR spectrum, coupling constants were calculated (Table 5.6).

Compound Number	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
57a	-73.6	27.3	297	-48	88	3

Table 5.6: $^{31}P\{^1H\}$ NMR data for a dppe based cyclic tetraphosphonium ion, **57a**

Attempts to synthesise cyclic tetraphosphonium ions from dppe with chlorophosphanes such as $^iPrPCl_2$ and $^tBuPCl_2$ were unsuccessful. Only broad signals were observed in the $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture when using $^iPrPCl_2$, and when using $^tBuPCl_2$ the only product of the reaction was the P-^{t}Bu derivative, **26b** (δP_A = -54.2 ppm (t), δP_B = 50.2 ppm (d), $^1J_{P\text{-}P}$ = 336 Hz).[14]

5.5 Synthesis of tetraphosphonium ions from other diphosphanes

Synthesis of cyclic tetraphosphonium ions from dmpm and depe in the presence of $AlCl_3$ were also successful. A reaction between dmpm and $EtPCl_2$ afforded two products, one being the desired tetraphosphonium ion (**58b**) as indicated by the presence of two identical multiplets in a $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture (δP_A = -38.3 ppm, δP_X = 62.1 ppm) (Table 5.7). The outer signals of the multiplet were not observed so coupling constants could not be calculated.

Diphosphane	Compound Number	R'PCl_2, R' =	δP_A, ppm	δP_X, ppm	J, Hz	J', Hz	J_A, Hz	J_X, Hz
dmpm	**58b**	Et	-38.3	62.1	-	-	-	-
depe	**59b**	Ph	-71.1	31.5	307	-30	140	-3

Table 5.7: $^{31}P\{^1H\}$ NMR data for other cyclic tetraphosphonium ions

The second product of the reaction was assigned as monochlorinated dmpm (**60**) (δP_A = -47.6 ppm (d), δP_B = 96.4 ppm (d), $^1J_{P\text{-}P}$ = 72 Hz) as the shift of P_A was consistent with that of the diphosphane itself, the shift of P_B was comparable with those reported for species with P-Me and P-Cl bonds, and also the coupling constant is a reasonable value for $^2J_{P\text{-}P}$ (Figure 5.4 Table 5.8).

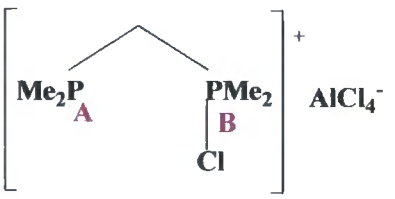


Figure 5.4: Monochlorinated dmpm, **60**

Compound	δP, ppm	Reference
dmpm	-53.5	-
Me_3P^+Cl	87.0	21, 22
$Me_2P^+(C_{18}H_{37})Cl$	94.7	21, 23
$ClPMe_2$	96.0	21

Table 5.8: $^{31}P\{^1H\}$ NMR data for the parent diphosphane dmpm and some R'-$^+PR_2Cl$ and PR_2Cl species

An analogous reaction was carried out between depe and $PhPCl_2$. The major product of the reaction was the tetraphosphonium ion, with two identical multiplet resonances observed in the $^{31}P\{^1H\}$ NMR spectrum (δP_A = -71.1 ppm, δP_X = 31.5 ppm). Coupling constants were calculated from the data obtained and were consistent with those previously reported for other systems (Table 5.7).[2, 3] Two doublet and two triplet resonances were also visible in the $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture. These were assigned to a small amount of the P_C-phenyl derivative containing three adjacent phosphorus atoms but with mixed counter-ions (δP_A = -86.9 ppm (t), δP_B = 58.1

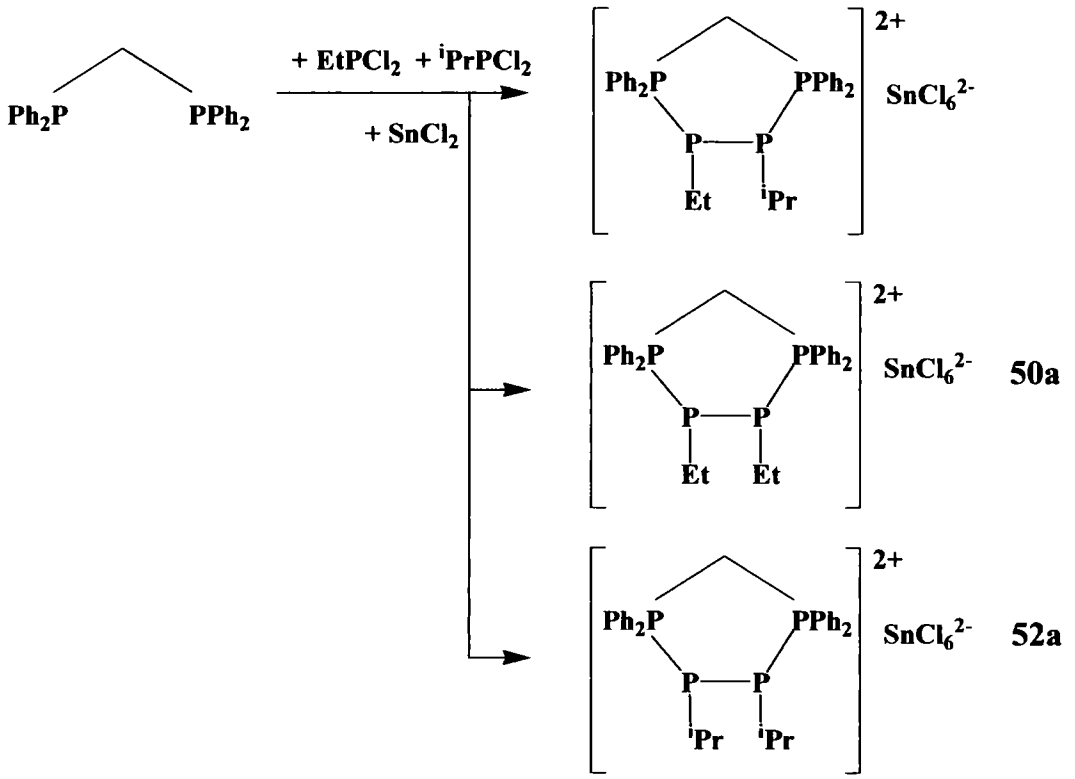
ppm (d), $^{1}J_{P\text{-}P}$ = 283 Hz, δP_A = -87.2 ppm (d), δP_B = 57.3 ppm (d), $^{1}J_{P\text{-}P}$ = 284 Hz) (**21c** and **21d**) (Scheme 5.3).[14]

Reactions involving the diphosphanes dppp and depp with $EtPCl_2$ and $SnCl_2$ did not lead to the formation of the cyclic tetraphosphonium ion. Instead the products of the reactions were the cyclic triphosphenium ion (due to PCl_3 impurity in the $EtPCl_2$) and the P-ethyl derivative in each case. It seems unlikely that the reason for this behaviour is due to steric or electronic effects, as tetraphosphonium ions have been synthesised from equivalent diphosphanes containing just one CH_2 less in their hydrocarbon backbone. This suggests that the main factor is the ring stability, as the cyclic triphosphenium ion and the P-ethyl derivatives are six-membered rings, whereas the tetraphosphonium ions would be seven-membered rings. In these cases the more stable six-membered rings are formed in preference to the less stable seven-membered rings.

5.6 Attempted synthesis of a 'mixed' tetraphosphonium ion

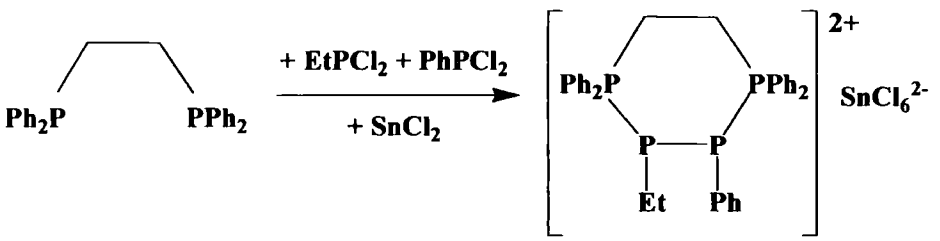
An attempt to synthesis a 'mixed' tetraphosphonium ion was carried out by reacting dppm with $EtPCl_2$ and $^{i}PrPCl_2$ (Scheme 5.4). Using this method, the formation of three products is possible: the 'mixed' species, the ethyl derivative **50a**, and/ or the *iso*-propyl derivative, **52a** (Scheme 5.5).

A $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after the addition of the two chlorophosphanes showed three singlets corresponding to dppm (-19.4 ppm), $EtPCl_2$ (198.3 ppm) and $^{i}PrPCl_2$ (δP 200.4 ppm). Clearly no reaction had taken place. Upon standing for two hours, colourless crystals had formed which were suitable for analysis by X-ray diffraction. Analysis showed the structure to be the ethyl derivative (**50ap**). The resulting molecular structure is described in Section 5.7.



Scheme 5.5: Proposed synthetic route to a 'mixed' cyclic tetraphosphonium ion and possible by-products

An attempt to synthesise a 'mixed' tetraphosphonium ion from dppe using one equivalent of $EtPCl_2$ and one equivalent of $PhPCl_2$ in the presence of $SnCl_2$ was also carried out (Scheme 5.6). Since cyclic tetraphosphonium ions with both ethyl and phenyl groups on the central phosphorus atoms, and the P-ethyl and P-phenyl 3P derivatives, had been successfully synthesised, it would be easy to identify known products if a mixture formed.



Scheme 5.6: Proposed synthesis of a 'mixed' cyclic tetraphosphonium ion

A $^{31}P\{^{1}H\}$ NMR spectrum was recorded soon after the addition of the chlorophosphanes and clearly indicated that a mixture of products had formed, including the dppe cyclic triphosphenium ion, **4b** (δP_A = -230.0 ppm (t), δP_B = 65.2 ppm (d), $^{1}J_{P\text{-}P}$ = 452 Hz) [15, 16, 18, 24, 25] and the P-ethylated derivative, **23b** (δP_A = -96.2 ppm (t), δP_B = 53.6 ppm(d), $^{1}J_{P\text{-}P}$ = 299 Hz) (Scheme 5.3).[14]

These two attempts to synthesise 'mixed' tetraphosphonium ions have been unsuccessful. Further investigations could involve reactions where acyclic intermediates were observed, *e.g.* dppm with $EtPCl_2$ in the presence of $AlCl_3$ (Section 5.2). It is possible that addition of a second dichlorophosphane at this stage could afford a 'mixed' species.

5.7 Molecular structures of cyclic tetraphosphonium ions derived from dppm and dcypm

Colourless crystals were obtained from a solution of **50a** formed from a reaction between dppm, $EtPCl_2$ and $SnCl_2$. The crystals were suitable for analysis by X-ray diffraction; the resulting molecular structure is shown in Figure 5.5. Within the unit cell there is one $SnCl_6^{2-}$ counter-ion for the dication and two molecules of $CHCl_3$.

The same dication was isolated from the attempted synthesis of a 'mixed' cyclic tetraphosphonium ion from dppm, $EtPCl_2$, $^{i}PrPCl_2$ and $SnCl_2$ (Figure 5.6). There are two half molecules of $SnCl_6^{2-}$ as counter-ions for the dication and no molecules of solvent, making this a pseudo-polymorph of **50a** and is designated **50ap**.

In both **50a** and **50ap** there is one molecule per asymmetric unit, meaning that there is not symmetry between the atoms in the dication. By overlaying the two structures it is clear that there is little difference in the five-membered rings consisting of four phosphorus atoms and one carbon atom, although there are some differences in the orientation of the substituents on the phosphorus atoms (Figure 5.7). This is not

surprising, as differences within the main ring would be caused by different electronic effects (*i.e.* none in this case), whereas changes in the packing/steric effects due to the presence of counter-ions and solvent molecules would account for the differences in the rest of the stuctures. There are no significant differences between **50a** and **50ap** in the packing, hydrogen bonding or contacts.

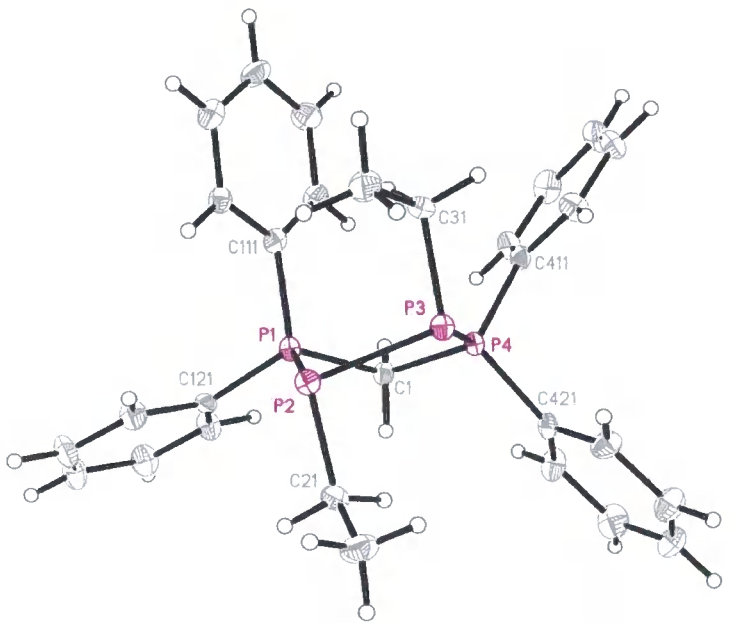


Figure 5.5: The crystal and molecular structure of the dication **50a**
The solvent and $SnCl_6^{2-}$ counter-ion have been omitted for clarity.
Thermal ellipsoids are drawn at 50% probability.

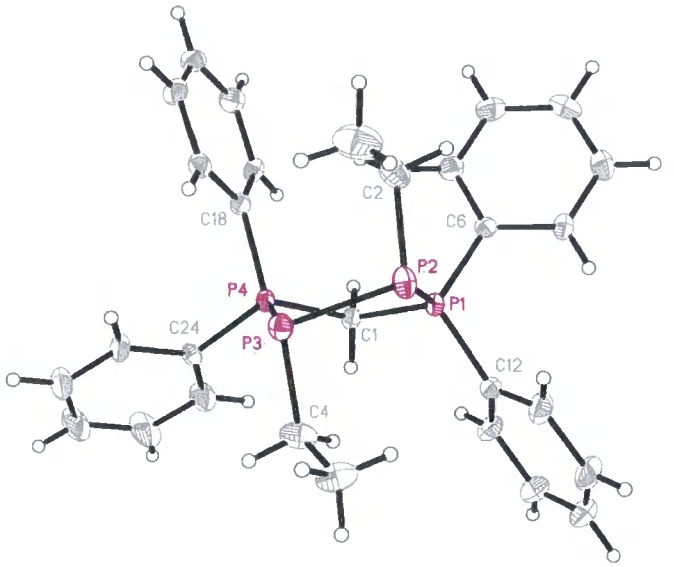


Figure 5.6: The crystal and molecular structure of the dication **50ap**
The two half molecules of $SnCl_6^{2-}$ as counter-ions have been omitted for clarity.
Thermal ellipsoids are drawn at 50% probability.

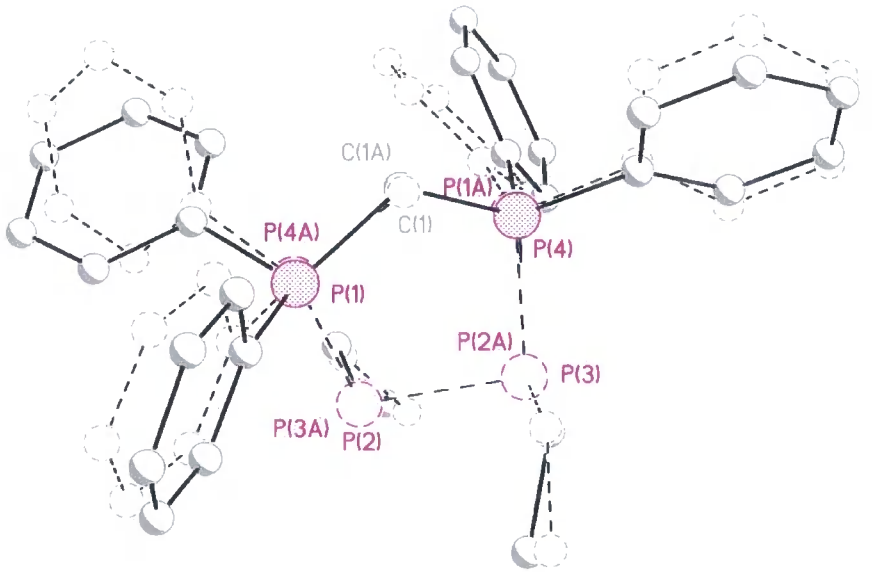


Figure 5.7: Overlap of the dications **50a** and **50ap**

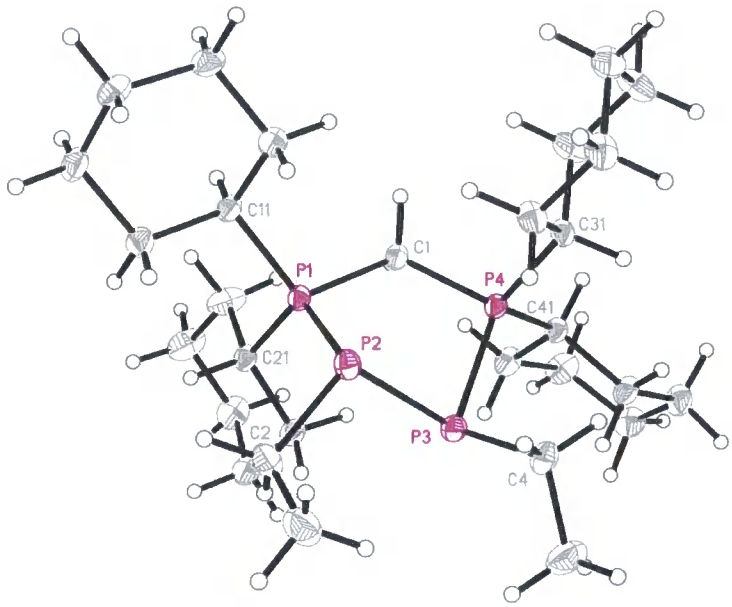


Figure 5.8: The crystal and molecular structure of the dication **54b**
Thermal ellipsoids are drawn at 50% probability.

Another five-membered ring cyclic tetraphosphonium ion, **54b**, formed from a reaction between dcypm, $EtPCl_2$ and $SnCl_2$, was isolated as a crystalline product. The crystals were suitable for analysis by X-ray diffraction; the resulting molecular structure is shown in Figure 5.8. Within the unit cell there two $AlCl_4^-$ counter-ions for the dication and one molecule of $CHCl_3$. Selected bond lengths and angles for **50a**, **50ap** and **54b** are shown in Table 5.9.

In all three structures the P-P bond lengths [average P-P bond = 2.2903 Å (**50a**), 2.200 Å (**50ap**) and 2.2066 Å (**54b**)] are typical values for normal P-P single bonds. They are similar to those found in the 3P-alkyl derivatives of cyclic triphosphenium ions (2.197(4)-2.2327(9)°),[14] and also those reported for other compounds containing four adjacent phosphorus atoms (2.185(7) and 2.2387(6) Å) (Figure 5.9).[4-8]

Bond Length /Å	50a	50ap	54b
P(1)–P(2)	2.2310(16)	2.2055(17)	2.1946(6)
P(2)–P(3)	2.2154(17)	2.2045(18)	2.2343(6)
P(3)–P(4)	2.1814(16)	2.1904(17)	2.1910(6)
P(1)–C(121)	1.801(5)	1.790(5)	1.8333(16)
P(2)–C(21)	1.8767(5)	1.855(5)	1.8560(18)
Bond Angle / °			
P(1)–P(2)–P(3)	97.74(6)	99.23(7)	92.25(2)
P(2)–P(3)–P(4)	97.10(6)	96.68(6)	92.23(2)

Table 5.9: Selected bond lengths and bond angles for dications **50a, 50ap** and **54b**

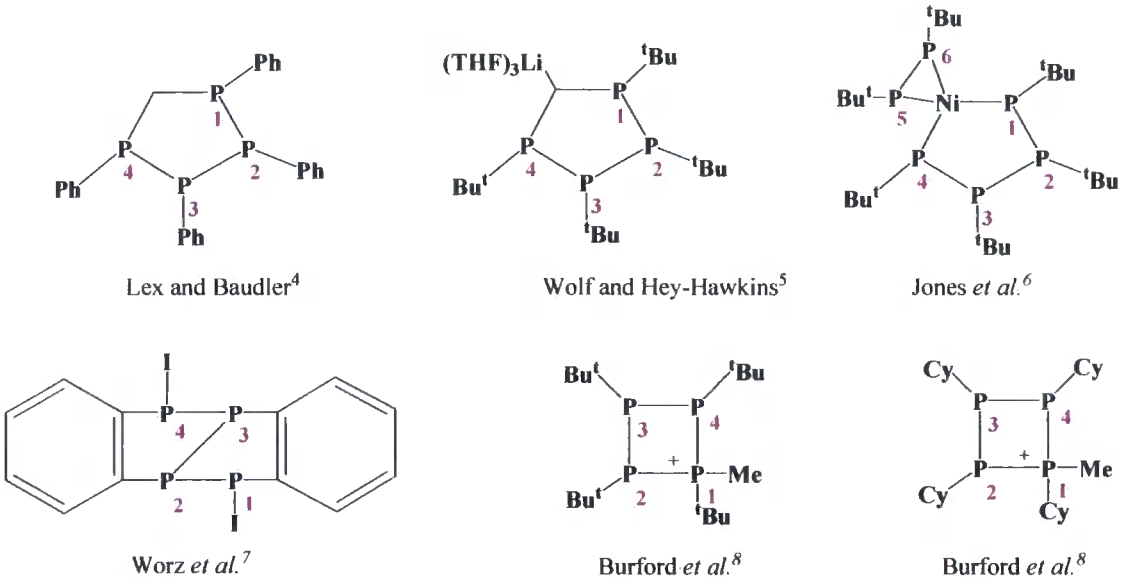


Figure 5.9: Other literature compounds containing four adjacent P atoms

For all three dications **50a, 50ap** and **54b**, the P-P-C bond angles are larger that the P-P-P angles, which suggests a large P-orbital contribution to the P-P bonding within the structures. For **54b**, the P-P-P bond angles are 92.25(2) and 92.23(3)°. These are close to the ideal bond angle, 90°, for bonding which involves P orbitals only, and no hybridisation. Similar bond lengths and angles are observed in the tetraphosphonium ion

derived from biphep by Boyall (Figure 1.12).[3] In this tetraphosphonium ion the P-P-P bond angles (91.196(6) and 94.45(7)°) are again much smaller than the P-P-C angles, and are close to 90°, suggesting a large P-orbital contribution to bonding.

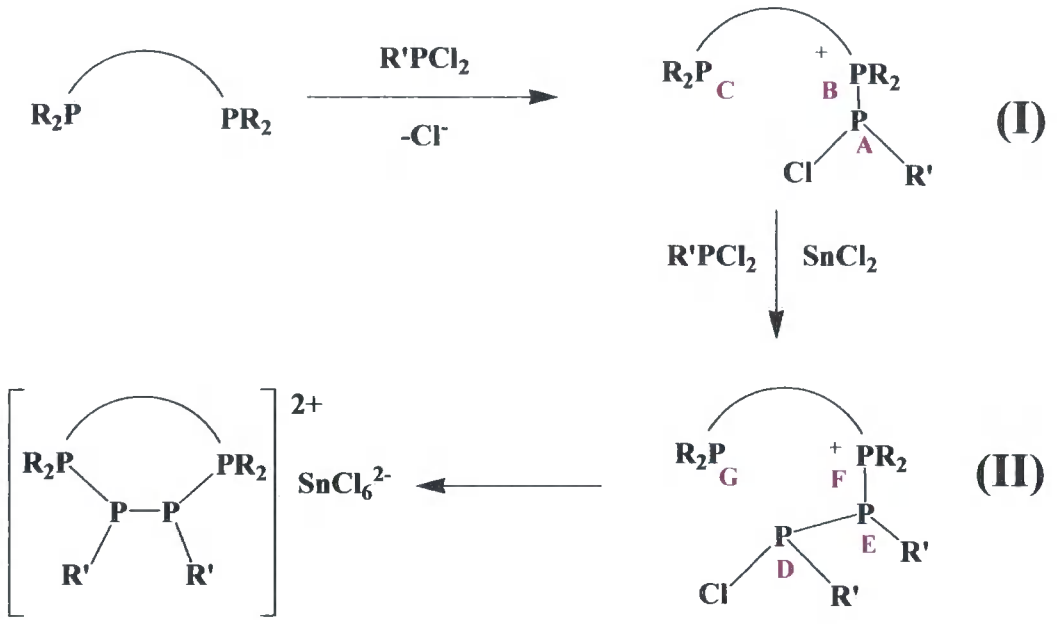
5.8 Conclusions

This study has shown that the formation of five- and six-membered cyclic triphosphenium ion derivatives containing various alkyl or aryl groups on the central P atoms and/or outer P atoms is possible, although reactions are slower when there are bulkier substituents on either the four-coordinate P atoms or the dichlorophosphane.

The synthesis of seven-membered tetraphosphonium ions has been unsuccessful. Several reactions have been carried out in an attempt to synthesise a seven-membered analogue but these reactions resulted in the formation of the more stable six-membered cyclic triphosphenium ion or P-alkyl derivative in preference.

These studies have also provided more evidence to support the proposed mechanism of formation of cyclic tetraphosphonium ions (Scheme 5.7). The first step necessarily involves the addition of the chlorophosphane to the diphosphane to form an acyclic intermediate (**I**). Evidence for this step was observed in reactions involving the diphosphane dppm, with both $EtPCl_2$ and $^{i}PrPCl_2$ in the presence of $AlCl_3$. The next step involves the formation of an unsymmetrical intermediate (**II**), as shown by Boyall.[2, 3] The final step is cyclisation to afford the tetraphosphonium ion.

While a reducing agent is required to synthesise these novel heterocycles, it has now been shown that using $SnCl_2$ is not necessary, however, as the diphosphanes themselves can act as reducing agents to allow the second addition to take place.



Scheme 5.7: Proposed mechanism of formation of cyclic tetraphosphonium ions

X-ray crystallographic studies carried out on two polymorphs of the cyclic tetraphosphonium ion synthesised from dppm, $EtPCl_2$ and $SnCl_2$, and also a tetraphosphonium ion derived from dcypm. These studies have confirmed the presence of single P-P bonds.

5.9 Experimental

Example reactions:

Using $AlCl_3$:

$PhPCl_2$ (0.27 mL, 0.44 mmol) was added via syringe to a solution of dppe (0.0598 g, 0.44 mmol), and $AlCl_3$ (0.5220 g, 0.87 mmol) under a nitrogen atmosphere. A $^{31}P\{^1H\}$ NMR spectrum was recorded soon after mixing.

Using $SnCl_2$:

$PhPCl_2$ (0.03 mL, 0.222 mmol) was added via syringe to a solution of dppe (0.0801 mL, 0.20 mmol), and $SnCl_2$ (0.0533 g, 0.40 mmol) under a nitrogen atmosphere. A $^{31}P\{^1H\}$ NMR spectrum was recorded soon after mixing.

Using two chlorophosphanes:

A solution of $EtPCl_2$ (0.04 mL, 0.44 mmol) and $PhPCl_2$ (0.06 mL, 0.44 mmol) was added via syringe to a solution of dppe (0.1720 g, 0.43 mmol), and $SnCl_2$ (0.1642 g, 0.87 mmol) under a nitrogen atmosphere. A $^{31}P\{^1H\}$ NMR spectrum was recorded soon after mixing.

Diphosphane	Compound number	Quantity of diphosphane		Quantity of $RPCl_2$		Quantity of $SnCl_2$/ $AlCl_3$	
		g	mmol	mL	mmol	g	mmol
dppm	**50a**	0.0503	0.13	0.030	0.28	0.0512	0.27
dppm	**50b**	0.0645	0.17	0.050	0.51	0.0476	0.35
dppm	**51a**	0.0577	0.15	0.040	0.30	0.0569	0.42
dppm	**52a**	0.0462	0.12	0.030	0.33	0.0460	0.34
dppm	**52b**	0.0493	0.13	0.050	0.39	0.0356	0.26
dppm	**53**	0.0307	0.08	0.0257†	0.16	0.0306	0.16
dcypm	**54a**	0.0497	0.12	0.030	0.28	0.0325	0.24
dcypm	**54b**	0.0419	0.10	0.010	0.10	0.0267	0.20
dcypm	**55a**	0.0360	0.09	0.028	0.27	0.0341	0.18
dcypm	**55b**	0.0394	0.10	0.013	0.10	0.0267	0.20
dcypm	**56b**	0.0402	0.10	0.012	0.10	0.0267	0.20
dppe *	**57a**	0.3306	0.83	0.230	1.69	0.2220	1.66
dppe	**57b**	0.0801	0.20	0.030	0.22	0.0533	0.40
dmpm	**58b**	0.0268	0.20	0.020	0.22	0.0533	0.40
depe*	**59b**	0.4037	1.96	0.270	1.96	0.5220	3.91

* reaction carried out in a Schlenk , † $RPCl_2$ is a solid so quantity is in g

Unsuccessful Reactions - Quantities of reagents used:

Reaction	Quantitiy of diphosphane		Quantity of $RPCl_2$		Quantity of $SnCl_2$/ $AlCl_3$	
	g	mmol	mL	mmol	g	mmol
dppe $EtPCl_2$ and $AlCl_3$	0.1372	0.34	0.070	0.68	0.0906	0.68
dppe $^{i}PrPCl_2$ and $SnCl_2$	0.1026	0.23	0.060	0.44	0.0992	0.52
dppe $^{t}BuPCl_2$ and $SnCl_2$	0.0657	0.17	0.050	0.33	0.0449	0.34
dppp $EtPCl_2$ and $SnCl_2$	0.0427	0.10	0.020	0.20	0.0492	0.26
depp $EtPCl_2$ and $SnCl_2$	0.0228	0.07	0.020	0.19	0.0270	0.14
dppm $^{i}PrPCl_2$ $EtPCl_2$ and $SnCl_2$	0.0263	0.07	0.007	0.07	0.0265	0.14
			0.009	0.07		
dppe $^{i}PrPCl_2$ $EtPCl_2$ and $SnCl_2$	0.1720	0.43	0.040	0.44	0.1642	0.87
			0.060	0.44		

Elemental analysis

Compound 50a:
Calculated: %C 34.65 %H 3.19 %N 0.00
Found: %C 34.71 %H 3.23 %N 0.00

Compound 50ap:
Calculated: %C 41.67 %H 3.86 %N 0.00
Found: %C 42.87 %H 3.84 %N 0.00

Isolation of compounds:

For compounds **50a**, **50ap** and **54b** crystals suitable for analysis by X-ray diffraction were obtained through evaporation of solvent in an inert atmosphere. It is noteworthy that these compounds, along with the other described in this chapter, are sensitive to both air and moisture.

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Chapter 6:

Synthesis and Characterisation of Some Pt(II) Complexes of Cyclic Triphosphenium Ions

6.1 Introduction

There have been limited investigations into the coordination properties of cyclic triphosphenium ions. Previous work has involved the reaction between some cyclic triphosphenium ions and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (Scheme 1.16).[1] The results obtained suggested that complexation with ring-retention did not take place if the cyclic triphosphenium ion had phenyl groups on both the four-coordinate phosphorus atoms. Instead ring scission and coordination of the diphosphane to the platinum centre occurred. In contrast, for cyclic triphosphenium ions with other groups on the four-coordinate phosphorus atoms (*e.g.* Et, Cy, ^{t}Bu) complexation with ring-retention does take place.[1]

For each of these cyclic triphosphenium ion complexes the most interesting and unusual feature was the $^1J_{Pt\text{-}P}$ coupling constant to the phosphenium central P, which had values between 1059 and 1222 Hz for *cis*, and 1023 Hz for the *trans* complex containing the

dcype cyclic triphosphenium ion, **3a**. These values are unusually small for a one-bond phosphorus-platinum coupling, and could indicate a long Pt-P bond. Unfortunately crystalline products were not obtained for any of these complexes, hence X-ray diffraction studies could not be used to probe the presence of a long Pt-P bond consistent with the small $^{1}J_{Pt\text{-}P}$ value. Preliminary calculations by Dr. M. A. Fox for the model compound $PtCl_2(PMe_3)[P(P(Me_2)_2(CH_2)_2]^+$ have suggested that the Pt-P bond length in *trans* isomers in particular might be as long as 2.39 or 2.43 Å.[2] Platinum is a difficult element to model, however, so no firm conclusions can be drawn until a crystal structure is obtained.

The longest reported Pt-P bond length in a Pt(II) compound with two chloro ligands and two P ligands is for trans-bis(di-t-butyl(isopropyl))phosphane dichloroplatinum(II) at 2.388(2) Å.[3, 4] The shortest Pt-P bond length in such compounds, 2.1337(19) Å, was reported by Carty *et al.* for a compound containing three bisphosphino diyne ligands which are bridging three *cis* square planar platinum centers (Figure 6.1).[4, 5]

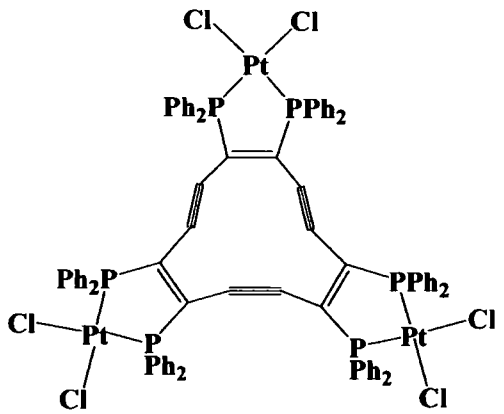


Figure 6.1: Structure reported by Carty *et al.* containing three bisphosphino diyne ligands which are bridging three *cis* square planar platinum centres[5]

For all reported Pt(II) complexes containing two P ligands and two chloro ligands, the mean Pt-P bond length is 2.250 Å. In 2005 Woollins *et al.* reported the synthesis and structure of (allylamino(diphenyl)phosphane)-dichloro-(dimethylphenylphosphine) platinum containing Pt-P bonds of 2.250 Å.[4, 6]

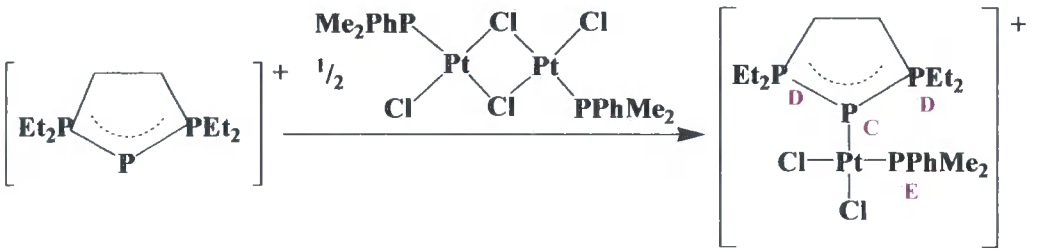
The first part of this chapter describes the reaction between cyclic triphosphenium ions and *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ (**61**), *trans*-[Pt($PPhMe_2$)Cl(μ-Cl)]$_2$ (**62**) and/or *trans*-[Pt(PPh_2Me)Cl(μ-Cl)]$_2$ (**63**). By changing the phosphane ligand from PEt_3 to $PPhMe_2$ or PPh_2Me using the different Pt dimers (**61-63**), several new Pt(II) complexes containing cyclic triphosphenium ions could be synthesised and it was hoped that crystal growth would be more favourable. The second part of this chapter describes the synthesis of some Pt(II) complexes containing chlorophosphanes, which were originally formed as by-products in reactions between *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ and cyclic triphosphenium ions if there was any residual PCl_3 in the reaction mixture. Also discussed is a study of the hydrolysis of these chlorophosphane complexes. In all the complexes synthesised in this chapter, Pt satellites were observed in the $^{31}P\{^1H\}$ NMR spectra, and the $^1J_{Pt\text{-}P}$ values are included in the appropriate tables.

6.2 Synthesis of Pt(II) complexes containing five-membered ring cyclic triphosphenium ions

6.2.1 Reaction of the depe cyclic triphosphenium ions 2a and 2b with *trans*-[Pt($PPhMe_2$)Cl(μ-Cl)]$_2$ and *trans*-[Pt(PPh_2Me)Cl(μ-Cl)]$_2$

Since previous reactions between the depe cyclic triphosphenium ion and the *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ had been successful,[1] but no materials suitable for a molecular structure determination were obtained, reactions were carried out using both **62** and **63**.

A reaction between *trans*-[Pt($PPhMe_2$)Cl(μ-Cl)]$_2$ (**62**) and the depe cyclic triphosphenium ion, **2b**, afforded two platinum complexes, one being the desired *cis* complex (**64b**) (Scheme 6.1). The $^{31}P\{^1H\}$ NMR data were consistent with those previously reported for *cis* complexes containing cyclic triphosphenium ions (Table 6.1).[1]



Scheme 6.1: Synthesis of the *cis* Pt(II) complex (**64b**) from the depe cyclic triphosphenium ion and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$

The second complex (**65**) observed in the $^{31}P\{^1H\}$ NMR spectrum was a minor component of the reaction mixture (δP_A 103.2 ppm, $^1J_{Pt\text{-}PA}$ = 5926 Hz, $^2J_{P\text{-}P}$ = 17 Hz, δP_B -5.5 ppm, $^1J_{Pt\text{-}PB}$ = 3142 Hz, $^2J_{P\text{-}P}$ = 17 Hz) and was formed in a side reaction between unreacted PCl_3 and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (Figure 6.2). This will be discussed in more detail in Section 6.7.1.1

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
69.3	d	$^1J_{PD\text{-}PC}$ = 359	P_D
-14.0	s	$^1J_{Pt\text{-}PE}$ = 3534	P_E
-113.2	t	$^1J_{PC\text{-}PD}$ = 359, $^1J_{Pt\text{-}PC}$ = 1120	P_C

Table 6.1: $^{31}P\{^1H\}$ NMR data for the *cis* Pt(II) complex (**64b**) from the reaction between the depe cyclic triphosphenium ion and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$

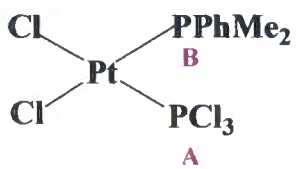


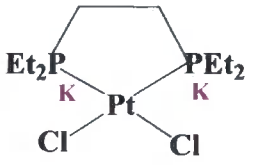
Figure 6.2: Product of the reaction between *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ and PCl_3 (**65**)

Complexation of the cyclic triphosphenium ion did not occur in a reaction between **2a** and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ (**63**). A $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture showed signals corresponding to unreacted cyclic triphosphenium ion, and two

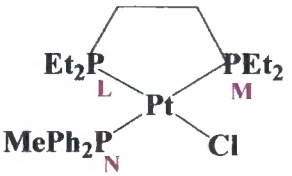
other Pt(II) complexes containing the diphosphane, **66** and **67** (Table 6.2, Figure 6.3). The data suggest that the cyclic triphosphenium ring broke up, allowing complexation of the diphosphane to the platinum centre to occur.

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
81.5	d	$^{1}J_{PB\text{-}PA} = 443$	P_B
71.7	d	$^{1}J_{PM\text{-}PN} = 375$, $^{1}J_{Pt\text{-}PM} = 2350$	P_M
58.9	s	$^{1}J_{Pt\text{-}PK} = 3551$	P_K
55.1	d	$^{2}J_{PL\text{-}PN} = 16$, $^{1}J_{Pt\text{-}PL} = 3338$	P_L
3.0	d	$^{1}J_{PN\text{-}PM} = 375$, $^{1}J_{Pt\text{-}PN} = 2261$, $^{2}J_{PN\text{-}PL} = 16$	P_N
-269.4	t	$^{1}J_{PA\text{-}PB} = 443$	P_A

Table 6.2: $^{31}P\{^{1}H\}$ NMR data for **66** and **67** formed in the reaction between the depe cyclic triphosphenium ion and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$



66



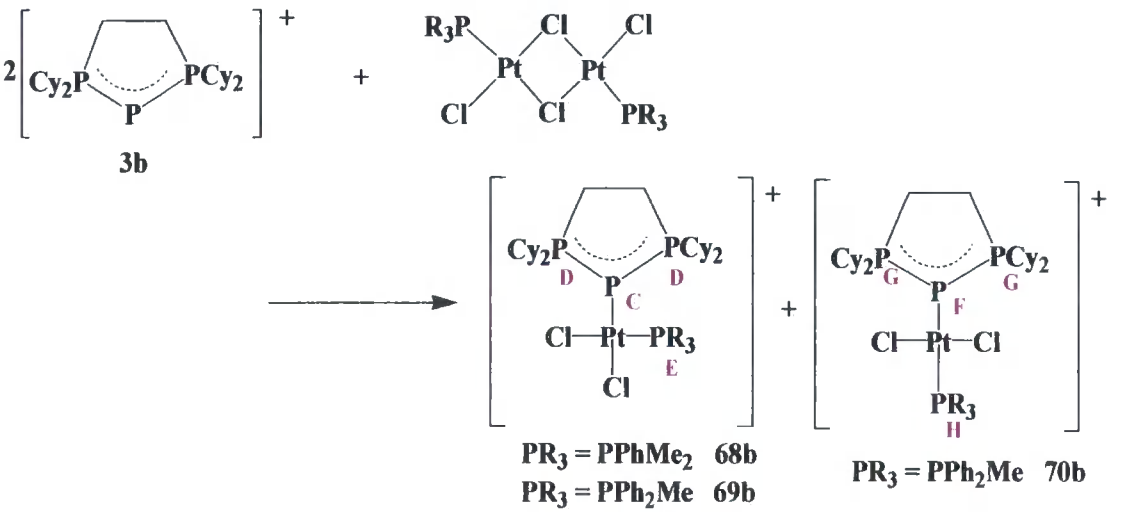
67

Figure 6.3: Products of the reaction between the **2a** and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$

A reaction between the depe cyclic triphosphenium ion as its hexachlorostannate salt, **2b**, and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ also resulted in the complexation of the diphosphane to the platinum centre to afford complexes **66** and **67**.

6.2.2 Reaction of the dcype cyclic triphosphenium ion, 3b, with *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$

Both the *cis* and *trans* complexes containing the dcype cyclic triphosphenium ion had been successfully synthesised from *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, but unfortunately no crystals were obtained.[1]



Scheme 6.2: Proposed reaction between the dcype cyclic triphosphenium ion and *trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$

In a reaction between **3b** and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (**62**), the $^{31}P\{^1H\}$ NMR spectrum recorded 15 minutes after the addition of the dimer showed signals corresponding to some un-reacted dimer (δP 16.9 ppm, $^1J_{Pt-P}$ = 3926 Hz) and the *cis* complex, **68b** (Scheme 6.2, Table 6.3). Subsequent $^{31}P\{^1H\}$ NMR spectra showed no further reaction.

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
69.9	d	$^1J_{PD\text{-}PC}$ = 381	P_D
-19.6	s	$^1J_{Pt\text{-}PE}$ = 3492	P_E
-111.6	t	$^1J_{PC\text{-}PD}$ = 381, $^1J_{Pt\text{-}PC}$ = 1179	P_C

Table 6.3: $^{31}P\{^1H\}$ NMR data for the *cis* complex **68b,** formed in the reaction between the dcype cyclic triphosphenium ion (**3b**) and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (**62**)

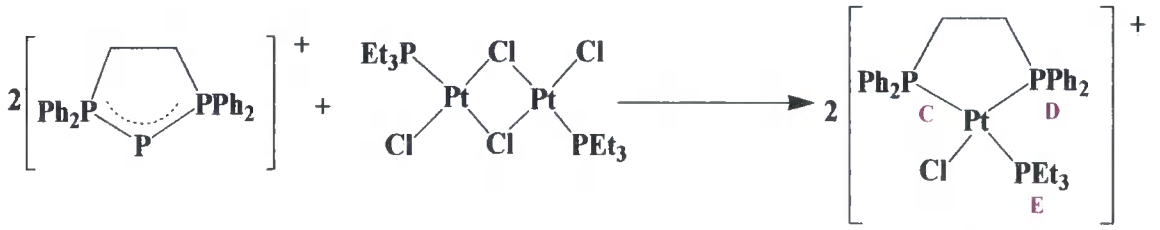
A reaction was also carried out using the dcype cyclic triphosphenium ion, **3b**, and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ (**63**). A $^{31}P\{^1H\}$ NMR spectrum recorded soon after mixing showed signals corresponding to unreacted cyclic triphosphenium ion, **3b**, (δ_{PA} = -288.9 ppm (t), δ_{PB} = 87.2 ppm (d), $^1J_{P\text{-}P}$ = 455 Hz), but also those corresponding to both the *cis* (**69b**) and *trans* (**70b**) complexes (Scheme 6.2, Table 6.4).

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
72.9	d	$^1J_{PD\text{-}PC}$ = 392	P_D
72.1	d	$^1J_{PG\text{-}PF}$ = 380	P_G
14.4	d	$^2J_{PH\text{-}PF}$ = 214, $^1J_{Pt\text{-}PH}$ = 2783	P_H
0.2	s	$^1J_{Pt\text{-}PE}$ = 3625	P_E
-104.1	t	$^1J_{Pt\text{-}PC}$ = 1183, $^1J_{PC\text{-}PD}$ = 392	P_C
-124.7	dt	$^1J_{PF\text{-}PG}$ = 380, $^2J_{PF\text{-}PH}$ = 215, $^1J_{Pt\text{-}PF}$ = 1032	P_F

Table 6.4: $^{31}P\{^1H\}$ NMR data for the *cis* (**69b**) and *trans* (**70b**) complexes formed in the reaction between *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ (**63**) and the dcype cyclic triphosphenium ion (**3b**)

6.2.3 Reaction of the dppe cyclic triphosphenium ion, 4a, with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$

Previous reactions between *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ (**61**) and the dppe cyclic triphosphenium ion **4a** had shown no evidence to support coordination of the ring to the platinum centre.[1] It appeared that the cyclic triphosphenium ion had broken up and coordination of the diphosphane had occurred (Scheme 6.3).[1] This reaction between **4a** and **61** was repeated to confirm ring scission. A $^{31}P\{^1H\}$ NMR spectrum was recorded as soon as possible after the addition of *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ to a solution of the dppe cyclic triphosphenium ion (Table 6.5).



4a **61** **71**

Scheme 6.3: Proposed reaction between the dppe cyclic triphosphenium ion, **4a**, and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, **61**

The spectrum showed several species to be present, including the dppe cyclic triphosphenium ion, **4a**, (δP_A = -229.5 ppm (t), δP_B = 65.0ppm (d), $^1J_{P\text{-}P}$ = 450 Hz). As previously reported, the ring did not coordinate to the platinum, but instead underwent ring scission, resulting in the coordination of the diphosphane in a bidentate fashion, **71** (Table 6.5). The chemical shifts and coupling constants were consistent with those previously reported.[1] The singlet resonance observed at 48.3 ppm ($^1J_{Pt\text{-}P}$ = 2356 Hz) corresponds to the [Pt (dppe)$_2$]$^{2+}$ complex, **72**.[7, 8]

δP, ppm	$^1J_{PA-PB}$, Hz	$^2J_{PC-PE}$, Hz	$^2J_{PE-PD}$, Hz	$^2J_{PC-PD}$, Hz	$^1J_{Pt-P}$, Hz	Assignment
53.5	-	369		7	2260	P_C
43.7	-	-	17	7	3542	P_D
17.2	-	369	17	-	2282	P_E

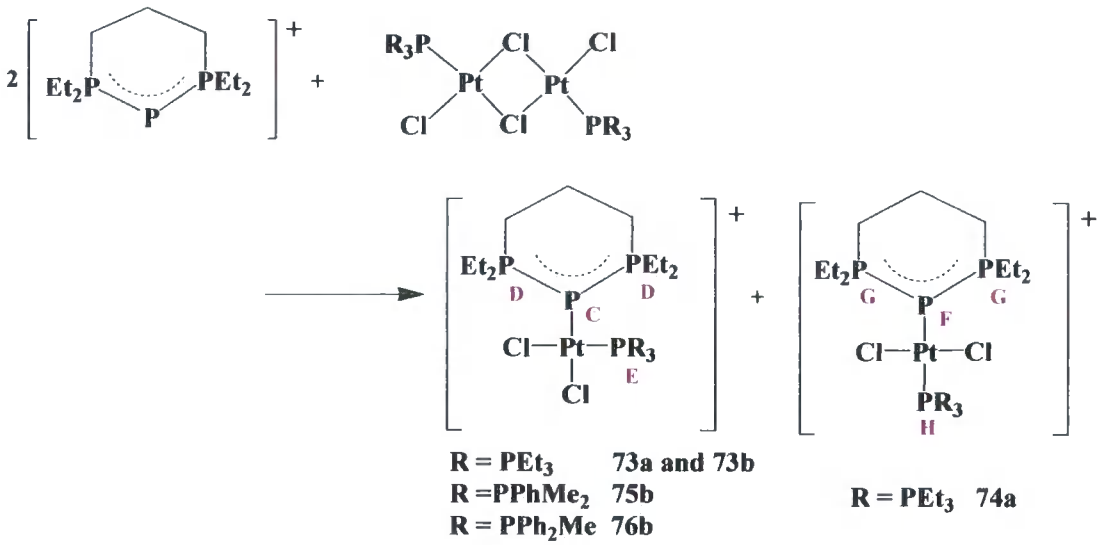
Table 6.5: $^{31}P\{^1H\}$ NMR data for **71** obtained from the reaction between the dppe cyclic triphosphenium ion, **4a**, and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ **61**.

6.3 Synthesis of Pt(II) complexes containing six-membered ring cyclic triphosphenium ions

6.3.1 Reactions of the depp cyclic triphosphenium ion, 6a and 6b, with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

Both the *cis* and *trans* complexes **73a** and **74a** have been successfully synthesised, previously, from the depp ring, **6a**, with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, **61**, although not all the Pt-P coupling constants were reported due to weak satellite peaks,[1] and unfortunately, crystalline products had not been obtained.

The reaction between **6a**, and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, **61**, was repeated to obtain further NMR data for the resulting products (Scheme 6.4). A $^{31}P\{^1H\}$ NMR spectrum was recorded soon after the addition of **61** to a solution of **6a** which showed signals corresponding to both the *cis*- (**73a**) and *trans*- (**74a**) complexes (Table 6.6). Also a doublet and triplet corresponding to some unreacted cyclic triphosphenium ion were observed (δP_A = -254.0 ppm (t), δP_B = 30.8 ppm (d), $^1J_{P\text{-}P}$ = 417 Hz). The $^{31}P\{^1H\}$ NMR spectrum clearly shows both the *cis* and *trans* isomers had formed, as previously reported,[1] although some of the Pt satellites were weak and so some $^1J_{Pt\text{-}P}$ values could not be obtained.



Scheme 6.4: Proposed synthesis of the *cis* and/or *trans* Pt(II) complex from the depp cyclic triphosphenium ions, **6a** and **6b**, and *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ (**61-63**)

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
26.1	d	$^1J_{PD\text{-}PC}$ = 348	P_G
19.1	d	$^1J_{PG\text{-}PF}$ = 340, $^2J_{Pt\text{-}PD}$ =105	P_D
9.3	d	$^2J_{PH\text{-}PF}$ = 172	P_H
3.2	s	$^1J_{Pt\text{-}PE}$ = 3369	P_E
-102.3	t	$^1J_{Pt\text{-}PC}$ = 1104, $^1J_{PC\text{-}PD}$ = 341	P_C
-136.0	dt	$^1J_{PF\text{-}PG}$ = 348, $^2J_{PF\text{-}PH}$ = 169,	P_F

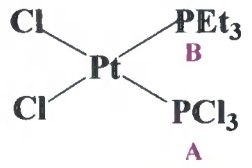
Table 6.6: $^{31}P\{^1H\}$ NMR data for the *cis*- (**73a**) and *trans*- (**74a**) complexes synthesised in the reaction between **6a**, and *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ (**61**)

Analogous reactions using the hexachlorostannate salt of the depp cyclic triphosphenium ion, **6b**, were carried out with each of the Pt(II) dimers (**61-63**). For each reaction the $^{31}P\{^1H\}$ NMR spectrum showed signals corresponding to the *cis* complex (Scheme 6.4, Table 6.7).

***trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$ PR$_3$ =**	**δ P$_C$, ppm**	**δ P$_D$, ppm**	**δ P$_E$, ppm**	**$^1J_{PC-PD}$, Hz**	**$^1J_{Pt-PC}$, Hz**	**$^1J_{Pt-PE}$, Hz**	**Compound Number**
PEt_3	-98.6	18.0	9.7	344	1117	3392	**73b**
$PPhMe_2$	-108.3	18.8	-14.1	338	1166	3550	**75b**
PPh_2Me	-111.6	18.8	-11.0	344	~ 1200	3642	**76b**

Table 6.7: $^{31}P\{^1H\}$ NMR data for the *cis* complexes synthesised in reaction between the depp cyclic triphosphenium ion, **6b**, and *trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$

In a reaction between **6b** and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, along with the *cis* complex, **73b**, a second complex, **77**, was also observed in the $^{31}P\{^1H\}$ NMR spectrum as a minor component of the reaction mixture (δP$_A$ 101.6 ppm, $^1J_{Pt-PA}$ = 6062 Hz, $^2J_{P-P}$ = 18 Hz, δP$_B$ 17.6 ppm, $^1J_{Pt-PB}$ = 2996 Hz, $^2J_{P-P}$ = 18 Hz) (Figure 6.4). **77** formed in a side reaction between the Pt dimer and residual PCl_3 and will be discussed in more detail in Section 6.7.1.1.

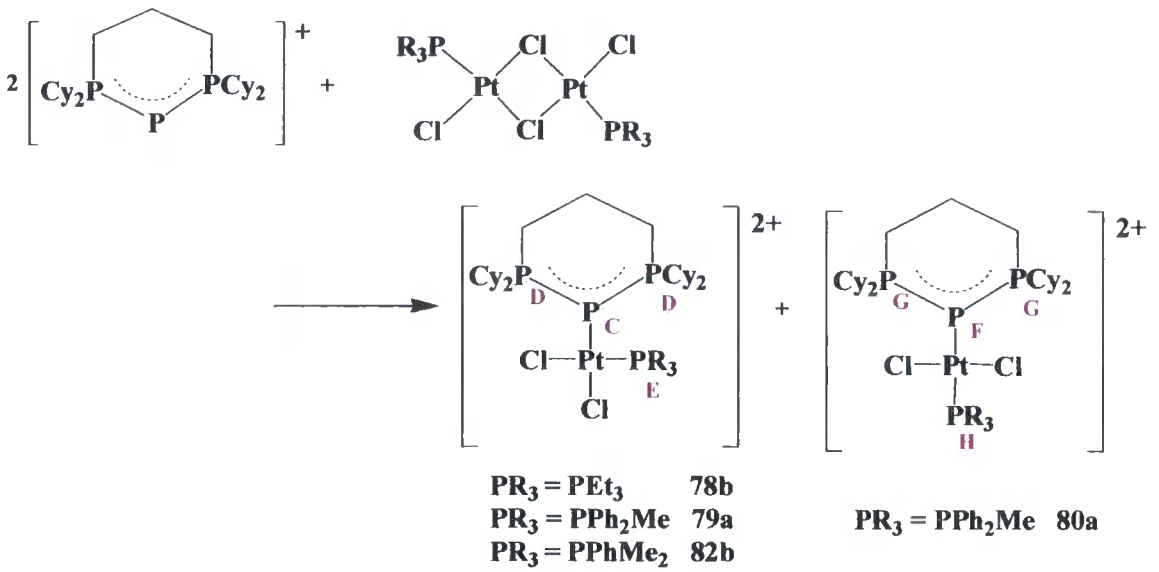


77

Figure 6.4: Product of the reaction between *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ and PCl_3

6.3.2 Reactions of the dcypp cyclic triphosphenium ions 7a and 7b with *trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$

To obtain missing $^1J_{Pt-P}$ coupling constants the reaction between the dcypp cyclic triphosphenium ion, **7b**, and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ was repeated in this complexation study, along with the synthesis of several new Pt(II) complexes using *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (Scheme 6.5).



Scheme 6.5: Proposed reaction between the dcypp cyclic triphosphenium ions, **7a** and **7b**, and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

The dcypp cyclic triphosphenium ion as a hexachlorostannate salt, **7b** was reacted with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ to afford the *cis* complex (**78b**) (Scheme 6.5, Table 6.8). The $^{31}P\{^1H\}$ NMR data are consistent with those previously reported by Deng *et. al.*[1] The $^1J_{Pt\text{-}PC}$ coupling was obtained, and is again unusually small for a one-bond platinum-phosphorus coupling at 1154 Hz. **77** was also observed as a minor component in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture (δP_A 101.6 ppm, $^1J_{Pt\text{-}PA}$ = 6062 Hz, $^2J_{P\text{-}P}$ = 18 Hz, δP_B 17.6 ppm, $^1J_{Pt\text{-}PB}$ = 2996 Hz, $^2J_{P\text{-}P}$ = 18 Hz).

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
20.5	d	$^1J_{PD\text{-}PC}$ =375	P_D
3.6	s	$^1J_{Pt\text{-}PE}$ = 3456	P_E
-102.3	t	$^1J_{PC\text{-}PD}$ = 375, $^1J_{Pt\text{-}PC}$ = 1154	P_C

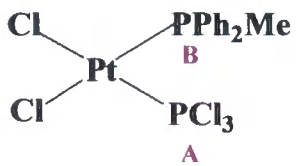
Table 6.8: $^{31}P\{^1H\}$ NMR data for the *cis* complex, **78b**, formed in the reaction between **7b** and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

An analogous reaction between the dcypp cyclic triphosphenium ion **7a** and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ showed the formation of both *cis* (**79a**) and *trans* (**80a**) complexes (Scheme 6.5, Table 6.9).

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
27.6	d	$^1J_{PG-PF}$ = 366	P_G
20.0	d	$^1J_{PD-PC}$ = 380	P_D
3.9	d	$^2J_{PH-PF}$ = 266	P_H
0.1	s	$^1J_{Pt-PE}$ = 3628	P_E
-97.0	t	$^1J_{Pt-PC}$ = 1267, $^1J_{PC-PD}$ = 380	P_C
-148.0	dt	$^1J_{PF-PG}$ = 366, $^2J_{PF-PH}$ = 266	P_F

Table 6.9: $^{31}P\{^1H\}$ NMR data for the *cis* (**79a**) and *trans* (**80a**) complexes synthesised in the reaction between **7a** and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$

A small amount of residual PCl_3 had been observed in the $^{31}P\{^1H\}$ NMR spectrum recorded after the synthesis of the cyclic triphosphenium ion. It was therefore not surprising that another complex, **81**, was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture as a minor component (δP_A 104.3 ppm, $^1J_{Pt-PA}$ = 5876 Hz, $^2J_{P-P}$ = 15 Hz, δP_B 5.5 ppm, $^1J_{Pt-PB}$ = 3229 Hz, $^2J_{P-P}$ = 15 Hz) and will also be discussed in more detail in Section 6.7.1.1 (Figure 6.5).



81

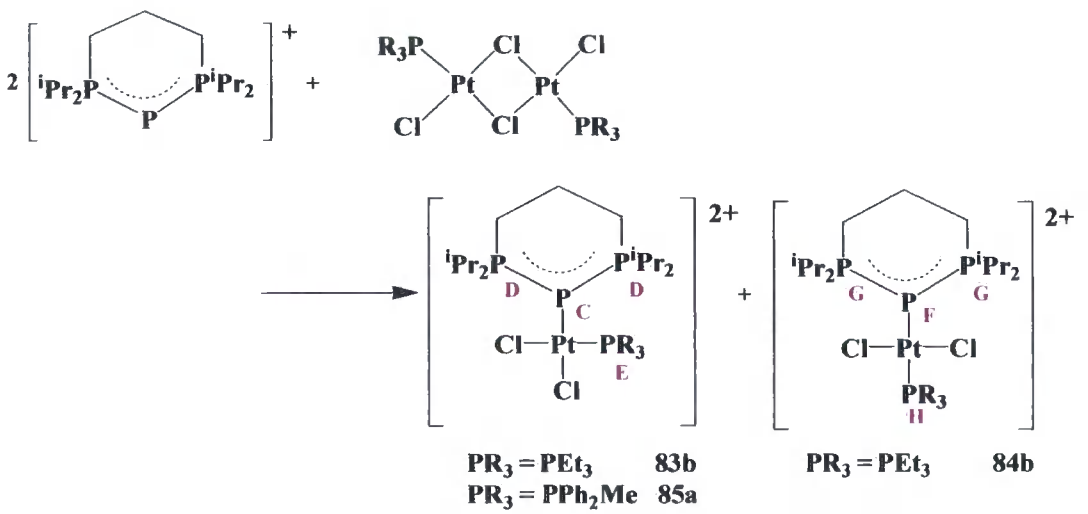
Figure 6.5: Product of the reaction between *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ and PCl_3

The *cis* complex, **82b**, was also obtained from a reaction of **7b** with *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (Scheme 6.5). The $^{31}P\{^1H\}$ NMR data are comparable with those reported for other complexes containing cyclic triphosphenium ions (Table 6.10).[1]

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
20.4	d	$^1J_{PD\text{-}PC} = 373$	P_D
-13.6	s	$^1J_{Pt\text{-}PE} = 3513$	P_E
-104.7	t	$^1J_{PC\text{-}PD} = 372$, $^1J_{Pt\text{-}PC} = 1227$	P_C

Table 6.10: $^{31}P\{^1H\}$ NMR data for the *cis* complex **82b** synthesised in the reaction between the dcypp cyclic triphosphenium ion (**7b**) and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$

6.3.3 Reactions of the dippp cyclic triphosphenium ions 8a and 8b with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$



Scheme 6.6: Proposed synthesis of the *cis* and *trans* Pt(II) complexes from the dippp cyclic triphosphenium ions **8a** and **8b** and *trans*-[Pt(PR$_3$)Cl(μ-Cl)]$_2$

Prior to this work there had been no coordination studies carried out using the dippp cyclic triphosphenium ion, **8**. These reactions were carried out to determine whether the *trans* complex would form initially then convert to the more thermodynamically stable *cis* complex, or whether the ^{i}Pr groups would be too bulky for conversion to the *cis* isomer to occur.

Reaction of the dippp cyclic triphosphenium ion **8b** with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ afforded both the *cis* (**83b**) and *trans* (**84b**) complexes (Scheme 6.6, Table 6.11). Signals corresponding to a small amount of unreacted cyclic triphosphenium ion were also observed (δP_A -298.6 ppm, δP_B 43.1 ppm, $^{1}J_{PA\text{-}PB}$ = 460 Hz) (Figure 6.6). The doublet resonance corresponding to P_H was not assigned due to numerous signals observed in the region of the spectra where this signal would be expected.

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
34.8	d	$^{1}J_{PG\text{-}PF}$ = 380	P_G
27.7	d	$^{1}J_{PD\text{-}PC}$ = 369	P_D
4.7	s	$^{1}J_{Pt\text{-}PE}$ = 3447	P_E
-99.1	t	$^{1}J_{Pt\text{-}PC}$ = 1133, $^{1}J_{PC\text{-}PD}$ = 369	P_C
-122.4	dt	$^{1}J_{PF\text{-}PG}$ = 380, $^{2}J_{PF\text{-}PH}$ = 172, $^{1}J_{Pt\text{-}PF}$ = 1115	P_F

Table 6.11: $^{31}P\{^{1}H\}$ NMR data for the *cis* (**83b**) and *trans* (**84b**) complexes formed in the reaction between the dippp cyclic triphosphenium ion (**8b**) and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

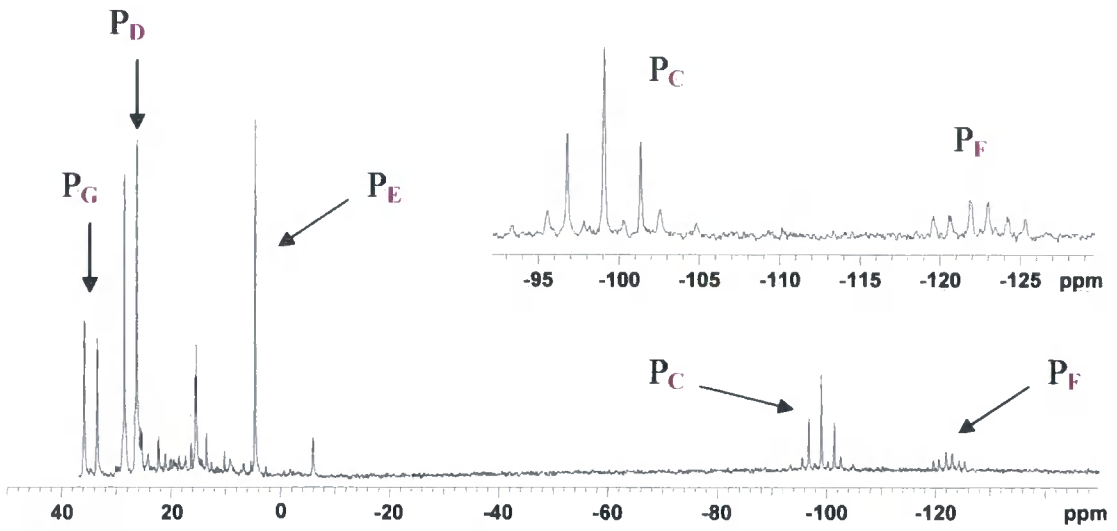


Figure 6.6: ^{31}P NMR spectrum of the reaction between dippp cyclic triphosphenium ion (**8b**) and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

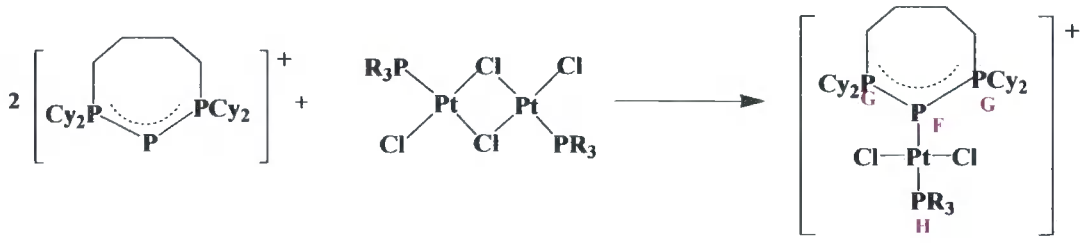
An analogous reaction carried out between **8a** *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ afforded a *cis* complex, **85a** (Scheme 6.6, Table 6.12). The $^{31}P\{^1H\}$ NMR spectrum also showed signals corresponding to the dippp cyclic triphosphenium ion (δP_A -298.4 ppm, δP_B 44.3 ppm, $^1J_{PA\text{-}PB} = 460$ Hz).

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
27.6	d	$^1J_{PD\text{-}PC} = 374$	P_D
0.2	s	$^1J_{Pt\text{-}PE} = 3628$	P_E
-94.6	t	$^1J_{PC\text{-}PD} = 374$ $^1J_{Pt\text{-}PC} = 1223$	P_C

Table 6.12: $^{31}P\{^1H\}$ NMR data for the *cis* complex **85a** synthesised in the reaction between the dippp cyclic triphosphenium ion and *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$

6.4 Synthesis of Pt(II) complexes containing seven-membered ring cyclic triphosphenium ions

6.4.1 Reactions of the dcypb cyclic triphosphenium ions 11a and 11b with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$



86b $PR_3 = PEt_3$
87b $PR_3 = PPhMe_2$
88a $PR_3 = PPh_2Me$

Scheme 6.7: Synthesis of *trans* Pt(II) complex from the dcypb cyclic triphosphenium ions **11a** and **11b** and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

Reactions of the dcypb cyclic triphosphenium ion as its chloride salt, **11a**, with *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$, and as its hexachlorostannate salt, **11b**, with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and *trans*-$[Pt(PPhMe_2)Cl(\mu\text{-}Cl)]_2$ all afforded *trans* complexes (**86b-88a**) (Scheme 6.7). The $^{31}P\{^1H\}$ NMR data for each complex were in good agreement with those previously obtained for other Pt(II) complexes containing cyclic triphosphenium ions (Table 6.13).[1]

In the reaction of **11b** with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ a singlet was also observed in the $^{31}P\{^1H\}$ NMR spectrum at 2.8 ppm which was assigned to $[Pt(PEt_3)Cl_3]^-$; the shift and coupling constants are consistent with those reported in the literature (Figure 6.7).[9-11] It is possible that this could be the counter-ion for the complex.

	***trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$ PR_3 =**		
	PEt_3	**$PPhMe_2$**	**PPh_2Me**
Cyclic Triphosphenium Ion	**11b**	**11b**	**11a**
δ P_F, ppm	-127.8	-124.1	-124.1
δ P_G, ppm	43.3	44.0	43.7
δ P_H, ppm	14.6	-3.4	2.3
$^1J_{P_F\text{-}P_G}$, Hz	423	420	421
$^2J_{P_F\text{-}P_H}$, Hz	281	291	287
$^1J_{Pt\text{-}P_F}$, Hz	1245	1017	1030
$^1J_{Pt\text{-}P_H}$, Hz	2842	2512	2586
Compound Number	**86b**	**87b**	**88a**

Table 6.13: $^{31}P\{^1H\}$ NMR data for the *trans* complexes synthesised in reactions between the dcypb cyclic triphosphenium ions **11a** and **11b** and *trans*-[Pt(PR_3)Cl(μ-Cl)]$_2$

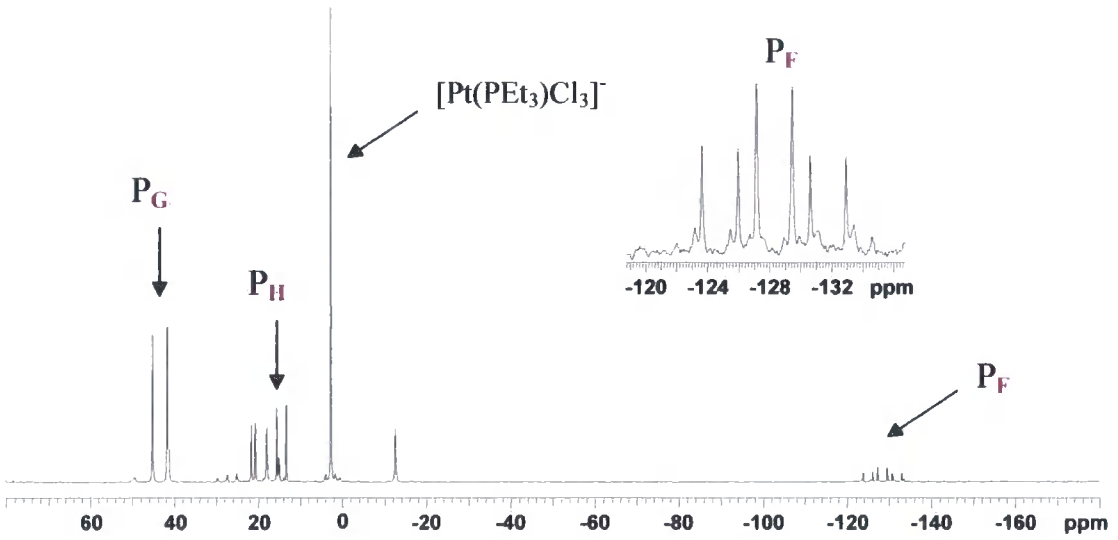


Figure 6.7: $^{31}P\{^1H\}$ NMR spectrum of the reaction between dcypb cyclic triphosphenium ion, **11b**, and *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$

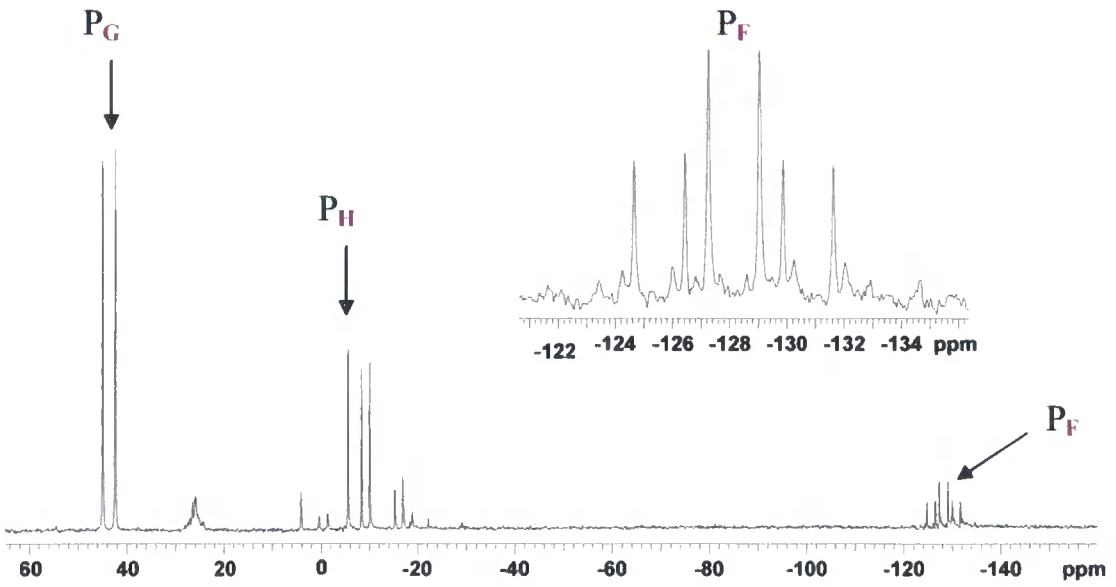
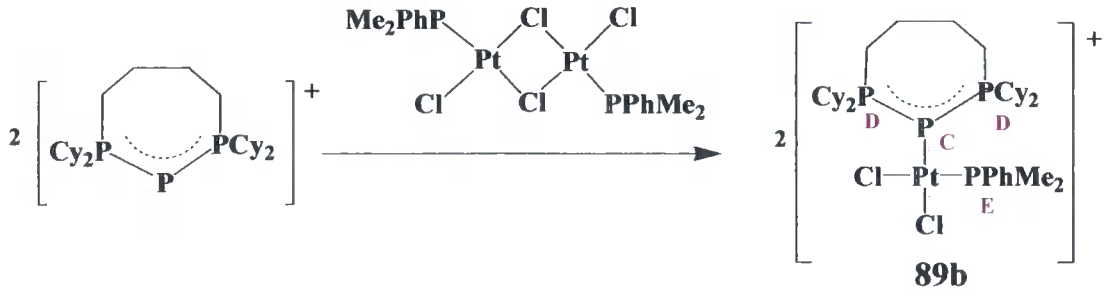


Figure 6.8: ^{31}P NMR spectrum of the reaction between dcypb cyclic triphosphenium ion and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$.

The reaction between **11b** and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ was repeated to ascertain whether the *trans* complex would convert to the *cis* isomer on standing. A $^{31}P\{^1H\}$ NMR spectrum recorded soon after mixing of the reagents showed signals corresponding to the cyclic triphosphenium ion (δP_A -260.5 ppm (t), δP_B 48.0 ppm (d), $^1J_{PA\text{-}PB}$ = 477 Hz) and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ (δP -14.6 ppm(s)), and very weak signals corresponding to the *cis* complex **89b** (Scheme 6.8, Table 6.14). There were no signals corresponding to the *trans* complex. Unfortunately due to weak satellite peaks, $^1J_{Pt\text{-}PC}$ was not obtained. A second $^{31}P\{^1H\}$ NMR spectrum was recorded the following day which showed no sign of the signals corresponding to the *cis* complex, only those for the cyclic triphosphenium ion and the unreacted dimer. There was no further reaction.



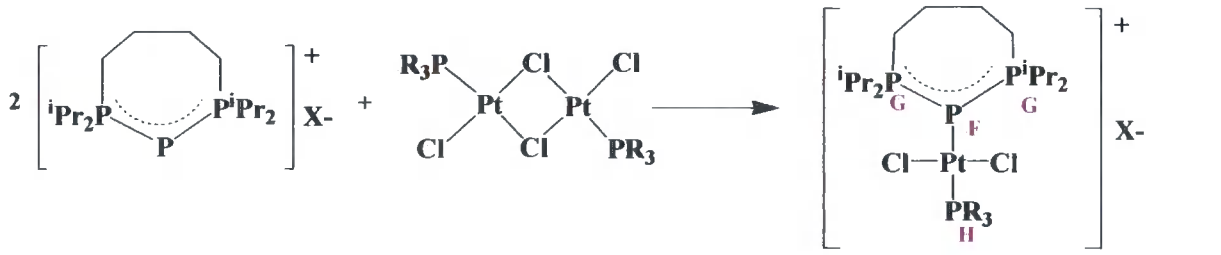
Scheme 6.8: Synthesis of the *cis* Pt(II) complex **89b** from the dcypb cyclic triphosphenium ion **11b** and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$

δ, ppm	Multiplicity	Coupling Constant, Hz	Assignment
40.0	d	$^1J_{PD\text{-}PC}$ = 420	P_D
-15.1	s	$^1J_{Pt\text{-}PE}$ = 3630	P_E
-78.5	t	$^1J_{PC\text{-}PD}$ = 422	P_C

Table 6.14: $^{31}P\{^1H\}$ NMR data for the *cis* complex **89b** formed in a reaction between the dcypb cyclic triphosphenium ion and *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$.

6.4.2 Reactions of the dippb cyclic triphosphenium ions 13a and 13b with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ and *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$

Reactions were carried out between *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ and both the chloride and hexachlorostannate salts of the dippb cyclic triphosphenium ion (**13a** and **13b**), and between *trans*-[Pt(PPh$_2$Me)Cl(μ-Cl)]$_2$ and the hexachlorostannate salt of the cyclic triphosphenium ion (**13b**) (Scheme 6.9). In the all three reactions, the *trans* complex was synthesised. $^{31}P\{^1H\}$ NMR data for these *trans* complexes (Table 6.15). Further $^{31}P\{^1H\}$ NMR spectra were recorded for each reaction but there was no evidence to suggest conversion from the *trans* complex to the *cis* complex.



90a $PR_3 = PEt_3$ $X = Cl^-$
90b $PR_3 = PEt_3$ $X = SnCl_6^{2-}$
91b $PR_3 = PPhMe_2$ $X = Cl^-$

Scheme 6.9: Synthesis of *trans* Pt(II) complex from the dippb cyclic triphosphenium ions (**13a** and **13b**) and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

	***trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ $PR_3 =$**		
	PEt_3	**PEt_3**	**PPh_2Me**
Cyclic triphosphenium ion	**13a**	**13b**	**13b**
δP_F, ppm	-133.1	-132.5	-127.7
δP_G, ppm	50.9	50.9	51.1
δP_H, ppm	15.7	15.6	5.1
$^1J_{PF\text{-}PG}$, Hz	418	420	417
$^2J_{PF\text{-}PH}$, Hz	275	275	287
$^1J_{Pt\text{-}PF}$, Hz	943	949	1013
$^1J_{Pt\text{-}PH}$, Hz	2840	2842	2873
Compound Number	**90a**	**90b**	**91b**

Table 6.15 $^{31}P\{^1H\}$ NMR data for the *trans* complexes synthesised in reactions between the dippb cyclic triphosphenium ions **13a** and **13b** and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

6.5 Reactions of diphosphanes and cyclic triphosphenium ions containing a ferrocene backbone with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$

The dippf cyclic triphosphenium ion (**9a**) was reacted with *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$. A $^{31}P\{^1H\}$ NMR spectrum was recorded soon after the addition of the Pt dimer, which showed signals corresponding to unreacted PCl_3 (δP -220.5 ppm (s)), some unreacted dippf cyclic triphosphenium ion (δP_A -146.7 ppm (t), δP_B 52.1 ppm (d), $^1J_{PA\text{-}PB}$ = 488 Hz), and signals corresponding to a Pt complex containing three inequivalent phosphorus atoms, one at significantly higher frequency than the others, **92** (Table 6.16).

δP, ppm	Multiplicity	$^1J_{P\text{-}P}$, Hz	$^1J_{Pt\text{-}P}$, Hz	Assignment
116.3	s	-	-	P_C
19.2	d	458	2440	P_D
11.4	d	458	2453	P_E

Table 6.16: $^{31}P\{^1H\}$ NMR data for the complex **92** formed in the reaction between the dippf cyclic triphosphenium ion **9a** and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, **61**

The data suggest that coordination of the diphosphane to platinum has occurred instead of coordinating of the cyclic triphosphenium ion. It is probable that the diphosphane originated from the decomposition of the cyclic triphosphenium ion occurred, similar to that observed in reactions between dppe- and dppf-derived cyclic triphosphenium ions and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$.[1] In similar systems previously reported where the diphosphane has bulky substituents on the outer phosphorus atoms, coordination of the diphosphane has occurred in a bidentate fashion.[12-15]

In this reaction between **9a** and *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$, the $^{31}P\{^1H\}$ NMR data indicate that the diphosphane, dippf, has coordinated to the platinum through only one of the phosphorus atoms, as a monodentate ligand, and that a *trans*-platinum complex has formed. Due to the high frequency shift of P_C (116.3 ppm), it seems likely that a chlorine atom is bound to the uncoordinated end of the diphosphane (Figure 6.9). The shift of P_C

suggests there is only one Cl bonded to the P atom, as it is consistent with those for other four-coordinate phosphonium salts (Table 6.17).

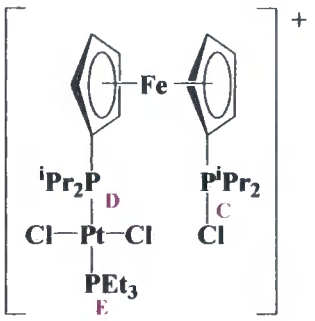


Figure 6.9: Proposed complex **92** formed in the reaction between the dippf cyclic triphosphenium ion and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$.

Compound	δ, ppm	Reference
$^{i}Pr_3P^{+}Cl\ Cl^{-}$	117.4 (nitromethane), 118.4 (MeCN)	16
$^{t}Bu_3P^{+}Cl\ Cl^{-}$	102.7 (DCM), 103.3 (nitromethane)	16
$Et_3P^{+}Cl\ Cl^{-}$	110.0 ($CHCl_3$), 112.1 (MeCN)	16
$Cy_3P^{+}Cl\ Cl^{-}$	103.2 (nitromethane), 104.2 (MeCN)	16

Table 6.17: $^{31}P\{^{1}H\}$ NMR literature data for some $R_3P^{+}Cl\ Cl^{-}$ phosphonium salts

Further investigation into this unusual behaviour involved the reaction of the diphosphane dippf with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$. A $^{31}P\{^{1}H\}$ NMR spectrum was recorded soon after the mixing of the reagents which showed the formation of a Pt complex containing three inequivalent phosphorus atoms (Table 6.18). The data confirm that the diphosphane coordinates in a unidentate fashion (Figure 6.10). δP_C (1.4 ppm) is

consistent with shifts for three-coordinate phosphorus compounds and the shift of the parent diphosphane, suggesting that unlike the previous reaction, the uncoordinated end of the diphosphane had not become chlorinated (Table 6.19). In the previous reaction between the dippf-derived cyclic triphosphenium ion and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ there had been excess PCl_3 present in solution, hence a supply of Cl^- that could allow chlorination of the un-coordinated end of the diphosphane to take place. In this reaction there was no source (except the Pt dimer) for the chloride ion so chlorination did not occur. The coupling constants show that the PEt_3 ligand is *trans* to the coordinated phosphorus of the ferrocene derivative. Further $^{31}P\{^1H\}$ NMR spectra were recorded but there was no evidence to suggest formation of a Pt(II) complex with the dippf as a bidentate ligand as seen when using dppf and dtbpf.

δP, ppm	Multiplicity	$^2J_{P\text{-}P}$, Hz	$^1J_{Pt\text{-}P}$, Hz	Assignment
20.6	d	459	2473	P_D
10.6	d	459	2420	P_E
1.4	s	-	-	P_C

Table 6.18: $^{31}P\{^1H\}$ NMR data for complex **93** formed in the reaction between dippf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

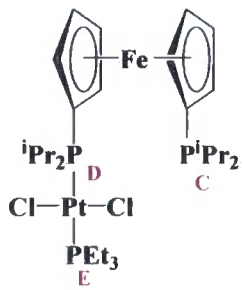
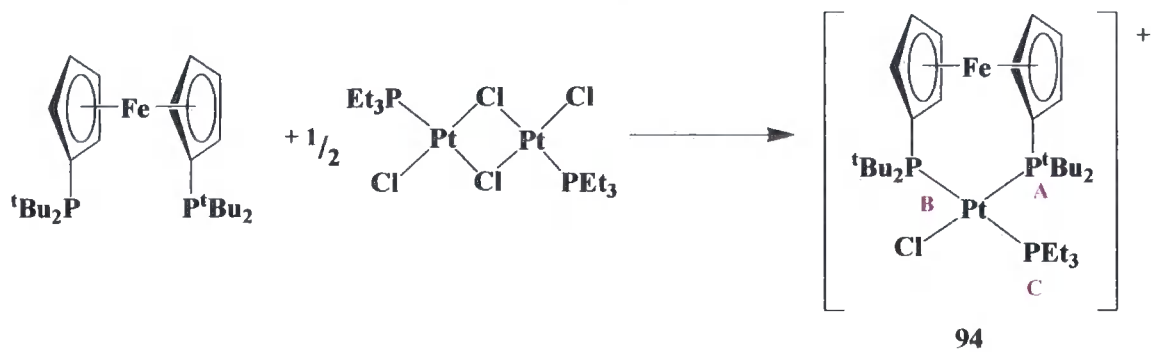


Figure 6.10: Proposed complex **93** formed in the reaction between dippf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$.

Compound	Chemical Shift, ppm	Reference
dippf	1.4	*
$^{i}Pr_2PCH_2CH_2CH_2Cl$	1.4	16
$^{i}Pr_2PCH_2PH\text{-}^{i}Pr$	-3.2	16
$^{i}Pr_2PCH_2PCl\text{-}^{i}Pr$	-5.2	16

Table 6.19: $^{31}P\{^{1}H\}$ NMR data for some three-coordinate phosphorus compounds, solvent DCM (* this work)

Further investigation into the coordination properties of diphosphanes containing a ferrocene backbone was carried out using the diphosphane dtbpf. A $^{31}P\{^{1}H\}$ NMR spectrum recorded soon after the mixing of the diphosphane dtpbf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ showed the signals corresponding to only one product, **94** (Scheme 6.10). The $^{31}P\{^{1}H\}$ data confirm the coordination of the diphosphane as a bidentate ligand (Table 6.20). The data are consistent with those previously reported for the similar complexes containing the diphosphanes dppe and dppf.[17]



94

Scheme 6.10: Synthesis of the Pt(II) complex **94** from the diphosphane dtbpf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$.

δP, ppm	Multiplicity	$^2J_{P-P}$, Hz	$^1J_{Pt-P}$, Hz	Assignment
43.0	d	457	2498	P_B
28.4	s	-	3861	P_A
9.7	d	456	2459	P_C

Table 6.20: $^{31}P\{^1H\}$ NMR data for the Pt(II) complex **94** from the reaction between dtbpf and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$.

6.6 Synthesis of Pt(II) complexes containing chlorophosphanes

Initial investigation into the formation of Pt(II) complexes containing chlorophosphanes was necessary, to confirm assignments of signals in the $^{31}P\{^1H\}$ NMR spectra for reactions between cyclic triphosphenium ions and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ with PCl_3 present as arising from *cis*-$PtCl_2(PCl_3)(PR_3)$ (see Sections 6.2.1, 6.3.1, and 6.3.2 for further details). Also previous work within the group had afforded crystalline material which, using single crystal X-ray diffraction studies, was determined to be *cis*-$PtCl_2(PEt_3)(P(OH)_3)$ (Figure 6.11).[18] It was proposed that this was produced by the hydrolysis of *cis*-$PtCl_2(PCl_3)(PEt_3)$ which had formed as a by-product in the original reaction.

Phosphorous acid, H_3PO_3, is dibasic and usually exists as $[HP(O)(OH)_2]$, with phosphorus in the +5 oxidation state. Similarly, hypophosphorus acid, H_3PO_2, usually exists as $[H_2P(O)(OH)]$. There are few reports of coordinated $P(OH)_3$ or $[H_2P(O)(OH)]$, though they have been identified in a few complexes where the P(III) form has been stabilized by coordination to a transition metal.[19-21]

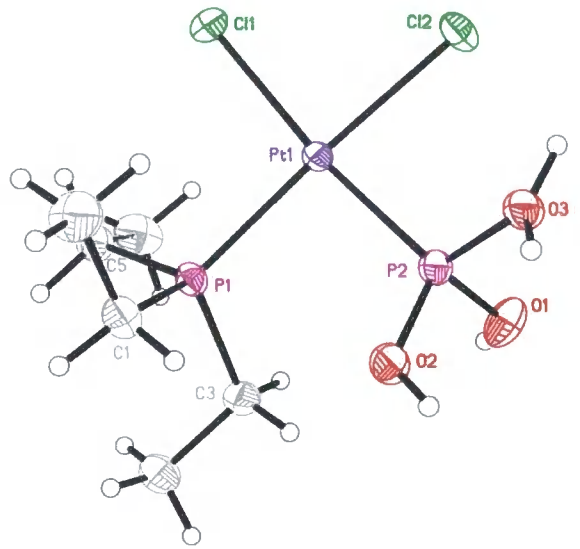


Figure 6.11: The molecular structure of *cis*-$PtCl_2(PEt_3)(P(OH)_3)$[18]

Fedin, Sokolov *et al.* reported the synthesis and isolation of a complex containing $P(OH)_3$ in 2001 (Scheme 6.11).[19]

$$[Mo_3(PdCl)S_4(H_2O)_9]^{3+} + PCl_3 + 3H_2O \longrightarrow [Mo_3(PdP(OH)_3)S_4(H_2O)_9]^{4+} + 3H^+ + 4Cl^-$$

Scheme 6.11: Synthesis of a complex containing $P(OH)_3$[19]

Addition of cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$) afforded the crystalline product $\{[Mo_3PdP(OH)_3S_4Cl_3(H_2O)_6]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2.20H_2O$.[19] The average P-O bond length in this complex is 1.561(12) Å, which is similar to those found in $Cl_2Pt(PEt_3)[P(OH)_3]$ (1.565(4) – 1.581(4) Å).[18] The bond lengths for these complexes containing $P(OH)_3$ are considerably shorter that those observed in most $P(OR)_3$ esters.[4]

Two complexes containing $[HP(OH)_2]$ were also isolated by Fedin, Sokolov *et al.* again using cucurbit[6]uril to obtain crystalline product (Scheme 6.12).[20] The P-O bond lengths in the Se complex are 1.585(11) and 1.622(12) Å, which are longer than those found in the $P(OH)_3$ complexes.[18, 19]

$$[W_3(NiCl)Q_4(H_2O)_9]^{3+} + H_3PO_2 \xrightarrow[\text{cucurbit[6]uril}]{\text{HCl}} [W_3(Ni(HP(OH)_2))Q_4(H_2O)_9]Cl_4.C_{36}H_{36}N_{24}O_{12}.11H_2O \qquad Q = \text{Se or S}$$

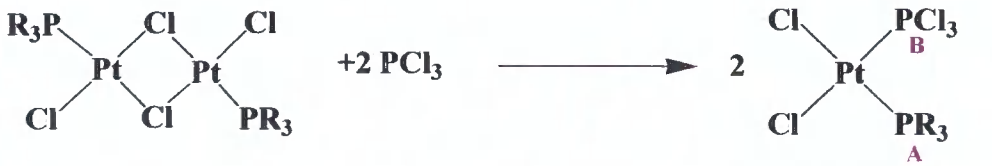
Scheme 6.12: Synthesis of complexes containing $[HP(OH)_2]$[19]

As there are few examples of complexes containing $P(OH)_3$, it was hoped to find a facile synthetic pathway to the formation of *cis*-$PtCl_2(PEt_3)(P(OH)_3)$, to obtain further details on its formation and analysis.

6.6.1 Synthesis and characterisation of the parent Pt(II) complexes

6.6.1.1 Reactions of *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ with PCl_3

In the synthesis of Pt(II) complexes containing cyclic triphosphenium ions, a second Pt(II) complex was observed as a minor component of the reaction mixture if there was any excess PCl_3 left from ring synthesis. These complexes were assigned to *cis*-$PtCl_2(PR_3)(PCl_3)$, formed in a side reaction with the Pt dimer used and PCl_3. To confirm these assignments these complexes were synthesised (Scheme 6.13). For each reaction, *cis*-$PtCl_2(PCl_3)(PR_3)$ was obtained as the only product of the reaction (Table 6.21 and Figure 6.12).



$PR_3 = PEt_3$ 77
$PR_3 = PPhMe_2$ 65
$PR_3 = PPh_2Me$ 81

Scheme 6.13: Synthesis of *cis*-$PtCl_2(PCl_3)(PR_3)$

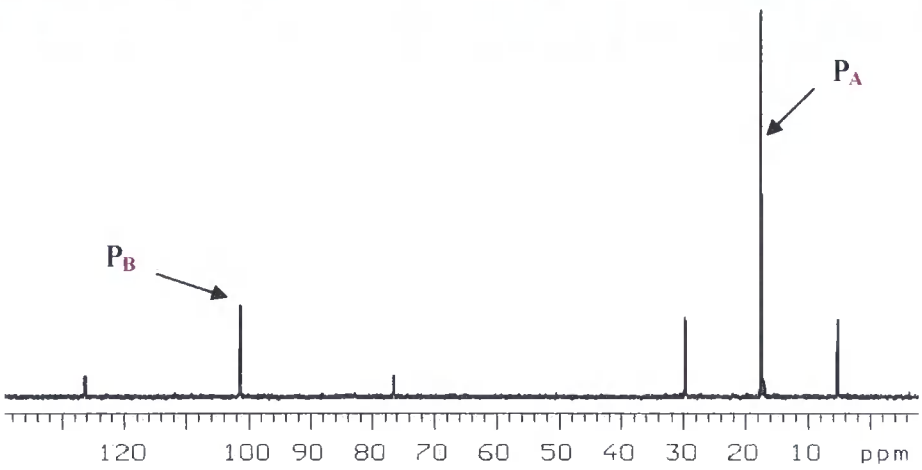


Figure 6.12: $^{31}P\{^1H\}$ NMR spectrum of *cis*-$PtCl_2(PEt_3)(PCl_3)$

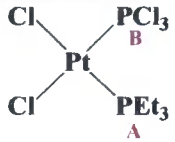
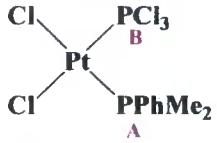
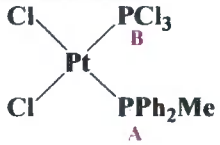
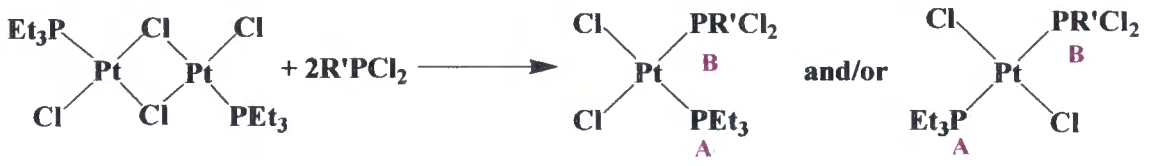
Complex	δP_A, ppm	δP_B, ppm	$^1J_{Pt\text{-}PA}$, Hz	$^1J_{Pt\text{-}PB}$, Hz	$^2J_{PA\text{-}PB}$, Hz
	17.6	101.6	2996	6062	18
	-5.6	103.2	3145	5922	17
	5.5	104.3	3229	5876	15

Table 6.21: $^{31}P\{^1H\}$ NMR data for *cis*-$PtCl_2(PEt_3)(PCl_3)$ (**77**), *cis*-$PtCl_2(PPhMe_2)(PCl_3)$ (**65**) and *cis*-$PtCl_2(PPh_2Me)(PCl_3)$ (**81**)

6.6.1.2 Reactions of *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ with $PR'Cl_2$

The aim of these reactions was to prepare a family of Pt(II) complexes that could potentially undergo hydrolysis, allowing comparisons to be made with the PCl_3 systems. By reacting *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ with various $R'PCl_2$, it was hoped that *cis* and/or *trans* complexes would be afforded in good yields, and suitable for further study (Scheme 6.14).



Scheme 6.14: General synthesis of *cis*- and/or *trans*- $PtCl_2(PEt_3)(PR'Cl_2)$

For reactions between *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and $R'PCl_2$ where R' = Et, ^nPr, ^iPr or Ph, *cis*-$PtCl_2(PCl_3)(PR'Cl_2)$, formed as the only product of the reaction (Table 6.22). However, reaction of $CyPCl_2$ or $^tBuPCl_2$ with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, afforded both the *cis* and *trans* isomers in each reaction (Table 6.22).

The $^{31}P\{^1H\}$ NMR spectra for the *cis* complexes are comparable with those obtained for the other $R'PCl_2$ systems, with a large $^1J_{Pt\text{-}P}$ coupling. For the *trans* isomer a large magnitude of $^2J_{P\text{-}P}$ is observed, and also the chemical shift of the *trans* complex (δP_B) is to higher frequency compared with that of the *cis* isomer. For these two reactions, the *trans* complex is the kinetic product of the reaction and forms initially, but then converts to the thermodynamically more stable complex, the *cis* isomer.

The reaction between $CyPCl_2$ with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ initially showed approximately 90% *cis* isomer (**99**) and 10% *trans* (**100**), compared to 40% *cis* isomer (**101**) and 60% *trans* (**102**) in the analogous $^tBuPCl_2$ reaction (Figure 6.13). Full conversion to afford only the *cis* complex occurred within seven days at room temperature for the $CyPCl_2$ derivative, whereas for the $^tBuPCl_2$ system full conversion was much slower, taking approximately three weeks.

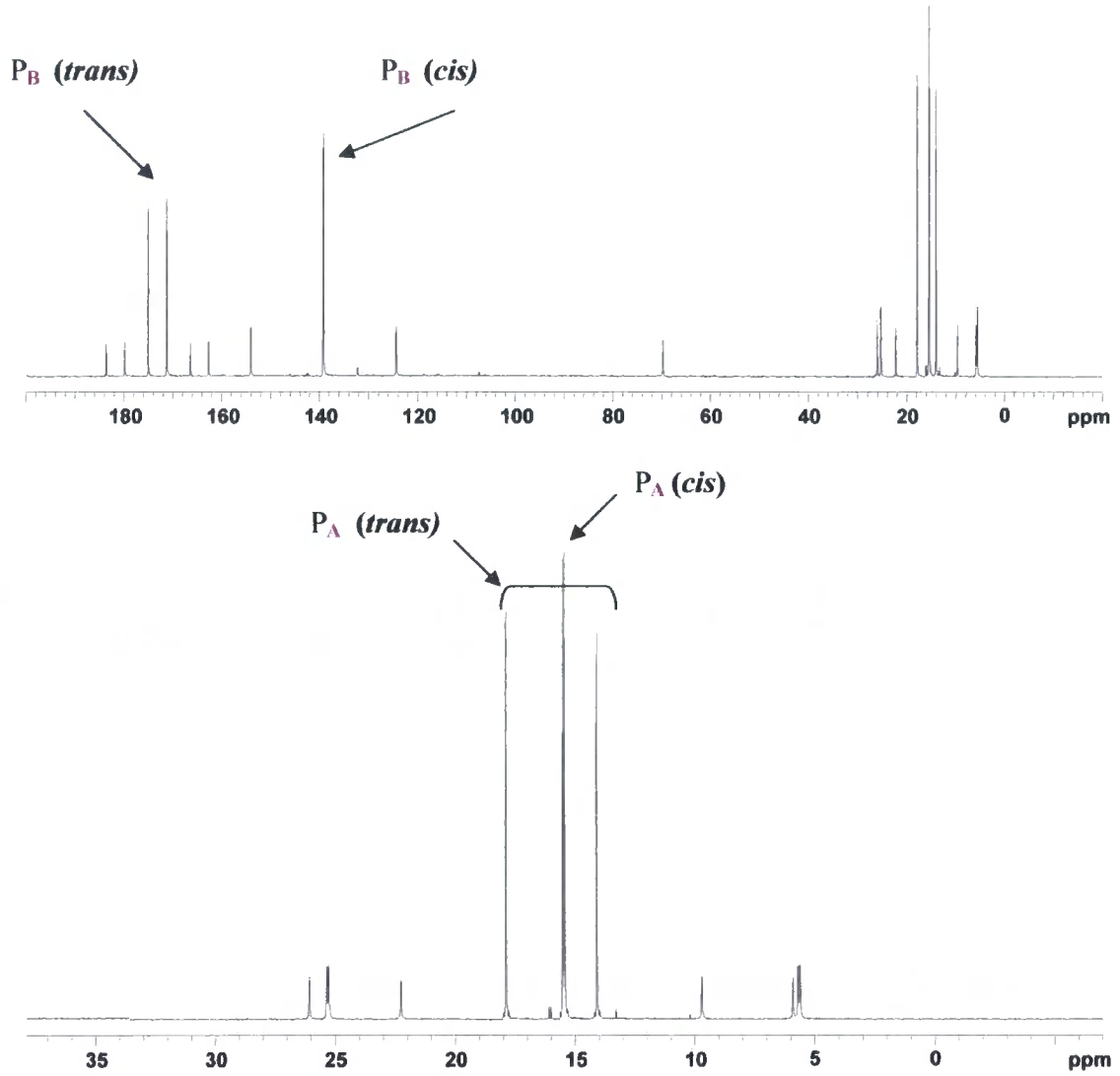


Figure 6.13: $^{31}P\{^{1}H\}$ NMR spectrum for a reaction between $^{t}BuPCl_2$ and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ showing both *cis* (**101**) and *trans*-$PtCl_2(PEt_3)(P^{t}BuCl_2)$ (**102**) complexes (top: full spectrum, bottom: expansion of the region between -7 and 38 ppm)

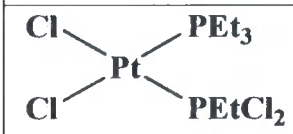
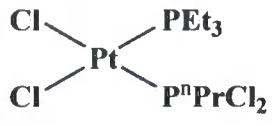
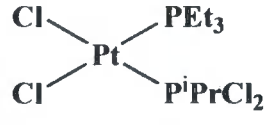
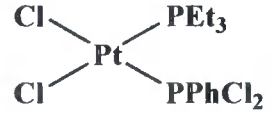
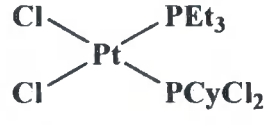
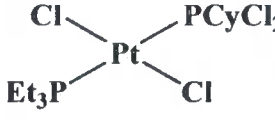
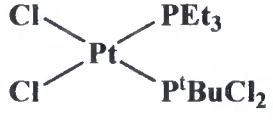
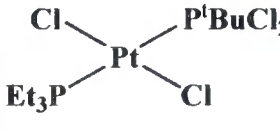
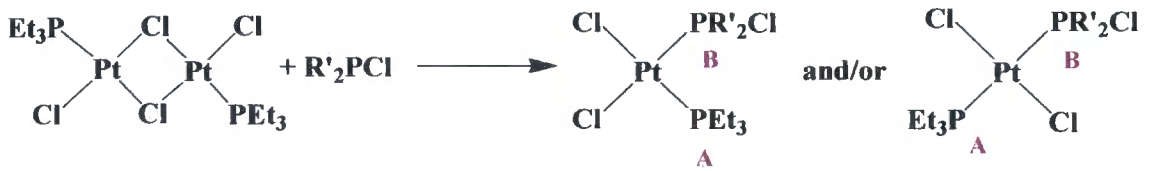
Complex	Compound Number	δP_A, ppm	δP_B, ppm	$^1J_{Pt\text{-}PA}$, Hz	$^1J_{Pt\text{-}PB}$, Hz	$^2J_{PA\text{-}PB}$, Hz
	**95**	16.6	117.4	3198	4965	14
	**96**	16.5	114.1	3207	4949	14
	**97**	16.9	130.4	3258	4848	14
	**98**	16.6	98.6	3160	5014	17
	**99**	17.2	125.4	3272	4823	14
	**100**	15.6	162.5	2700	2799	629
	**101**	15.5	139.2	3181	4803	13
	**102**	16.0	173.2	2651	2781	614

Table 6.22: $^{31}P\{^1H\}$ NMR data for *cis*- and *trans*-$PtCl_2(PEt_3)(PR'Cl_2)$, $P_A = PEt_3$

6.6.1.3 Reactions of *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ with PR'_2Cl

By reacting *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ with various R'_2PCl it was hoped that *cis* and/or *trans* complexes would be afforded in good yields, and suitable for further study (Scheme 6.15). The purpose of these reactions was to prepare a family of Pt(II) complexes which could potentially undergo hydrolysis, allowing comparisons to be made with the PCl_3 and PR'_2Cl systems.



Scheme 6.15: General synthesis of *cis*- and/or *trans*-$PtCl_2(PEt_3)(PR'_2Cl)$

A reaction between Et_2PCl and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ showed that the *cis* complex (**103**) had formed initially although the signals corresponding to P_A were very broad (Table 6.23). A week later a second $^{31}P\{^1H\}$ NMR spectrum was recorded at -50°C to try and resolve these signals. The parent complex was still present, but several new peaks were apparent. Two sets of doublets (with Pt satellites) were assigned to the *trans* isomer (**104**) (Table 6.24). Also apparent were two singlets (δP 98.5 ppm $^1J_{Pt\text{-}P}$ = 3982 Hz; δP 114.2 ppm $^1J_{Pt\text{-}P}$ = 3859 Hz (weak)). The singlet at 98.5 ppm was assigned to the product resulting from ligand scrambling, *cis*-$PtCl_2(PEt_2Cl)_2$ (**114**) which had previously been reported (δP 100.9 ppm $^1J_{Pt\text{-}P}$ = 3936 Hz in THF),[22] as there was also a very weak signal at 10.2 ppm that was assigned to another product resulting from ligand scrambling, $PtCl_2(PEt_3)_2$ (**115**).[23]

The reaction between Ph_2PCl and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ afforded the *cis* complex **107** (Table 6.24). The data are in good agreement with those reported by Berry *et al.*[22] Two other signals were also apparent in the $^{31}P\{^1H\}$ NMR spectrum which were assigned to products resulting from ligand scrambling, *cis*-$PtCl_2(PPh_2Cl)_2$ (**116**)[22] and *cis*-$PtCl_2(PEt_3)_2$ (**115**),[23] respectively (Table 6.24).

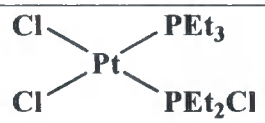
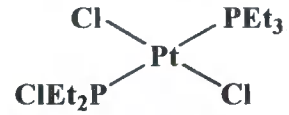
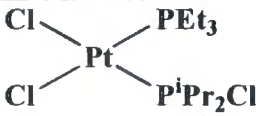
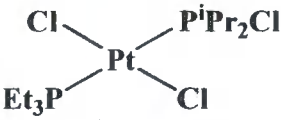
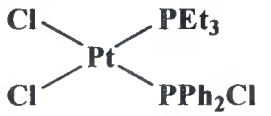
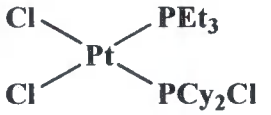
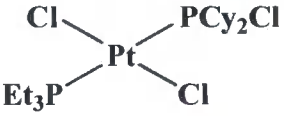
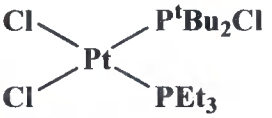
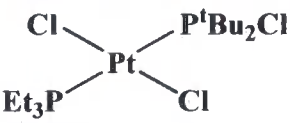
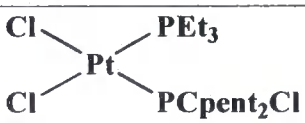
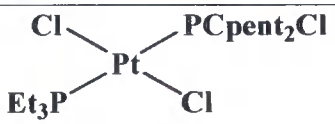
Complex	Compound Number	δP_A, ppm	δP_B, ppm	$^1J_{Pt-PA}$, Hz	$^1J_{Pt-PB}$, Hz	$^2J_{P-P}$, Hz
	**103**	15.8	117.4	3469	4042	13
	**104**	23.0	122.0	2144	2420	402
	**105**	13.6	125.8	3477	4056	12
	**106**	14.1	134.1	2266	2581	513
	**107**	14.5	72.0	3314	4341	15
	**108**	13.7	117.5	3492	4039	12
	**109**	13.9	122.2	2503	2567	512
	**110**	10.8	134.3	3490	4075	11
	**111**	12.7	139.2	2511	2543	494
	**112**	13.6	113.0	3506	4024	13
	**113**	13.7	122.8	2491	2599	520

Table 6.23: $^{31}P\{^1H\}$ NMR data for both *cis*- and *trans*-$PtCl_2(PEt_3)(PR_2Cl)$ complexes, P_A=PEt_3

In the reactions between *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and $^iPr_2PCl$, Cy_2PCl and $Cpent_2PCl$, both the *cis* and *trans* complexes were initially observed in $^{31}P\{^1H\}$ NMR spectra recorded 15 minutes after the addition of the chlorophosphane (Table 6.24). Figure 6.14 shows the $^{31}P\{^1H\}$ NMR spectrum obtained showing both *cis* and *trans*-$PtCl_2(PEt_3)(P^iPr_2Cl)$ complexes (**105** and **106**). In the time taken for full conversion to the *cis* complex to occur other signals corresponding to products resulting from ligand scrambling were observed in each reaction mixtures (Table 6.24 and Table 6.25). These additional products are in good agreement with those previously reported for *cis*-$PtCl_2(PEt_3)_2$,[23] *cis*-$PtCl_2(PPh_2Cl)_2$ and *cis*-$PtCl_2(PEt_2Cl)_2$.[22] For *trans*-$PtCl_2(PEt_3)(P^tBu_2Cl)$, initially only the *trans* complex was observed (Figure 6.15). At room temperature, conversion to the *cis* isomer began after approximately one week, although after three months there was approximately 15% *cis* complex and 85% *trans*.

Complex	δP, ppm	$^1J_{Pt\text{-}P}$, Hz	Compound Number
cis-$PtCl_2(PEt_2Cl)_2$	98.5	3982	**114**
cis-$PtCl_2(PEt_3)_2$	10.2	3513	**115**
cis-$PtCl_2(PPh_2Cl)_2$	72.3	3780	**116**
cis-$PtCl_2(P^iPr_2Cl)_2$	129.4	3996	**117**
cis-$PtCl_2(PCy_2Cl)_2$	110.7	4000	**118**
cis-$PtCl_2(PCpent_2Cl)_2$	108.1	4037	**119**

Table 6.24: $^{31}P\{^1H\}$ NMR for products resulting from ligand scrambling observed in reactions between *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and Ph_2PCl, $^iPr_2PCl$, Cy_2PCl and $Cpent_2PCl$

R'$_2$PCl	Initial % *cis*	Initial % *trans*	Time taken for full conversion
$^iPr_2PCl$	30	70	5 days
Cy_2PCl	50	50	3 days
$Cpent_2PCl$	50	50	5 days

Table 6.25: Ratios of *cis* : *trans* complexes in reactions between *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ and $^iPr_2PCl$, Cy_2PCl and $Cpent_2PCl$, and time for full conversion to the *cis* isomer at RT

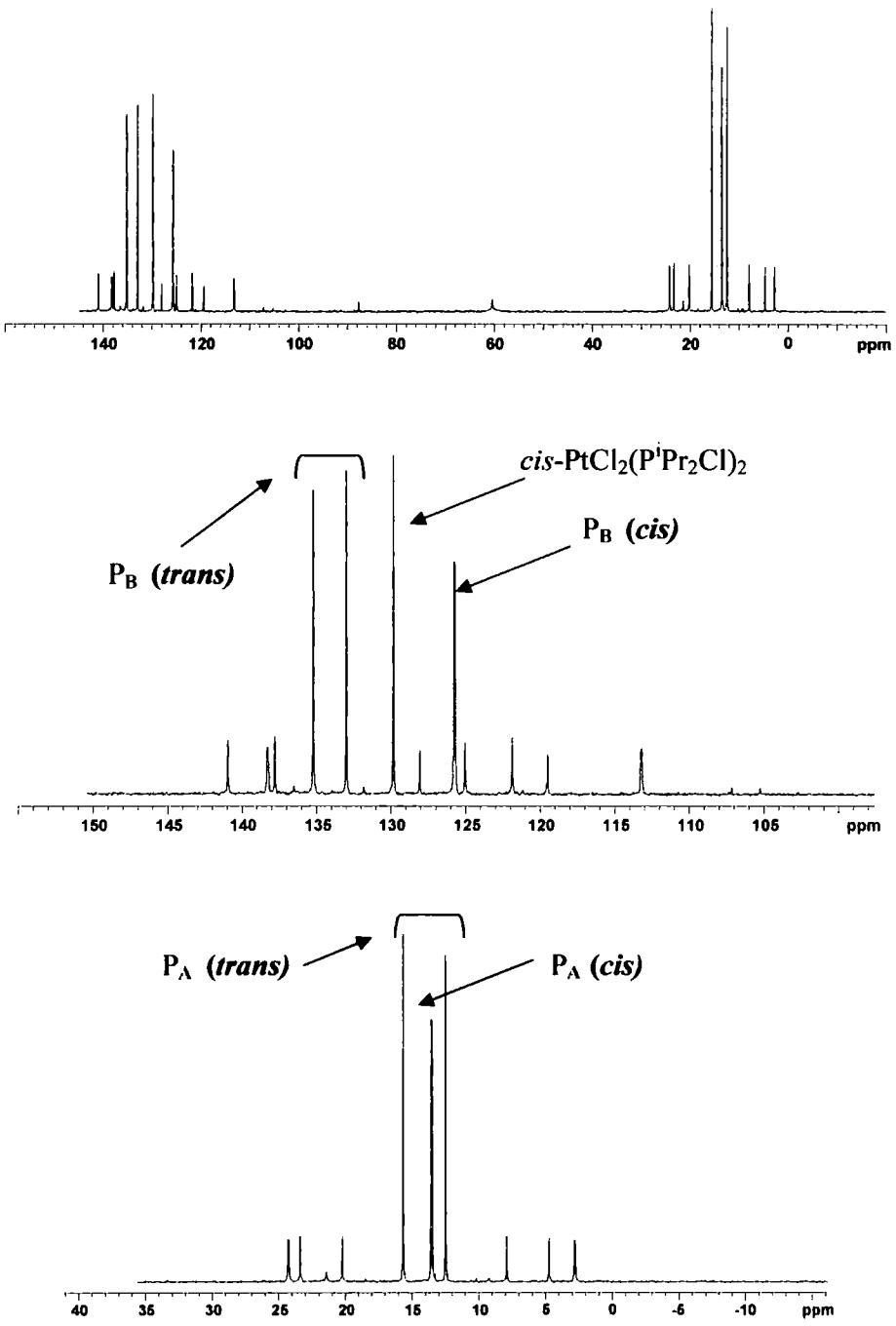


Figure 6.14: Initial $^{31}P\{^{1}H\}$ NMR spectrum for the reaction between $^{i}Pr_2PCl$ and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ showing both *cis* and *trans*-$PtCl_2(PEt_3)(P^{i}Pr_2Cl)$ complexes (top: full spectra, middle: expansion of the region between 98 and 165 ppm, bottom: expansion of the region between -16 and 41 ppm)

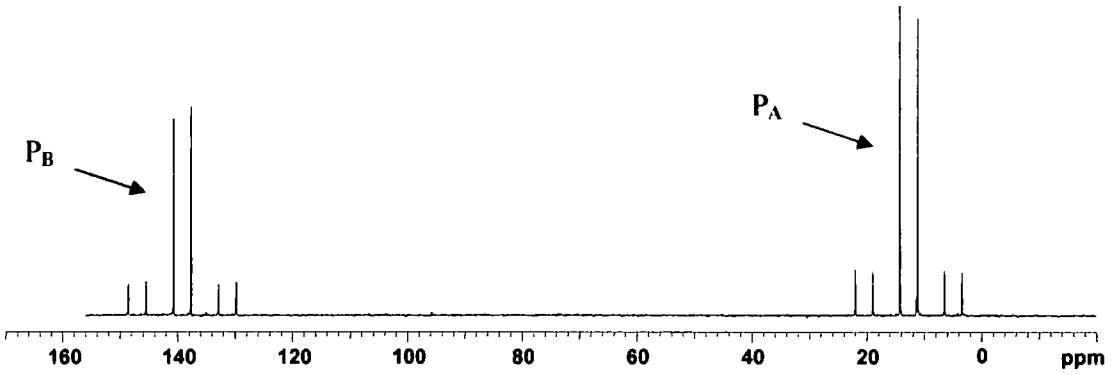
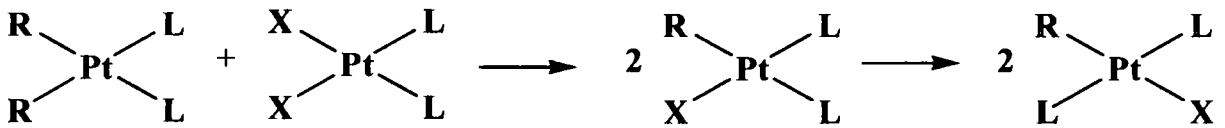


Figure 6.15: $^{31}P\{^{1}H\}$ NMR spectrum for the reaction between $^{t}Bu_2PCl$ and *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ showing the *trans*-$PtCl_2(PEt_3)(P^{t}BuCl_2)$ complex

Puddephatt and Thompson reported ligand scrambling reactions to occur between two Pt complexes, one with halide/anionic ligands and the other with alkyl/aryl ligands (Scheme 6.16).[24-26]



R = alkyl/aryl
X = halide/anionic ligand
L = tertiary phosphine/arsine

Scheme 6.16: Symmetrisation reactions summary showing ligand scrambling[24-26]

For the palladium complexes *cis*- and *trans*-$[Pd(C_6F_5)_2(tht)_2]$, Minniti has shown that they spontaneously isomerise to a *cis/trans* mixture, with the *cis* isomer predominating.[27] This suggests that the *cis* isomer is the more thermodynamically stable species.

Two possible mechanisms were proposed for this isomerisation, an associative process (through a five coordinate intermediate), or a dissociative process (through a three

coordinate intermediate). The results obtained by Minniti suggested that the associative pathway remains the favoured method of substitution.[27]

It is probable that a similar process is involved to afford ligand scrambling products **114-119**, although there was no evidence of conversion from the *cis* to the *trans* isomer in any of the reactions.

6.6.1.4 Molecular structures of the parent Pt(II) complexes containing chlorophosphane ligands

Crystals suitable for X-ray diffraction of three of the parent Pt(II) complexes were isolated (**77, 95** and **105**); the resulting molecular structures are shown in Figures 6.16-6.18. Selected bond distances and angles for each molecule are listed in Table 6.26.

Each molecule shows *cis* geometry at platinum that was inferred from the $^{31}P\{^{1}H\}$ NMR data, and also shows near square-planar platinum centres [sum of angles: (**77**) = 360.00, (**95**) = 360.22, (**105**) = 360.01°]. There is some distortion around the square-planar platinum center in each complex, with the angles around platinum varying from 85.34(4) to 97.05(4)° (**77**), 86.07(5) to 98.46(5)° (**95**) and 81.82(7) to 98.53(6)° and 82.90(7) to 99.24(7)° (**105**), with the larger P(1)–Pt(1)–P(2) angle to accommodate the bulk of the phosphane groups.

The Pt(1)-P(1) bond lengths in **77**, **95** and **105** (2.2935(10) Å, 2.2801(14) Å and 2.2596(18) Å respectively) are similar in magnitude to those observed for other $PtCl_2(P1)(P2)$ complexes where (P1) = PEt_3 (*e.g.* 2.2550(13) Å in *cis*-$[PtCl_2(PEt_3)(P(OH)_3)]$[18], 2.264(2) and 2.261(2) Å in *cis*-$PtCl_2(PEt_3)_2$[28] or 2.305(6) Å in *cis*-$PtCl_2(PEt_3)(PCy)_3$).[29]

However, the Pt(1)-P(2) bond length for each complex is much shorter (2.1746(10) Å (**77**), 2.1835(14) (**95**) and 2.2312(18) (**105**) suggesting a stronger Pt-P bond. This is also

consistent with the larger $^{1}J_{Pt\text{-}P(1)}$ coupling constant observed for these complexes. As expected the Pt(1)-P(2) bond length decreases $P^{i}Pr_2Cl$ > $PEtCl_2$ > PCl_3 as there are more electronegative substituents on the phosphane. The Pt-P(2) bond length in *cis*-$PtCl_2(PEt_3)(PF_3)$ is even shorter than that in $PtCl_2(PEt_3)(PCl_3)$ at 2.142(3) Å.[30]

Bond Length /Å	**77**	**95**	**105**
Pt(1)–P(1)	2.2935(10)	2.2801(14)	2.2596(18)
Pt(1)–P(2)	2.1746(10)	2.1835 (14)	2.2312(18)
Pt(1)–Cl(1)	2.3253(10)	2.3304(13)	2.3459(18)
Pt(1)–Cl(2)	2.3394(10)	2.3653(13)	2.3791(18)
Pt(2)–P(3)	-	-	2.2681(18)
Pt(2)–P(4)	-	-	2.2332(19)
Pt(2)–Cl(4)	-	-	2.3500(18)
Pt(2)–Cl(5)	-	-	2.3583(18)
Bond Angle /°			
P(1)–Pt(1)–P(2)	97.05(4)	98.46(5)	99.24(7)
P(1)–Pt(1)–Cl(1)	85.34(4)	89.16(5)	91.11(7)
P(2)–Pt(1)–Cl(2)	90.86(4)	86.07(5)	82.90(7)
Cl(1)–Pt(1)–Cl(2)	86.75(4)	86.53(5)	86.76(7)
P(3)–Pt(2)–P(4)	-	-	98.53(6)
P(3)–Pt(2)–Cl(4)	-	-	91.73(7)
P(4)–Pt(2)–Cl(5)	-	-	81.82(6)
Cl(4)–Pt(2)–Cl(5)	-	-	87.99(6)

*Table 6.*26: Selected bond lengths and angles for **77, 95** and **105**

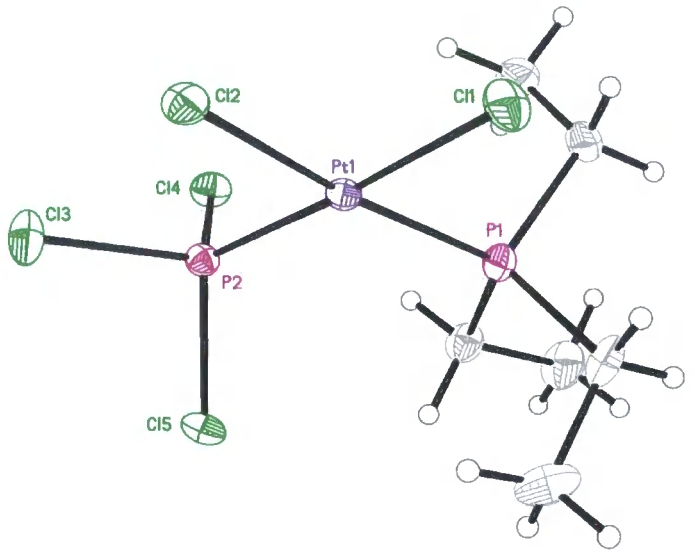


Figure 6.16: The molecular structure of **77**, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

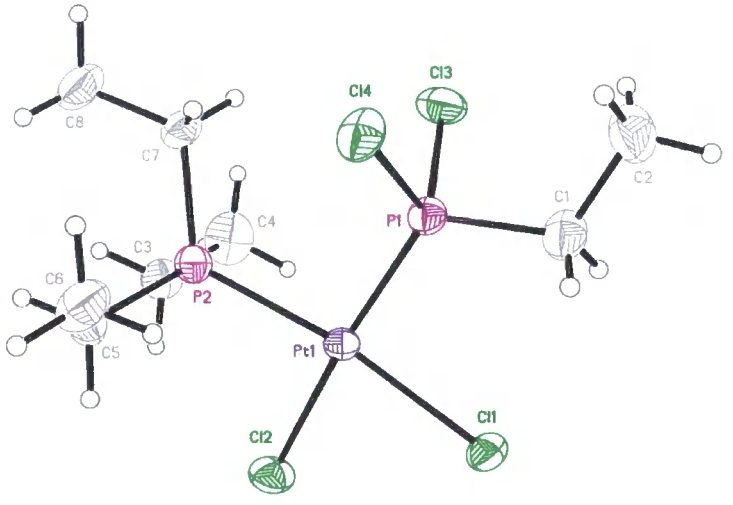


Figure 6.17: The molecular structure of **95**, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

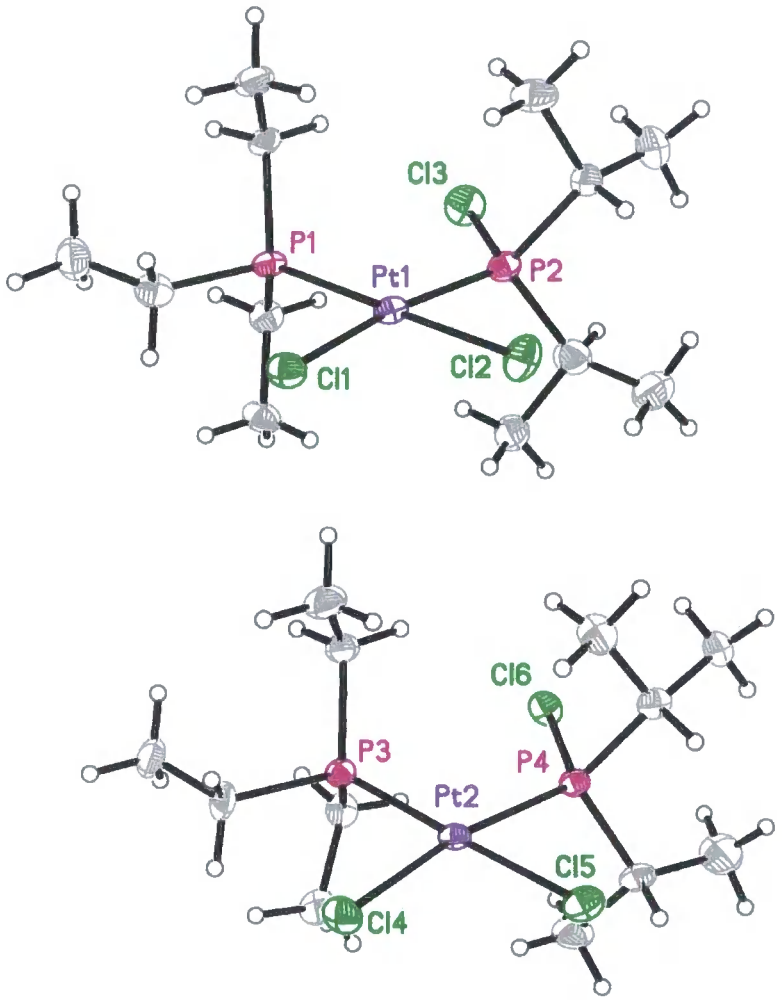
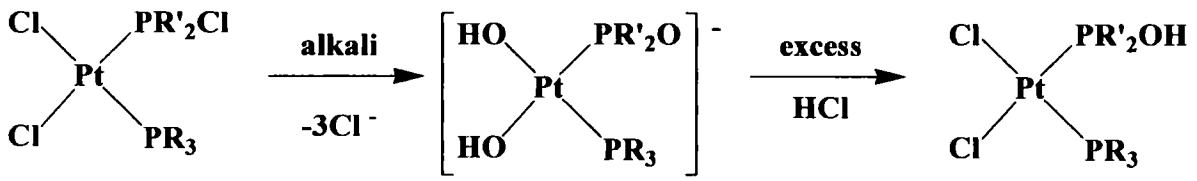


Figure 6.18: The molecular structure of **105**, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

6.6.2 Investigation into the hydrolysis of Pt(II) chlorophosphane complexes

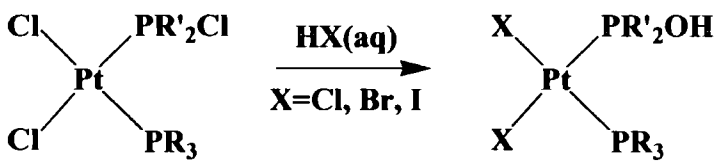
Several Pt(II) complexes containing chlorophosphanes have been previously reported, but there has been limited investigation into the hydrolysis of these complexes.[22, 31-33] Reported investigations have shown that these hydrolysis reactions, and those of similar complexes, are quite complicated, frequently resulting in multiple product formation and/or products containing P-O-P and P-O-H-O-P linkages.[22, 33-40]

Investigation into the hydrolysis of some Pt(II) chlorophosphane complexes was carried out by Chatt and Heaton.[33] Due to limited ^{31}P NMR facilities at this time, the majority of analysis was carried out using IR and elemental analysis. Two methods were used to synthesise the hydrolysed products. The first, a two-step process, involved the addition of alkali to remove all three halogens, followed by addition of excess hydrochloric acid (Scheme 6.17). [33]



Scheme 6.17: Two-step synthesis of the hydrolysed Pt(II) complex [33]

The second, perhaps more convenient method, involved boiling an acetone solution of the parent complex with aqueous HX (Scheme 6.18).



Scheme 6.18: One-pot synthesis of the hydrolysed Pt(II) complex

Seven hydrolysed complexes of the type $[PtX_2(PR_3)(PR'_2OH)]$ were reported (X=Cl, R' = Ph, R = Me, Et; X = Br, R' = Ph, R = Me, Et; X = I, R' = Ph, R = Et; X = Cl, R' = Et, R = Et; X = Cl, R' = Bu, R = Ph). $^{31}P\{^1H\}$ NMR data were obtained for $[PtCl_2(PBu_3)(PPh_2OH)]$ (Table 6.27).

Investigations into the hydrolysis of $[PtCl_2(PEt_3)(PPh_2Cl)]$ and $[PtCl_2(PEt_3)(P(OEt)_2Cl)]$ were carried out by Berry *et al.*[22] The addition of two molar equivalents of water to a solution of $[PtCl_2(PEt_3)(PPh_2Cl)]$ in THF afforded the hydrolysed product (Table 6.27).

However, an analogous reaction with $[PtCl_2(PEt_3)(P(OEt)_2Cl)]$ afforded a mixture of products, but the desired hydrolysis product was not isolated. Both $[PtCl_2(PEt_3)(PPh_2OH)]$ and $[PtCl_2(PEt_3)(P(OEt)_2OH)]$, however, were synthesised by reaction of $Ph_2P(O)H$ or $(EtO)_2P(O)H$ with $[PtCl_2(COD)]$ (Table 6.27).

R =	R' =	δP_A, ppm	δP_B, ppm	$^1J_{Pt\text{-}PA}$, Hz	$^1J_{Pt\text{-}PB}$, Hz	$^2J_{PA\text{-}PB}$, Hz	Reference
Bu	Ph	50.2	116.5	3502	4172	NR	33
Et	OEt	14.9	63.2	3414	5623	23	22
Et	Ph	10.3	72.9	3497	3890	17	22

Table 6.27: $^{31}P\{^1H\}$ NMR literature data for the hydrolysis products, *cis*-$[PtCl_2(PR_3)(PR'_2OH)]$ (NR – not recorded)

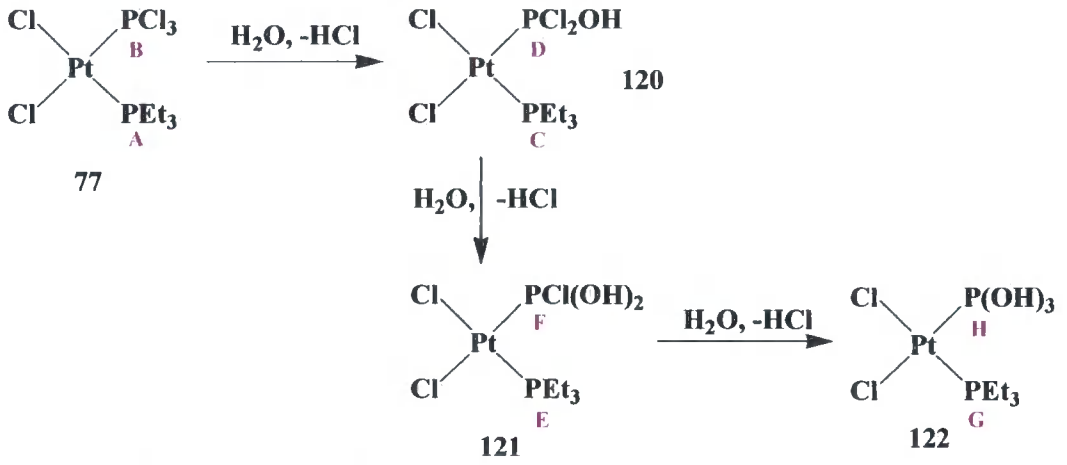
6.6.2.1 Hydrolysis of Pt(II) chlorophosphane complexes through exposure to air and 'wet' solvents

The hydrolysis reactions of Pt(II) chlorophosphane complexes described in this section were carried out by exposure to air and moisture through stirring of the solution in an open vessel. The solutions were topped up with 'wet' DCM as the solvent evaporated. These reactions proceeded very slowly and were monitored using $^{31}P\{^1H\}$ NMR spectroscopy.

6.6.2.1.1 Hydrolysis of $PtCl_2(PEt_3)(PCl_3)$ - Synthesis of *cis*-$PtCl_2(PEt_3)[P(OH)_3]$

It was proposed that the hydrolysis of the PCl_3 group would occur in three stages (Scheme 6.19). Careful hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ was carried out, and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction

proved to be very slow at room temperature and had not gone to completion after 12 months. However, over this period of time there were peaks in the $^{31}P\{^{1}H\}$ NMR spectra corresponding to four different complexes (Table 6.28).



Scheme 6.19: Proposed synthesis of *cis*-$PtCl_2(PEt_3)[P(OH)_3]$

δ, ppm	Mulitplicity	$^{1}J_{Pt\text{-}P}$, Hz	$^{2}J_{P\text{-}P}$, Hz	Assignment
101.6	d	6062	18	P_B
47.3	d	6495	23	P_D
39.6	d	5951	24	P_F
36.7	d	5823	23	P_H
17.6	d	2996	18	P_A
16.9	d	3245	23	P_C
15.0	d	3506	23	P_G
14.5	d	3493	24	P_E

Table 6.28: $^{31}P\{^{1}H\}$ NMR data for the hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$

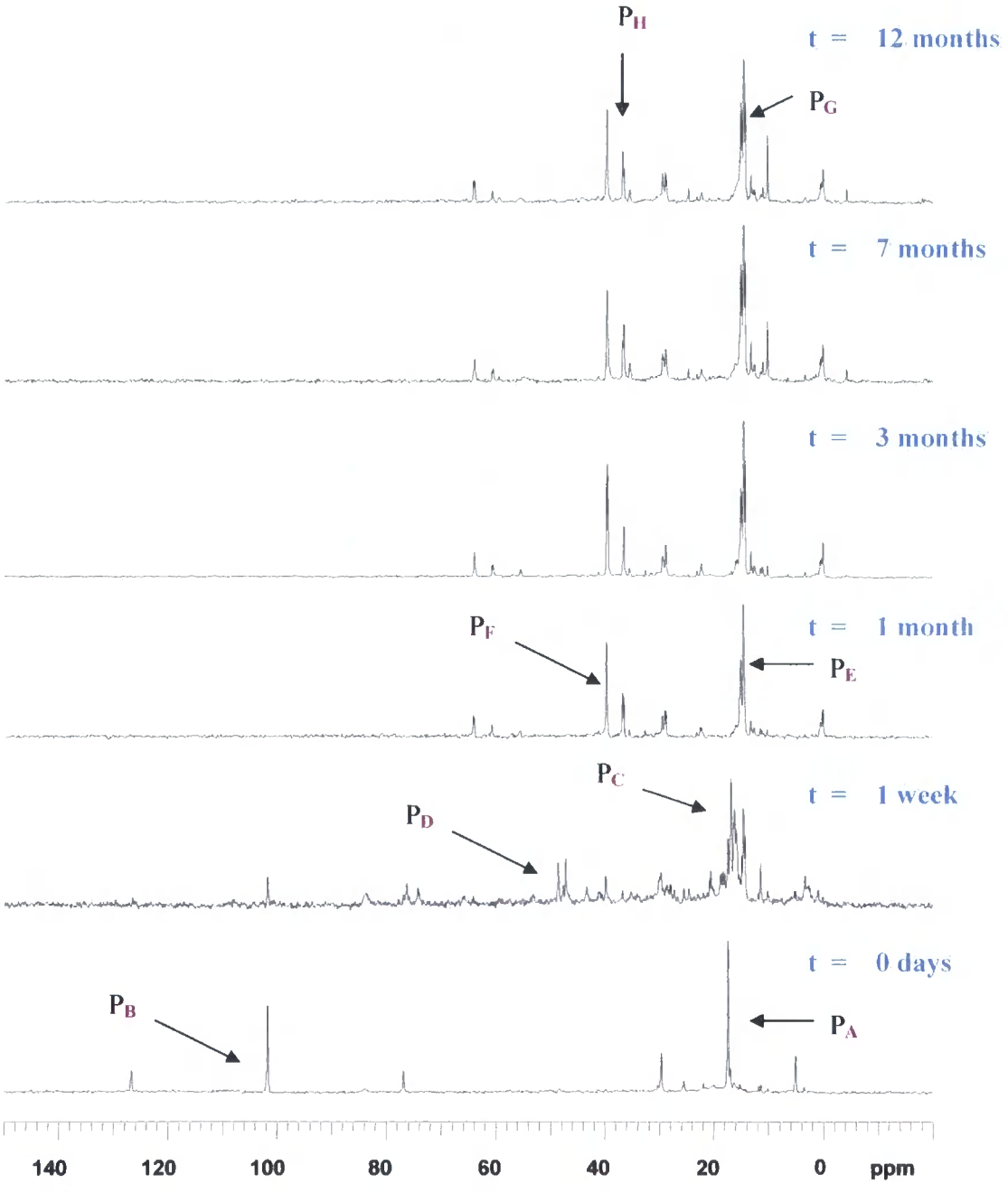
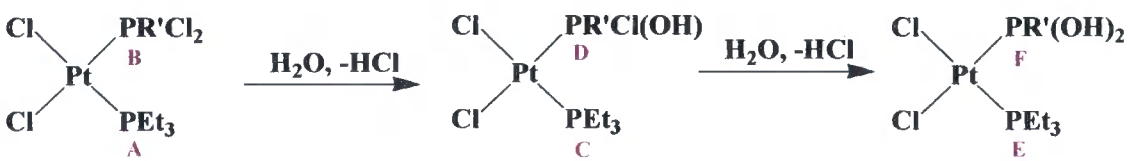


Figure 6.19: Stackplot of $^{31}P\{^{1}H\}$ NMR spectra for the exposure of $PtCl_2(PEt_3)(PCl_3)$ to air and 'wet' solvent over a period of 12 months - synthesis of *cis*-$PtCl_2(PEt_3)[P(OH)_3]$. t = 0 is when $PtCl_2(PEt_3)(PCl_3)$ was synthesised.

The NMR spectra show firstly the disappearance of the peaks corresponding to P_A and P_B and the appearance of those corresponding to P_C and P_D. Over time these peaks also disappeared and peaks corresponding to P_E and P_F, and then finally P_G and P_H, appeared (Figure 6.19). As each chlorine is replaced by OH, a shift to lower frequency is observed for the doublet corresponding to the phosphorus atom is seen, compared with the P_B resonance of the parent complex, *cis*-$PtCl_2(PEt_3)(PCl_3)$. This is consistent with the data reported for the hydrolysis of *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ and *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ using NaOH.[33] This spectroscopic evidence clearly supports the proposed pathway (Scheme 6.19).

6.6.2.1.2 Hydrolysis of $PtCl_2(PEt_3)(PR'Cl_2)$ – Attempted synthesis of *cis*-$PtCl_2(PEt_3)[PR'(OH)_2]$

The attempted hydrolysis of several *cis*-$PtCl_2(PR'Cl_2)(PEt_3)$ complexes was carried out and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. It was proposed that the hydrolysis of the $PRCl_2$ group would occur in two stages (Scheme 6.20). For the *cis*-$PtCl_2(PR'Cl_2)(PEt_3)$ complexes where R'= Et, ^{i}Pr or Ph, the first hydrolysis product was obtained and there was no evidence of the second hydrolysis product after 2 months (Table 6.29).



Scheme 6.20: Proposed synthesis of *cis*-$PtCl_2(PEt_3)[PEt(OH)_2]$

***cis*-$PtCl_2(PEt_3)$[PR'Cl(OH)] R' =**	**δP_C, ppm**	**δP_D, ppm**	**$^1J_{Pt\text{-}PC}$, Hz**	**$^1J_{Pt\text{-}PD}$, Hz**	**$^2J_{P\text{-}P}$, Hz**	**Compound Number**
Et	15.6	94.6	3614	4387	20	**123**
^{i}Pr	15.4	96.5	3638	4323	19	**124**
Ph	13.0	75.9	3553	4484	21	**125**

Table 6.29: $^{31}P\{^1H\}$ NMR data for *cis*-$PtCl_2(PEt_3)$[PR'Cl(OH)] where R' = Et, ^{i}Pr and Ph

For the three hydrolysis products obtained, a shift to lower frequency is seen for the doublet corresponding to P_D, compared with that for P_B of the parent complex, *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$, as the chlorine is replaced by OH. This is consistent with the data reported for the hydrolysis of *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ and *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ using NaOH,[33] and for the hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ (Section 6.6.2.1.1). The NMR spectra for each reaction, over a period of time, showed firstly the disappearance of the resonances corresponding to P_A and P_B and the growth of those corresponding to P_C and P_D. This is again consistent with the proposed hydrolysis pathway.

During the monitoring period, ligand scrambling occurred for all reactions except that involving *cis*-$PtCl_2(P^tBuCl_2)(PEt_3)$, probably because of the bulky phosphane ligand. The ligand scrambling products are shown in Table 6.30.

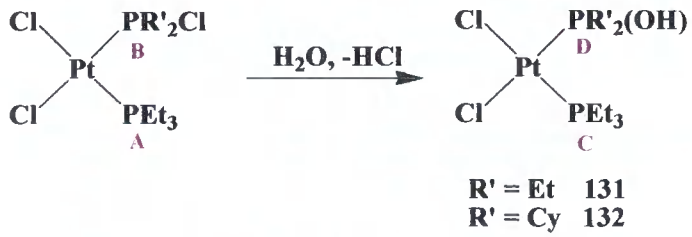
The $^{31}P\{^1H\}$ NMR data for both *cis* and *trans*-$PtCl_2(PEt_3)(PRCl_2)$ complexes are consistent with those previously reported.[13, 23] In the attempted hydrolysis of *cis*-$PtCl_2(PEtCl_2)(PEt_3)$, the singlet at 84.3 ppm was assigned to *cis*-$PtCl_2[PEtCl(OH)]_2$ as the shift was significantly to lower frequency compared with that of the $PEtCl_2$ in the parent Pt(II) complex, suggesting a hydrolysis product. The assignment of *cis*-$PtCl_2[P^iPrCl(OH)]_2$ was made due to the chemical shift being similar to that for *cis*-$PtCl_2(PEt_3)[P^iPrCl(OH)]$, and also to lower frequency compared to the parent complex.

Parent Complex	Ligand scrambling product	δP_C, ppm	δP_D, ppm	$^1J_{Pt-PC}$, Hz	$^1J_{Pt-PD}$, Hz	$^2J_{P-P}$, Hz	Compound Number
95, 97, 98, 99	*cis*-$PtCl_2(PEt_3)_2$	10.3	-	3518	-	-	**115**
95, 97	*trans*-$PtCl_2(PEt_3)_2$	13.3	-	2394	-	-	**126**
95	*cis*-$PtCl_2[PEtCl(OH)]_2$	-	84.3	-	4470	-	**127**
95	*trans*-$PtCl_2(PEt_3)(PEtCl_2)$	19.7	119.2	2110	3064	422	**128**
97	*cis*-$PtCl_2[P^iPrCl(OH)]_2$	-	86.7	-	4484	-	**129**
97	*trans*-$PtCl_2(P^iPrCl_2)_2$	20.1	114.1	3213	3626	418	**130**

Table 6.30: $^{31}P\{^1H\}$ NMR data for products resulting from ligand scrambling in the attempted hydrolysis of *cis*-$PtCl_2(PR'Cl_2)(PEt_3)$ where R' = Et, ^{i}Pr, Cy and Ph ($P_C = PEt_3$)

6.6.2.1.3 Hydrolysis of $PtCl_2(PEt_3)(PR_2'Cl)$ – Attempted synthesis of *cis*-$PtCl_2(PEt_3)[PR_2'(OH)]$

The attempted hydrolysis of several *cis*-$PtCl_2(PEt_3)(PR_2'Cl)$ complexes were carried out and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. It was proposed that the hydrolysis of the PEt_2Cl group would occur as shown in Scheme 6.21. For the *cis*-$PtCl_2(PR_2'Cl)(PEt_3)$ complexes where R'= Et or Cy, the hydrolysis product was obtained (Table 6.31).



Scheme 6.21: Proposed synthesis of *cis*-$PtCl_2(PEt_3)[PR'_2(OH)]$

***cis*-$PtCl_2(PEt_3)(PR_2'(OH))$ R' =**	**δP_C, ppm**	**δP_D, ppm**	**$^1J_{Pt\text{-}PC}$, Hz**	**$^1J_{Pt\text{-}PD}$, Hz**	**$^2J_{P\text{-}P}$, Hz**
Et	15.8	93.5	3672	4005	16
Cy	13.1	97.5	3704	4023	16

Table 6.31: $^{31}P\{^1H\}$ NMR data for *cis*-$PtCl_2(PEt_3)[PR_2'(OH)]$ where R' = Et or Cy

Ligand scrambling was observed in all reactions, except that involving *cis*-$PtCl_2(P^tBu_2Cl)(PEt_3)$. Again this is probably because of the bulky phosphane ligand. The products resulting from ligand scrambling are shown in Table 6.32.

Parent Complex	**Ligand scrambling product**	**δP_C, ppm**	**δP_D, ppm**	**$^1J_{Pt\text{-}PC}$, Hz**	**$^1J_{Pt\text{-}PD}$, Hz**	**Compound Number**
103, 105, 107, 108	*cis*-$PtCl_2(PEt_3)_2$	10.3	-	3518	-	**115**
105	*cis*-$PtCl_2(P^iPr_2Cl)_2$	-	119.3	-	3995	**133**
107	*cis*-$PtCl_2(PPh_2(OH))_2$	-	51.4	-	4098	**134**
108	*trans*-$PtCl_2(PCy_2Cl)_2$	-	110.5	-	3967	**135**

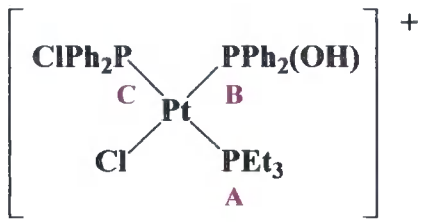
Table 6.32: $^{31}P\{^1H\}$ NMR data for products resulting from ligand scrambling in the attempted hydrolysis of *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ where R' = Et, ^{i}Pr, Cy and Ph ($P_C = PEt_3$)

In the attempted hydrolysis of *cis*-$PtCl_2(PEt_3)(PPhCl_2)$, a third platinum complex (**136**) containing three phosphane ligands was also observed in the $^{31}P\{^1H\}$ NMR spectrum (Table 6.33, Figure 6.20).

δ, ppm	Multiplicity	$^1J_{Pt\text{-}P}$, Hz	$^2J_{PA\text{-}PC}$, Hz	$^2J_{P\text{-}P}$, Hz	Assignment
79.5	dd	2774	402	18	P_C
62.0	t	3886	-	18	P_B
13.1	dd	2156	402	18	P_A

Table 6.33: $^{31}P\{^1H\}$ NMR data for a by-product in the hydrolysis of *cis*-$PtCl_2(PEt_3)(PPh_2Cl)$

From the chemical shifts of the signals the three phosphane ligands must be different. P_A and P_C have similar shifts to PEt_3 and PPh_2Cl in the parent complex. The third phosphane can be assigned to PPh_2OH as the signal is to lower frequency than that for PPh_2Cl, as previously observed for hydrolysed chlorophosphanes.[16, 21-23] The $^1J_{Pt\text{-}P}$ coupling constants also agree with this assignment as P_A and P_C have values typical for *trans* complexes, which dominates coupling, and P_B has a typical value for a *cis* complex.



136

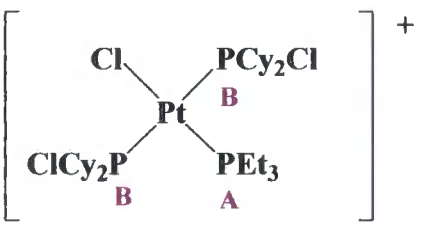
Figure 6.20: Proposed by-product in the hydrolysis of *cis*-$PtCl_2(PEt_3)(PPh_2Cl)$

A third platinum complex containing three phosphane ligands was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the attempted hydrolysis of *cis*-$PtCl_2(PPhCl_2)(PEt_3)$ (Table 6.34). The $^{31}P\{^1H\}$ NMR data clearly show that there are three phosphane ligands, and that two of the phosphanes are identical and are *trans* to each other. The shifts suggest that the phosphanes are Cy_2PCl and PEt_3, as they are similar to those observed for the

parent complex, with the proposed complex (**137**) (Figure 6.21). Upon standing crystalline material was obtained. However single crystal X-ray diffraction studies showed the structure to be *cis*-$PtCl_2(PEt_3)_2.CDCl_3$, a product of ligand scrambling, which will be discussed in more detail in Section 6.6.2.2.3.

δ, ppm	Multiplicity	$^1J_{Pt-P}$, Hz	$^2J_{PA-PB}$, Hz	Assignment
114.9	d	2546	17	P_B
14.5	t	3622	18	P_A

Table 6.34: $^{31}P\{^1H\}$ NMR data for a by-product in the hydrolysis of *cis*-$PtCl_2(PEt_3)(PCy_2Cl)$ (**137**)



137

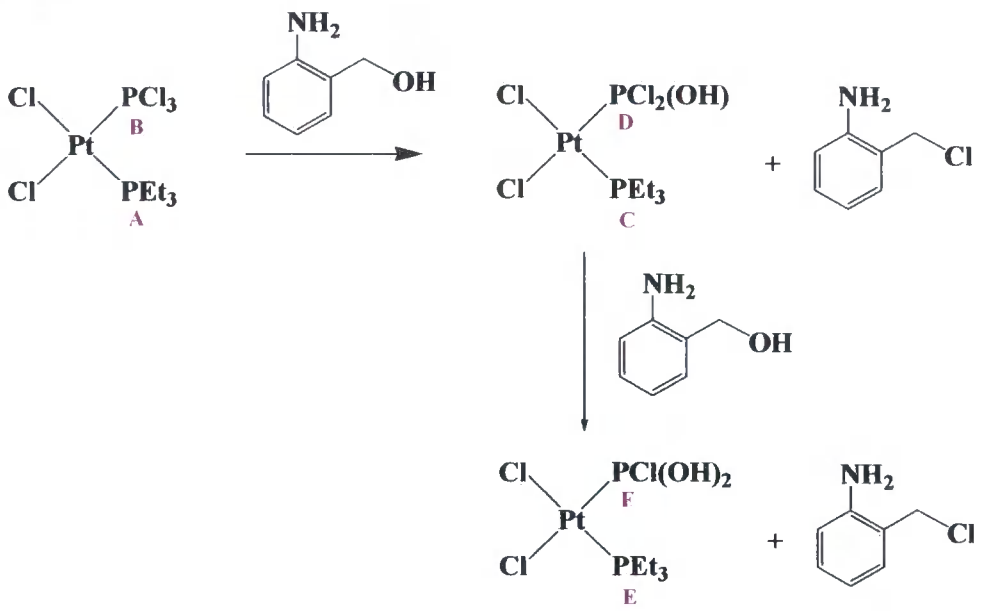
Figure 6.21: Proposed by-product in the hydrolysis of *cis*-$PtCl_2(PEt_3)(PCy_2)$

6.6.2.2 Hydrolysis reactions using 2-aminobenzyl alcohol

Reactions carried out by Dyer and Wright suggested that 2-aminobenzyl alcohol could be used as a mild, anhydrous source of OH^-.[41] This prompted an investigation into the potential application of 2-aminobenzyl alcohol in hydrolysis reactions of Pt(II) chlorophosphane complexes.

6.6.2.2.1 Hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ using 2-aminobenzyl alcohol -Synthesis of *cis*-$PtCl_2(PEt_3)[PCl_2(OH)]$ and *cis*-$PtCl_2(PEt_3)[PCl(OH)_2]$

A mixture of two complexes were observed in a $^{31}P\{^1H\}$ NMR spectrum recorded 15 minutes after the addition of 2-aminobenzyl alcohol to a solution of *cis*-$PtCl_2(PEt_3)(PCl_3)$. The proposed reaction is shown in Scheme 6.22. The main component (70%) was the parent complex, *cis*-$PtCl_2(PEt_3)(PCl_3)$ (d, δP_A 101.5 ppm, $^1J_{Pt\text{-}P}$ = 6044 Hz, $^2J_{P\text{-}P}$ = 18 Hz, d, δ P_B 17.8 ppm, $^1J_{Pt\text{-}P}$ =2979 Hz, $^2J_{P\text{-}P}$ = 18 Hz). The other complex (30%) was assigned to a product of hydrolysis (**138**). Complete conversion to this hydrolysed product occurred in 5 hours (Figure 6.22).



Scheme 6.22: Proposed hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ using 2-aminobenzyl alcohol

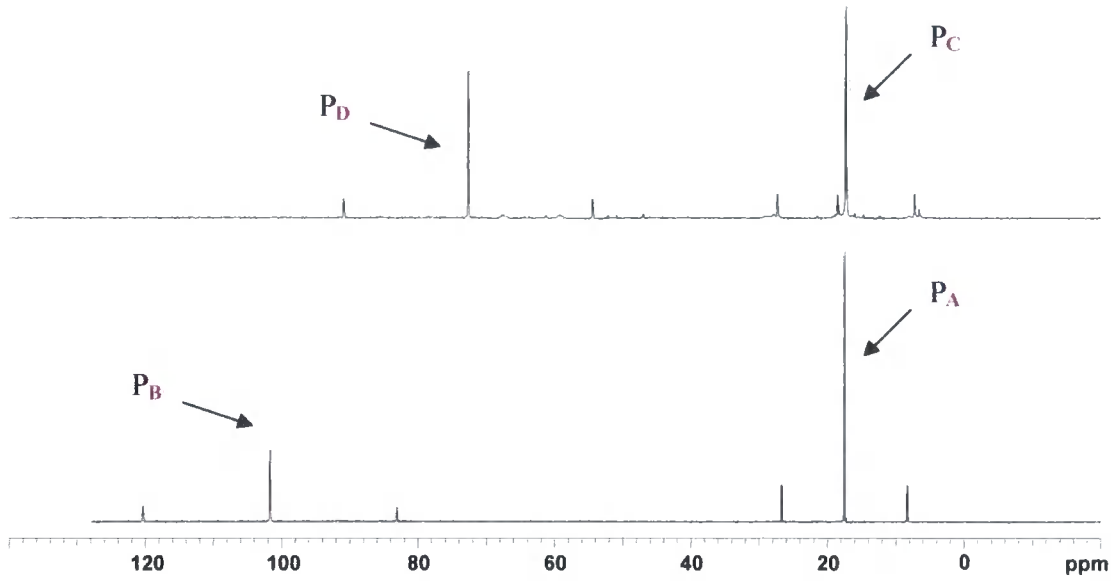


Figure 6.22: $^{31}P\{^{1}H\}$ NMR data for the reaction between *cis*-$PtCl_2(PEt_3)(PCl_3)$ and 2-aminobenzyl alcohol. Bottom: parent complex, top: spectrum after 5 hours of reaction

Upon standing, a solution of **138** afforded colourless crystals that were suitable for analysis by X-ray diffraction, the resulting molecular structure being shown in Figure 6.23. Selected bond lengths and angles are shown in Table 6.35.

As observed with the parent Pt(II) complex, **77**, the molecular structure of **138** reveals a near square planar platinum centre (sum of angles = 359.98°). There is some distortion around the Pt(II) centre, with the angles around Pt varying from 86.25(7) to 93.97(10)° and the larger P(1)-Pt(1)-P(2) angle to accommodate the bulkier phosphane groups. The Pt(1)-P(1) bond is shorter that the Pt(1)-P(2) bond length, which is consistent with more electronegative substituents on P(1).

The P(1)-O(1) bond length is significantly shorter than P-O bond lengths in complexes containing $[P(OH)_3]$ (*e.g.* 1.565(4) – 1.581(4) Å in *cis*-$[PtCl_2(PEt_3)(P(OH)_3]$[18] or 1.561(12) Å in $\{[Mo_3PdP(OH)_3S_4Cl_3(H_2O)_6](C_{36}H_{36}N_{24}O_{12})\}Cl_2.20H_2O)$)[19], compounds containing P-O-H-O-P links (*e.g.* 1.562 and 1.581 Å in $[Mo(CO)_4\{(PPh_2O)_2H\}]^-$)[42] or in

other products of hydrolyis (*e.g.* 1.581(4) and 1.597(5) Å in *cis*-$[PtCl_2(PPh_2OH)_2]$)[22]. This is expected since the product is a salt.

Hydrogen bonding is present within this structure, with the NH_3 group on the protonated 2-aminobenzylchloride hydrogen bonding to the oxygen in the hydrolysed Pt(II) complex, as well as to chlorine atoms in other molecules.

	Bond Length /Å		**Bond Angle /°**
Pt(1)–P(1)	2.217(2)	P(1)–Pt(1)–P(2)	93.97(10)
Pt(1)–P(2)	2.267(3)	P(1)–Pt(1)–Cl(4)	89.96(8)
P(1)–Cl(2)	2.041(4)	P(2)–Pt(1)–Cl(5)	89.80(9)
P(1)–O(1)	1.474(6)	Cl(4)–Pt(1)–Cl(5)	86.25(7)

Table 6.35: Selected bond lengths and angles for **138**

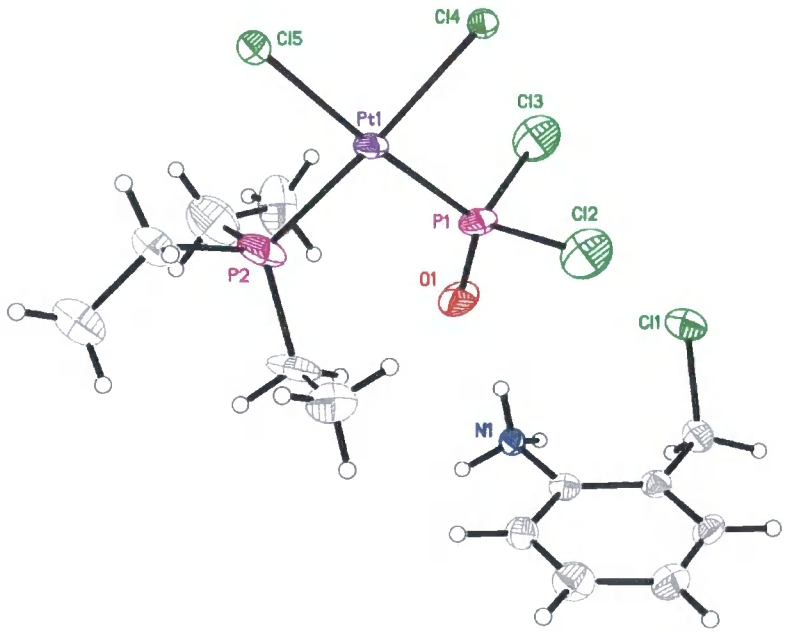


Figure 6.23: The molecular structure of **138**, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

The difference in chemical shifts is obviously due to the product of hydrolysis from exposure to air and 'wet' solvent, *cis*-$PtCl_2(PEt_3)[PCl_2OH]$ (**120**) is not a salt, whereas the product of the hydrolysis reaction using 2-aminobenzyl alcohol is the salt, $[PtCl_2(PEt_3)(PCl_2O)]^-[1,2\text{-}C_6H_4(CH_2Cl)(NH_3)]^+$ (**138**), A similar change in shift has been reported in other systems (Table 6.36).[16]

First product of hydrolysis				Second product of hydrolysis		
	120	**138**			**121**	**139**
δP_C, ppm	16.9	17.3		δP_E, ppm	14.5	18.6
δP_D, ppm	47.3	72.7		δP_F, ppm	39.6	62.1*
$^1J_{Pt\text{-}PC}$, Hz	3245	3237		$^1J_{Pt\text{-}PE}$, Hz	3493	3390
$^1J_{Pt\text{-}PD}$, Hz	6495	5904		$^1J_{Pt\text{-}PF}$, Hz	5823	~6000
$^2J_{PC\text{-}PD}$, Hz	23	22		$^2J_{PE\text{-}PF}$, Hz	24	24

Table 6.36: $^{31}P\{^1H\}$ NMR data for the first and second hydrolysis products of *cis*-$PtCl_2(PEt_3)(PCl_3)$ obtained through exposure to air and 'wet' solvent and using 2-aminobenzyl alcohol (* broad signal)

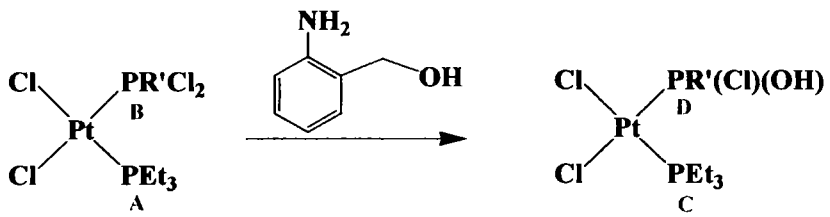
Since the reaction using 2-amino benzyl appeared to be selective, with only one Cl being replaced by OH with the addition of one equivalent, it was proposed that by adding two equivalents of 2-aminobenzyl alcohol the second stage of hydrolysis product, *cis*-$PtCl_2(PEt_3)[PCl(OH)_2]$ (or the corresponding salt), would be obtained.

Fifteen minutes after the addition of 2-aminobenzyl alcohol, a $^{31}P\{^1H\}$ NMR spectrum showed no signals corresponding to the parent complex, *cis*-$PtCl_2(PEt_3)(PCl_3)$. The main product of the reaction was the first hydrolysis product **138**, although signals corresponding to a second platinum-containing complex (a minor product) were apparent. The data suggest that this could be the second stage of hydrolysis product, as the shift of the P_D resonance is to lower frequency, while there is a decrease in the value of $^1J_{Pt\text{-}PD}$ and also there is an increase in the value of $^1J_{Pt\text{-}PC}$. The broad signals suggest that exchange is taking place.

However the $^{31}P\{^{1}H\}$ NMR data for this second hydrolysis product are not consistent with those obtained for **121** from the slow hydrolysis of the parent complex through exposure to air and 'wet' solvent (Table 6.36). As seen in the previous reaction, there is a difference in shift for P_F of the product obtained when using 2-aminobenzyl alcohol compared to that obtained by slow hydrolysis. This suggests that the product obtained is again a salt, $[PtCl_2(PEt_3)(PCl(OH)O)]^-[1,2\text{-}C_6H_4(CH_2Cl)(NH_3)]^+$ (**139**)

6.6.2.2.2 Hydrolysis of *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ using 2-aminobenzyl alcohol

Following the successful hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ using 2-aminobenzyl alcohol, it was proposed that hydrolysis of *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ complexes would also occur in a stepwise fashion (Scheme 6.23).



Scheme 6.23: Proposed synthesis of *cis*-$PtCl_2(PEt_3)(PR'(Cl)(OH))$ using 2-aminobenzyl alcohol

Addition of one equivalent of 2-aminobenzyl alcohol to *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ complexes afforded the hydrolysed product although 100% conversion was not achieved, even after one week (Table 6.37, Table 6.38). Formation of hydrolysed products is much faster compared to those by exposure to air and 'wet' solvent discussed in Section 6.6.2.1. However some ligand scrambling was observed to afford a small amount of *cis*-$PtCl_2(PEt_3)_2$ in all the reactions (s, δ 10.2 ppm, $^{1}J_{Pt\text{-}P}$ = 3515 Hz)[13, 23] For the hydrolysis products of *cis*-$PtCl_2(PEt_3)(PR'Cl_2)$ complexes where R' = Et and ^{i}Pr, the

$^{31}P\{^{1}H\}$ NMR data obtained is comparable to those from the products of hydrolysis through exposure to air and 'wet' solvents. This suggests that the products are non-salts.

However, the $^{31}P\{^{1}H\}$ NMR spectrum for the product of hydrolysis of *cis*-$PtCl_2(PEt_3)(PPhCl_2)$ using 2-aminobenzyl alcohol suggests that it is the salt $[PtCl_2(PEt_3)(PPhCl(O)]^-$ $[1,2\text{-}C_6H_4(CH_2Cl)(NH_3)]^+$ (**143**), as there is a large difference in shift of P_D compared to **125** obtained by slow hydrolysis (Table 6.39).

***cis*-$PtCl_2(PEt_3)$[PR'Cl(OH)] R' =**	**δP_C, ppm**	**δP_D, ppm**	**$^1J_{Pt\text{-}PC}$, Hz**	**$^1J_{Pt\text{-}PD}$, Hz**	**$^2J_{P\text{-}P}$, Hz**	**Compound Number**
Et	17.1	95.7	3576	4421	16	**123**
^{n}Pr	17.1	93.5	3549	4404	17	**140**
^{i}Pr	16.7	101.3	3601	4367	16	**124**
Cy	16.5	99.0	3615	4087	16	**141**
^{t}Bu	16.3	106.9	3540	4358	15	**142**

Table 6.37: $^{31}P\{^{1}H\}$ NMR data for *cis*- $PtCl_2(PEt_3)$[PR'Cl(OH)] complexes synthesised using 2-aminobenzyl alcohol

R'=	**Initial Spectrum Parent : Hydrolysis**	**Spectrum after 1 week Parent : Hydrolysis**
$EtPCl_2$	1:1	-
$^n PrPCl_2$	2:1	2:1
$^i PrPCl_2$	2:1	2:3
Ph	1:2	-
Cy	1:2	-

Table 6.38: Ratios of parent complex to *cis*- $PtCl_2(PEt_3)$[PR'Cl(OH)] complexes

	cis-$PtCl_2(PEt_3)$[PPhCl(OH)]	$[PtCl_2(PEt_3)(PPhCl(O)]^-$ $[1,2\text{-}C_6H_4(CH_2Cl)(NH_3)]^+$
Compound number	**125**	**143**
δP_C, ppm	13.0	13.7
δP_D, ppm	75.9	92.7
$^1J_{Pt\text{-}PC}$, Hz	3553	3350
$^1J_{Pt\text{-}PD}$, Hz	4484	4698
$^2J_{PC\text{-}PD}$, Hz	21	19

Table 6.39: $^{31}P\{^1H\}$ NMR data for the hydrolysis products *cis*-$PtCl_2(PEt_3)$[PPhCl(OH)] and $[PtCl_2(PEt_3)(PPhCl(O)]^-[1,2C_6H_4(CH_2Cl)(NH_3)]^+$

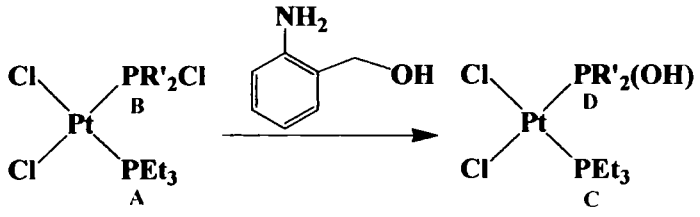
In the reaction between *cis*-$PtCl_2(PEt_3)(PPhCl_2)$ and one equivalent of 2-aminobenzyl alcohol, a small amount of the second hydrolysis product, *cis*-$PtCl_2(PEt_3)(PR'(OH)_2)$ was synthesised (**146**) (Table 6.40). By replacing Cl with OH, there is a shift to lower frequency of the doublet resonance corresponding to P_F in the $^{31}P\{^1H\}$ NMR spectrum, a reduction in the magnitude of $^1J_{Pt\text{-}PF}$ and an increase in $^1J_{Pt\text{-}PE}$ compared to that determined for the parent complex, and the first hydrolysis product (**143**).

δ, ppm	**Mulitplicity**	$^1J_{Pt\text{-}P}$, **Hz**	$^2J_{P\text{-}P}$, **Hz**	**Assignment**
78.2	d	4614	18	P_F
16.4	d	3504	18	P_E

Table 6.40: $^{31}P\{^1H\}$ NMR data for the second hydrolysis product of *cis*-$PtCl_2(PEt_3)(PPhCl_2)$ using 2-aminobenzyl alcohol (**146**)

6.6.2.2.3 Hydrolysis of cis-$PtCl_2(PEt_3)(PR_2'Cl)$ using 2-aminobenzyl alcohol

It was proposed that hydrolysis of *cis*-$PtCl_2(PEt_3)(PR_2'Cl)$ complexes using 2-aminobenzyl alcohol would also occur to afford only one product (Scheme 6.24).



Scheme 6.24: Proposed hydrolysis of *cis*-$PtCl_2(PEt_3)(PR'_2Cl)$ using 2-aminobenzyl alcohol

Reaction of *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ with 2-aminobenzyl alcohol should afford only one hydrolysis product (Scheme 6.24). A $^{31}P\{^1H\}$ NMR spectrum recorded soon after the addition of 2-aminobenzyl alcohol showed signals corresponding to the parent complex, **103** (d, δ 106.4 ppm, $^1J_{Pt\text{-}P}$ = 4042 Hz, $^2J_{P\text{-}P}$ = 13 Hz, d, δ 15.8 ppm, $^1J_{Pt\text{-}P}$ = 3467 Hz, $^2J_{P\text{-}P}$ = 13 Hz) and *cis*-$PtCl_2(PEt_3)_2$, **114** (s, δ 10.3 ppm, $^1J_{Pt\text{-}P}$ = 3515 Hz), showing that some ligand scrambling was already taking place. However, there were signals corresponding to a *cis*-platinum complex, which was assigned as the hydrolysis product, *cis*-$PtCl_2(PEt_3)[PEt_2(OH)]$, **131** (Table 6.41). The $^{31}P\{^1H\}$ NMR data is similar to those obtained from the product obtained through exposure of *cis*-$PtCl_2(PEt_3)(PEt_2Cl)$ to air and 'wet' solvent. This suggests the product is a non-salt.

δ, ppm	Multiplicity	$^1J_{Pt\text{-}P}$, Hz	$^2J_{PC\text{-}PD}$, Hz	Assignment
34.6	d	3947	15	P_D
10.7	d	3645	15	P_C

Table 6.41: $^{31}P\{^1H\}$ NMR data for *cis*-$PtCl_2(PEt_3)[PEt_2(OH)]$, **131**

Analogous reactions between *cis*-$PtCl_2(PEt_3)(PR_2'Cl)$ (where R'= ^{i}Pr, ^{t}Bu, Cy or Cpent) and 2-aminobenzyl alcohol did not afford the expected hydrolysis products, and for the ^{i}Pr and ^{t}Bu systems no reaction at all was observed. This has been attributed to the presence of the bulky phosphane ligands. However, in the reaction between *cis*-$PtCl_2(PEt_3)(PCy_2'Cl)$ and 2-aminobenzyl alcohol, signals were seen corresponding to *cis*-$PtCl_2(PEt_3)_2$ (**114**) (s, δ 10.3 ppm, $^1J_{Pt\text{-}P}$ = 3513 Hz).[13, 23] Similarly in the reaction between *cis*-$PtCl_2(PEt_3)(PCpent_2'Cl)$ and 2-aminobenzyl alcohol, signals corresponding to **114** and *cis*-$PtCl_2(PCpent_2Cl)_2$ (**119**) (s, δ 108.1 ppm, $^1J_{Pt\text{-}P}$ = 4037 Hz) were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, indicating that ligand scrambling was taking place.

Upon standing, the *cis*-$PtCl_2(PEt_3)(PCpent_2'Cl)$ and 2-aminobenzyl alcohol reaction mixture afforded colourless crystals of *cis*-$PtCl_2(PEt_3)_2.CDCl_3$ (**115**) that were suitable for analysis by X-ray diffraction; data were collected at 120K. The resulting molecular structure is shown in Figure 6.24. This compound is a pseudo-polymorph (or solvate) of *cis*-$PtCl_2(PEt_3)_2$ previously reported by Otto and Muller,[28] where no solvent was present.

Single crystal X-ray diffraction studies were also carried out at 220K on **115**, the resulting molecular structure being shown in Figure 6.25. The Pt-P and Pt-Cl bond lengths and angles are similar to those reported by Otto and Muller.[28] Selected bond distances and angles for all three pseudo polymorphs are listed in Table 6.42.

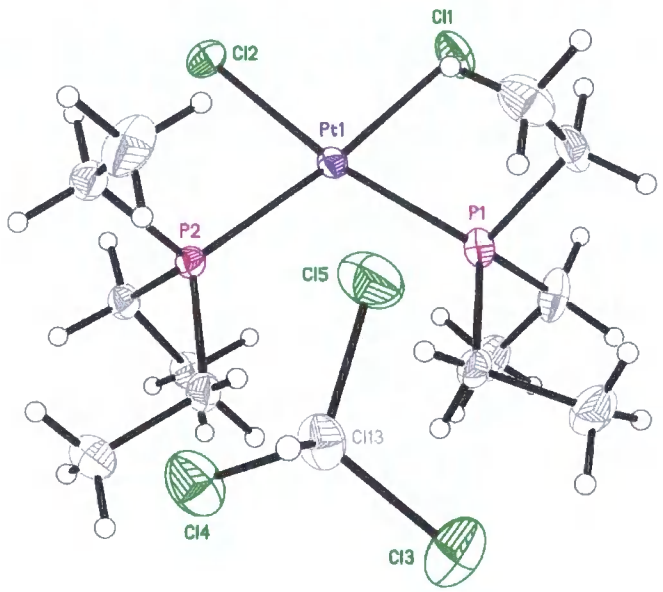


Figure 6.24: The molecular structure of **115** at 120K, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

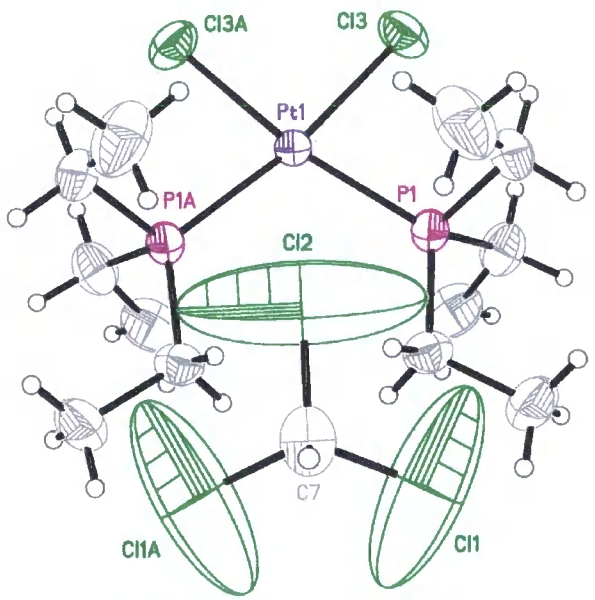


Figure 6.25: The molecular structure of **115p** at 220K, showing the numbering scheme for the key atoms. Thermal ellipsoids are drawn at 50 % probability.

	120K	220K	Otto and Muller[28]
Space Group	Orthorhombic	Pmna	Monoclinic
Bond Length /Å			
Pt(1)–P(1)	2.2562(11)	2.2525(16)	2.264(2)
Pt(1)–P(2)	2.2529(11)	2.2525(16)	2.262(2)
Pt(1)–Cl(4)	2.3673(11)	2.3618(17)	2.364(2)
Pt(1)–Cl(5)	2.3699(10)	2.3618(17))	2.374(2)
Bond Angle /°			
P(1)–Pt(1)–P(2)	103.87(4)	104.82(9)	98.39(7)
P(1)–Pt(1)–Cl(1)	85.17(4)	84.63(6)	84.63(9)
P(2)–Pt(1)–Cl(2)	85.10(4)	84.63(6)	91.33(7)
Cl(1)–Pt(1)–Cl(2)	85.93(4)	85.92(10)	85.66(9)

Table 6.42: Selected bond lengths and angles for *cis*-$PtCl_2(PEt_3)_2.CDCl_3$, at 120K and 220K, and for *cis*-$PtCl_2(PEt_3)_2$.[28]

The change in space group for *cis*-$PtCl_2(PEt_3)_2.CDCl_3$ at different temperatures is due to the $CDCl_3$ molecule spinning at higher temperature. This forms a mirror plane through both the Pt(II) complex and the $CDCl_3$ molecule. At lower temperatures the $CDCl_3$ stops spinning but not on the mirror plane. This results in the disappearance of the mirror plane, which changes the space group.

6.7 Conclusions

Numerous Pt(II) complexes containing five-, six- and seven-membered ring cyclic triphosphenium ions have now been synthesised *via* a reaction between the cyclic triphosphenium ion and *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$, where PR_3 is PEt_3, PPh_2Me or $PPhMe_2$. Using this method the *cis* and/or *trans* complexes can form (Scheme 6.1). If the substituents are very bulky, *e.g.* using the cyclic triphosphenium ion derived from dtbpox, only the *trans* isomer forms.[1] However, with less bulky substituents the *trans* complex often forms initially as the kinetic product of the reaction, but then converts to the more thermodynamically stable *cis* complex.

An important and interesting feature of both *cis* and *trans* complexes containing cyclic triphosphenium ions is the $^{1}J_{Pt\text{-}P}$ coupling constant to the phosphenium central P. The magnitudes of these couplings are unusually small with values between 1104-1267 Hz for *cis* and 981-1245 for *trans* Hz. The other $^{1}J_{Pt\text{-}P}$ coupling constant to the PR_3 within the complexes are as expected for *cis* or *trans* couplings. This suggests that the bond between the phosphenium central P atom and the Pt centre is long, which is not surprising due to the cationic nature of the cyclic triphosphenium ion ligand. Unfortunately isolation of crystalline products was unsuccessful for any of these complexes, and so the reason for the small $^{1}J_{Pt\text{-}P}$ value has not yet been established conclusively.

Further supporting evidence for the proposal of a long Pt-P bond is found when comparing $^{1}J_{Pt\text{-}PH}$ coupling constants for the *trans* cyclic triphosphenium ion complexes, with literature values for *trans* phosphorus ligands. The $^{1}J_{Pt\text{-}PH}$ couplings observed for the *trans* cyclic triphosphenium ion complexes are much larger than those observed for phosphanes containing alkyl groups, and are more consistent with those reported for more electronegative ligands on platinum (Table 6.43). This could be due to a shortening of the Pt-PR_3 bond because the Pt-P_C bond *trans* to it is long. There would not be as significant an effect in the *cis* complexes.

This study into the synthesis of some Pt(II) chlorophosphane complexes, and their hydrolysis reactions, has led to some interesting results. For *cis*-complexes, large values of $^{1}J_{Pt\text{-}P}$ were observed in all cases (2996-6062 Hz), along with small values of $^{2}J_{P\text{-}P}$ (12-18 Hz). For the *trans*-complexes the $^{2}J_{P\text{-}P}$ values are much larger (494-614 Hz), whereas $^{1}J_{Pt\text{-}P}$ values are much smaller (2266-2781 Hz). This is consistent with the data reported by Pidock *et al.*[43] and Grim *et al.*[44] for similar complexes. As expected, with more electronegative substituents on the phosphane, the shift is to higher frequency and $^{1}J_{Pt\text{-}P}$ is much larger.[43] Where both *cis* and *trans* parent complexes were synthesised, the chemical shift of the chlorophosphane ligand (P_B) of the *trans* complex was always to higher frequency than that for the *cis*. Also the *cis* complexes had significantly larger $^{1}J_{Pt\text{-}P}$ coupling constants compared to those for the corresponding *trans* complexes.

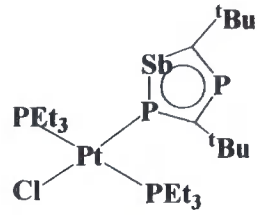
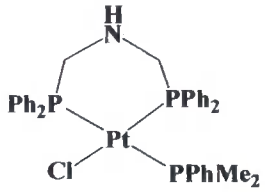
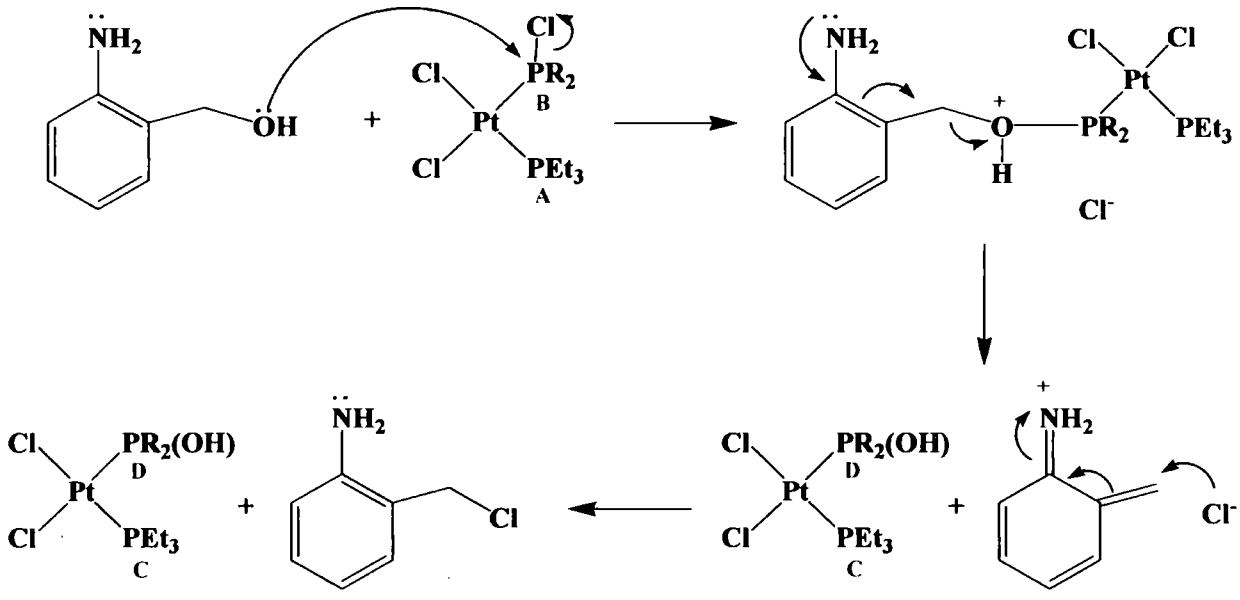
Complex	P_1	P_2	$^1J_{Pt-P2}$	Reference
70b	**3b**	PPh_2Me	2783	*
86b	**11b**	PEt_3	2842	*
87b	**11b**	$PPhMe_2$	2512	*
88a	**11a**	PPh_2Me	2586	*
90a	**13a**	PEt_3	2840	*
90b	**13b**	PEt_3	2842	*
91b	**13b**	PPh_2Me	2873	*
	PEt_3	PEt_3	2372	45
	PPH_2-	$PPhMe_2$	2371	46
trans-$PtCl_2(PEt_3)(ArPCl_2)$	$ArPCl_2$	PEt_3	2886	47
trans-$PtCl_2(PEt_3)(Ar'PF_2)$	$Ar'PF_2$	PEt_3	2723	48
trans-$PtCl_2(PEt_3)(Ar''PCl)$	Ar''PCl	PEt_3	2686	49
trans-$PtCl_2(PEt_3)(Ar''PH)$	Ar''PH	PEt_3	2677	49
trans-$PtCl_2(PEt_3)(Ar''PBr)$	Ar''PBr	PEt_3	2638	49

Table 6.43: $^{31}P\{^1H\}$ NMR data for *trans* complexes obtained in this work and literature data for similar *trans* complexes (* this work)

Using the parent complexes containing the chlorophosphanes $EtPCl_2$, $^iPrPCl_2$, $PhPCl_2$, Et_2PCl and Cy_2PCl, a hydrolysed product was observed in each case. However, none of these reactions resulted in complete conversion to the hydrolysed product.

As each chlorine is replaced by OH, a shift to lower frequency for the doublet corresponding to P_D, compared to P_B of the parent complex, *cis*-$PtCl_2(PEt_3)(PCl_3)$ is observed. This shift to lower frequency is due to the Cl being replaced by the less electronegative OH. Also $^1J_{Pt\text{-}PD}$ decreases in value and $^1J_{Pt\text{-}PC}$ increases in value compared to that of the parent complex. In most cases, with the exception of the complexes containing $^tBuPCl_2$ and $^tBu_2PCl$, ligand scrambling occurred. This method is obviously not the optimum route to the hydrolysis of the P-Cl bond(s) in the coordination sphere of Pt(II).

Using 2-aminobenzyl alcohol as a mild source of OH^- was more successful, and in most cases ligand scrambling did not occur. It is thought that the reaction proceeds as shown in Scheme 6.25.



Scheme 6.25: Proposed reaction pathway for the hydrolysis of *cis*-$PtCl_2(PEt_3)$(chlorophosphane) using 2-aminobenzyl alcohol

Single crystal X-ray diffraction studies carried out on the product of the reaction between *cis*-$PtCl_2(PEt_3)(PCl_3)$ and one equivalent of 2-aminobenzyl alcohol showed the

hydrolysed product to be a salt. This accounts for the discrepancy in the $^{31}P\{^{1}H\}$ NMR data for the compound compared to those obtained through exposure of the parent complex to air and 'wet' solvent. Although the isolated product from the hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ using 2-aminobenzyl alcohol was a salt, the $^{31}P\{^{1}H\}$ NMR data obtained for other systems suggests that a salt is not always formed as the product of the hydrolysis reaction (Table 6.44).

***cis*-$Cl_2Pt(PEt_3)(L)$ L =**	**Exposure to air and 'wet' solvents**					**Using 2-aminobenzyl alcohol**				
	δP_D, ppm	**$^1J_{PtPD}$, Hz**	**δP_C, ppm**	**$^1J_{PtPC}$, Hz**	**$^2J_{P\text{-}P}$, Hz**	**δP_D, ppm**	**$^1J_{PtPD}$, Hz**	**δP_C, ppm**	**$^1J_{PtPC}$, Hz**	**$^2J_{P\text{-}P}$, Hz**
$PCl_2(OH)$*	47.3	6495	16.9	3245	23	72.7	5904	17.3	3237	22
$PCl(OH)_2$*	39.6	5951	14.5	3493	24	62.1	~6000	18.6	3390	24
$P(OH)_3$	36.7	5823	15.0	3506	23	-	-	-	-	-
PEtCl(OH)	94.6	4397	15.6	3614	20	95.7	4421	17.1	3576	16
$P^iPrCl(OH)$	96.5	4323	15.4	3638	19	101.3	4367	16.7	3601	16
PPhCl(OH)*	75.9	4484	13.0	3553	21	92.7	4698	13.7	3350	19
$PEt(OH)_2$	93.5	4005	15.8	3672	16	34.6	3947	10.7	3645	15
$PCy_2(OH)$	97.5	4023	13.1	3704	16	-	-	-	-	-
$P^nPrCl(OH)$	-	-	-	-	-	93.5	4404	17.1	3549	17
$PPh(OH)_2$*	-	-	-	-	-	78.2	4614	16.4	3504	18
PCyCl(OH)	-	-	-	-	-	99.0	4087	16.5	3615	16
$P^tBuCl(OH)$	-	-	-	-	-	106.9	4358	16.3	3540	15

Table 6.44: Table containing $^{31}P\{^{1}H\}$ NMR data for hydrolysis products of Pt(II) complexes containing chlorophosphanes (* salts formed when using 2-aminobenzyl alcohol)

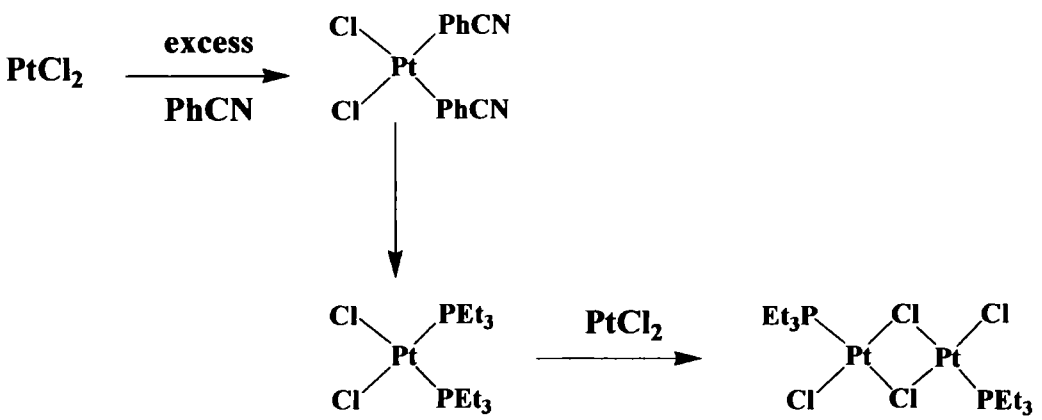
Ligands which are stronger acids, *e.g.* PCl_3, favour formation of a salt as the product. However weaker acids, *e.g.*ligands containing ethyl or *iso*-propyl groups, seem to favour non-salt formation (or possibly equilibrate between salt and non-salt). Comparisons between $^{31}P\{^{1}H\}$ NMR data obtained for the hydrolysis reactions through exposure to air

and 'wet' solvent, and when using 2-aminobenzyl alcohol (Table 6.44) suggest that salt formation has occurred for L = $PCl_2(OH)$, $PCl(OH)_2$, PPhCl(OH) and probably $PPh(OH)_2$. In the other cases it seems likely that the product is a non-salt or perhaps in an equilibrium as the $^{31}P\{^1H\}$ NMR data (where obtained) are very similar when the hydrolysis was carried out by both methods.

6.8 Experimental

6.8.1 Three-stage synthesis of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$

A three step literature method was followed to synthesise *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (Scheme 6.26). [50]



Scheme 6.26: Synthesis of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, a three step reaction[50]

Step 1: Synthesis of *cis*-$[PtCl_2(PhCN)_2]$ [50]

$PtCl_2$ (6.1956 g, 23.3 mmol) was added to PhCN (60 mL). The resulting solution was dark brown and was heated to 100°C for 30 minutes until the solution was yellow in colour. The solution was then cooled overnight. A yellow precipitate formed so the

solution was filtered, the crystals washed with petroleum ether and dried under vacuum. Yield = 8.94 g (81%).

Step 2: Synthesis of *cis*-$[PtCl_2(PEt_3)_2]$ [50]

PEt_3 (6.0 mL, 4.8 g, 40.6 mmol) was added to a solution of *cis*-$[PtCl_2(PhCN)_2]$ (8.94 g, 19.0 mmol) dissolved in CH_2Cl_2 (50 mL). The reaction mixture was then stirred for 18 hours at RT. Solvent was removed *in vacuo*, upon which white crystals formed along with a yellow oil. Hexane (20 mL) was then added and the suspension stirred at RT for 30 minutes, after which time the colour had changed from yellow to white. The reaction was filtered *via* a cannula filter, yielding a thick white oil. A $^{31}P\{^1H\}$ NMR spectrum showed that along with the desired product, *cis*-$[PtCl_2(PEt_3)_2]$, a trisubstituted Pt complex also formed, $[PtCl(PEt_3)_3]^+$ (d, δP 18.3 ppm $^1J_{Pt\text{-}P}$ = 2278, t, δP 11.3 ppm $^1J_{Pt\text{-}P}$ = 3439).[13] This mixture was used in Step 3 without separation.

Step 3: Synthesis of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ [50]

cis-$[PtCl_2(PEt_3)_2]$, (9.95 g, 19.9 mmol - assuming all the product was $PtCl_2(PEt_3)_2$), was added to a solution of $PtCl_2$ (10.52 g, 39.7 mmol) dissolved in $(CHCl_2)_2$ (20 mL). The solution was then heated to 150°C for two hours. During this time the solution turned black in colour. When the solution was cooled, orange crystals formed. The black solution was assumed to be platinum black. 100 mL of DCM was added to dissolve the crystals. A very fine filter cannula was then used to remove the solution containing the crystals. The solution was bright yellow. The solvent was then removed *in vacuo* and recrystallised using DCM. Yield = 7.87 g (79%).

^{31}P (300 MHz, $CDCl_3$): δ 11.4 ppm (s, $^1J_{Pt\text{-}P}$ = 3844 Hz)

Elemental Analysis: Calculated: %C 18.76, %H 3.94, %N 0.0
Actual: %C 18.52, %H 3.91, %N 0.0

The $^{31}P\{^{1}H\}$ NMR data were in good agreement with those previously reported, and the analysis results were in good agreement with calculated values, so the dimer was used without further purification.[1, 49]

6.8.2 Synthesis of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ – An alternative method[51]

$PtCl_2$ (4.53 g, 17.1 mmol) and PEt_3 (2.4 mL, 16.0 mmol) were added to p-chlorotoluene (15mL) and the mixture was stirred to give a dark brown muddy coloured solution. This was then heated to 250°C for 120 minutes. The solvent was then removed *in vacuo* to afford a dark brown solid. DCM (20 mL) was then added and the solution was filtered through celite. The solid was washed with further quantities of DCM until the filtrate ran clear. Upon standing overnight bright orange crystals formed. These were recrystallised from DCM. Yield = 10.56 g (76%).

^{31}P (300 MHz, $CDCl_3$): δ 11.5 ppm (s, $^{1}J_{Pt\text{-}P}$ = 3839 Hz)

Elemental Analysis: Calculated: %C 18.76, %H 3.94, %N 0.0
Actual: %C 18.89, %H 3.95, %N 0.0

6.8.3 Synthesis of *trans*-$[Pt(PPh_2Me)Cl(\mu\text{-}Cl)]_2$ dimer[51, 52]

$PtCl_2$ (2.11 g, 7.96 mmol) and PPh_2Me (1.4 mL, 7.41 mmol) were added to p-chlorotoluene (10mL) and the mixture was stirred to give a dark brown muddy coloured solution. This was then heated to 180°C for 90 minutes. The solvent was then removed *in vacuo* to afford a dark brown solid. DCM (20 mL) was then added and the solution was filtered through celite. The solid was washed with further quantities of DCM until the filtrate ran clear. The yellow filtrate was then concentrated to approximately 10 mL and pentane (40 mL) added. Upon addition of pentane, a yellow precipitate formed. The solution was then filtered to isolate the yellow solid. Yield = 9.12 g (54 %).

^{31}P (300 MHz, $CDCl_3$): δ -6.4 ppm (s, $^1J_{Pt\text{-}P}$ = 4003 Hz)

Elemental Analysis: Calculated: %C 33.49, %H 2.81, %N 0.0
Actual: %C 33.19, %H 2.87, %N 0.0

6.8.4 Synthesis of *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ dimer[51]

$PtCl_2$ (2.1 g, 7.96 mmol) and $PPhMe_2$ (1.4 mL, 7.41 mmol) were added to p-chlorotoluene (10mL) and the mixture was stirred to give a dark brown muddy coloured solution. This was then heated to 180°C for 90 minutes. The solvent was then removed *in vacuo* to afford a dark brown solid. DCM (30 mL) was then added and the solution was filtered through celite. The solid was washed with further quantities of DCM until the filtrate ran clear. The filtrate was then concentrated to approximately 10 mL and pentane (40 mL) added. Upon addition of pentane, a yellow precipitate formed. The solution was then filtered to isolate the yellow solid. Yield = 11.33 g (77%)

^{31}P (300 MHz, $CDCl_3$): δ -70.0 ppm (s, $^1J_{Pt\text{-}P}$ = 3928 Hz)
Elemental Analysis: Calculated: %C 23.78, %H 2.74, %N 0.0
Actual: %C 23.76, %H 2.75, %N 0.0

6.8.5 Synthesis of Pt(II) complexes containing cyclic triphosphenium ions

It is noteworthy that these compounds are sensitive to both air and moisture so reactions were carried out in an inert atmosphere.

Example Reaction:

Reaction of the depe cyclic triphosphenium ion with *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$
depe (0.0300 g, 0.14 mmol) and $SnCl_2$ (0.0265 g, 0.14 mmol) were dissolved in 1.0 mL $CDCl_3$. PCl_3 (0.014 mL, 0.14 mmol) was then added and a $^{31}P\{^1H\}$ NMR spectrum recorded soon after mixing to confirm the formation of the cyclic triphosphenium ion. When necessary residual PCl_3 was removed *in vacuo*. *trans*-[Pt(PPhMe$_2$)Cl(μ-Cl)]$_2$ dimer (0.0560 g, 0.07 mmol) was then added to the solution.

Quantities of reagents used:

Compound Number	Quantity of diphosphane		Quantity of PCl_3		Quantity of $SnCl_2$		Quantity of Pt dimer	
	g	mmol	mL	mmol	g	mmol	g	mmol
64b	0.0300	0.14	0.014	0.14	0.0265	0.14	0.0560	0.07
2a repeat	0.0427	0.21	0.020	0.22	0.0392	0.21	0.0996	0.11
68b	0.0193	0.05	0.004	0.05	0.0095	0.05	0.0202	0.03
69b/70b	0.0310	0.07	0.010	0.11	0.0139	0.07	0.0342	0.04
73a/74a	0.0642	0.19	0.015	0.15	-	-	0.0456	0.05
73b	0.0230	0.10	0.010	0.11	0.0197	0.10	0.0398	0.05
75b	0.0140	0.06	0.005	0.06	0.0114	0.06	0.0242	0.03
76b	0.0210	0.10	0.010	0.11	0.0190	0.10	0.0242	0.06
78b	0.0239	0.05	0.005	0.06	0.0157	0.08	0.0192	0.03
79a/80a	0.0446	0.10	0.010	0.11	-	-	0.0466	0.05
82b	0.0260	0.06	0.005	0.06	0.0114	0.06	0.0242	0.03
83b/84b	0.0136	0.05	0.004	0.05	0.0100	0.05	0.0191	0.03
85a	0.0397	0.14	0.010	0.11	-	-	0.0513	0.06
86b	0.0900	0.20	0.018	0.20	0.0400	0.20	0.1532	0.10
87b	0.0196	0.04	0.004	0.04	0.0145	0.08	0.0162	0.02
88a	0.0569	0.13	0.010	0.11	-	-	0.0498	0.05
89b	0.0733	0.16	0.014	0.16	0.0303	0.16	0.0647	0.08
90a	0.0305	0.11	0.010	0.11	-	-	0.0466	0.05
90b	0.0280	0.10	0.010	0.11	0.0291	0.15	0.0583	0.08
91b	0.0235	0.08	0.007	0.08	0.0151	0.08	0.0323	0.04
92	0.0252	0.06	0.010	0.11	-	-	0.0235	0.03
93	0.0312	0.07	-	-	-	-	0.0271	0.04
94	0.0290	0.06	-	-	-	-	0.0230	0.03

6.8.6 Synthesis of parent Pt(II) complexes containing chlorophosphanes

Example Reactions

Synthesis of *cis*-$PtCl_2(PEt_3)(PCl_3)$ (77)

trans-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (0.0416 g, 0.054 mmol) was dissolved in $CDCl_3$ (1.0 mL) to afford an orange solution. PCl_3 (0.01 mL, 0.11 mmol) was added *via* a syringe. Upon addition of PCl_3 the solution became colourless.

Synthesis of *cis*- and *trans*-$PtCl_2(PEt_3)(P^tBuCl_2)$ (101 and 102)

trans-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (0.1532 g, 0.20 mmol) was dissolved in $CDCl_3$ (0.7 mL) to afford an orange solution. A solution of P^tBuCl_2 (0.0671 g; 0.42 mmol) in 0.3 mL was added *via* a syringe. Upon addition of P^tBuCl_2 the solution became pale yellow in colour.

Synthesis of *cis*- and *trans*-$PtCl_2(PEt_3)(P^iPr_2Cl)$ (105 and 106)

trans-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (0.1302 g, 0.17 mmol) was dissolved in $CDCl_3$ (1.0 mL) to afford an orange solution. P^iPr_2Cl (0.0570 g, 0.34 mmol) was added *via* a syringe. Upon addition of P^iPr_2Cl the solution became pale yellow in colour.

Crystals of **77**, **95** and **105** were obtained by slow evaporation of solvent in an inert atmosphere. It is noteworthy that these compounds, along with the other described in this section, are sensitive to both air and moisture.

Quantities of reagents used:

Compound Number	Quantity of chlorophosphane used		Quantity of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ used		Colour of resulting solution
	mL	mmols	g	mmols	
77	0.010	0.11	0.0416	0.05	colourless
65	0.016	0.18	0.0727	0.09	colourless
81	0.014	0.16	0.0709	0.08	colourless
95	0.017	0.16	0.0595	0.08	colourless
96	0.010	0.13	0.0340	0.05	colourless
97	0.030	0.24	0.0828	0.11	colourless
98	0.033	0.24	0.0933	0.12	colourless
99/100	0.045	0.30	0.1095	0.14	colourless
101/102	0.0671*	0.42	0.1532	0.20	pale yellow
103/104	0.040	0.34	0.1273	0.17	colourless
105/106	0.0570*	0.34	0.1302	0.17	pale yellow
110/111	0.0500*	0.28	0.1055	0.14	pale yellow
107	0.043	0.24	0.0902	0.12	colourless
108/109	0.084	0.11	0.0420	0.06	colourless
112/113	0.045	0.20	0.0765	0.10	colourless

* chlorophosphane was solid not liquid so quantity is in g.

6.8.7 Hydrolysis reactions

Example Hydrolysis Reaction through exposure to air and 'wet' solvent

Hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$

trans-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (0.0416 g, 0.054 mmol) was dissolved in $CDCl_3$ (1 mL) to afford an orange solution. PCl_3 (0.01 mL, 0.11 mmol) was added *via* a syringe. Upon addition of PCl_3 the solution became colourless. A $^{31}P\{^1H\}$ NMR spectrum confirmed the formation of the complex as the only product. The solution was then transferred to a large

necked open vial. 'Wet' DCM was then added (15.0 mL). A magnetic stirrer was added, and the solution stirred continuously. 'Wet' DCM was added when the level of solvent dropped to approximately 5.0 mL. To monitor the reaction by $^{31}P\{^{1}H\}$ NMR all the solvent was allowed to evaporate before $CDCl_3$ was added to provide a deuterium lock.

Quantities of reagents used:

Chlorophosphane Used	Quantity of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ used		Quantity of chlorophosphane used	
	mL	mmol	mL	mmol
PCl_3	0.0416	0.05	0.010	0.11
$EtPCl_2$	0.0595	0.08	0.017	0.16
$^{i}PrPCl_2$	0.0828	0.11	0.030	0.24
$PhPCl_2$	0.0470	0.06	0.016	0.12
$CyPCl_2$	0.0855	0.11	0.035	0.23
$^{t}BuPCl_2$*	0.1532	0.20	0.0671	0.42
Et_2PCl	0.1273	0.17	0.040	0.34
$^{i}Pr_2PCl$*	0.1302	0.17	0.0570	0.34
$^{i}Pr_2PCl$*	0.1299	0.17	0.0600	0.34
$^{t}Bu_2PCl$*	0.1055	0.14	0.050	0.28
Ph_2PCl	0.0902	0.12	0.043	0.24
Cy_2PCl	0.0765	0.10	0.045	0.20

* chlorophosphane was solid not liquid so quantity is in g.

Example hydrolysis reaction using 2-aminobenzyl alcohol

Hydrolysis of *cis*-$PtCl_2(PEt_3)(PCl_3)$

trans-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ (0.1116 g, 0.15 mmol) was dissolved in $CDCl_3$ (1.0 mL) to afford an orange solution. PCl_3 (0.41 mL, 0.30 mmol) was added *via* a syringe. Upon addition of PCl_3 the solution became colourless. A $^{31}P\{^{1}H\}$ NMR spectrum confirmed the

formation of the complex as the only product. 2-aminobenzyl alcohol (0.0363 g, 0.30 mmol) was then added and the solution was agitated. The reaction was monitored using $^{31}P\{^{1}H\}$ NMR spectroscopy. Crystals were obtained by slow evaporation of solvent in an inert atmosphere.

Quantities of reagents used:

Compound Number	Chloro-phosphane Used	Quantity of *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ used		Quantity of chlorophosphane used		Quantity of 2-aminobenzyl alcohol used	
		g	mmols	mL	mmols	g	mmols
138	**PCl_3**	0.1116	0.15	0.041	0.30	0.0363	0.30
139	**PCl_3**	0.0780	0.10	0.018	0.20	0.0492	0.40
140	**$EtPCl_2$**	0.0715	0.09	0.019	0.18	0.0221	0.18
141	**$^{n}PrPCl_2$**	0.1000	0.13	0.034	0.26	0.0320	0.26
142	**$^{i}PrPCl_2$**	0.0501	0.07	0.017	0.14	0.0172	0.14
143	**$PhPCl_2$**	0.0933	0.12	0.033	0.24	0.0299	0.24
144	**$CyPCl_2$**	0.0606	0.08	0.024	0.16	0.0197	0.16
145	**$^{t}BuPCl_2$***	0.0957	0.13	0.0400	0.25	0.0303	0.25
147	**Et_2PCl**	0.0656	0.09	0.022	0.18	0.0221	0.18
-	**$^{i}Pr_2PCl$***	0.1762	0.23	0.0700	0.46	0.0283	0.23
-	**$^{t}Bu_2PCl$***	0.1685	0.22	0.0800	0.44	0.0271	0.22
-	**Ph_2PCl**	0.0916	0.12	0.043	0.24	0.0152	0.12
-	**$Cpent_2PCl$**	0.0840	0.11	0.042	0.22	0.0271	0.22
-	**Cy_2PCl**	0.0600	0.08	0.035	0.16	0.0197	0.16

* chlorophosphane was solid not liquid so quantity is in g.

Additional analysis of compounds

cis-$PtCl_2(PEt_3)(PCl_3)$ (77)

^{1}**H** (300 MHz, $CDCl_3$): δ 2.23 (3H, dt, J = 7.4 Hz, $PCH_2C\mathbf{H_3}$), 4.28 (2H, m, $PC\mathbf{H_2}CH_3$).

^{13}**C a** (63 MHz, $CDCl_3$): δ 8.4 ($PC\mathbf{H_2}CH_3$), 15.7 ($PCH_2C\mathbf{H_3}$).

Elemental Analysis: Calculated: C% 13.82 H% 2.90 N %0

Actual: C% 13.81 H% 2.91 N% 0

cis-$PtCl_2(PPhMe_2)(PCl_3)$ (65)

^{1}**H** (300 MHz, $CDCl_3$): δ 2.10 (6H, dt, J = 12 Hz, $P(C\mathbf{H_3})_2$), 7.42-7.84 (5H, m, PPh**H**).

cis-$PtCl_2(PPh_2Me)(PCl_3)$ (81)

^{1}**H** (300 MHz, $CDCl_3$): δ 2.35 (3H, dt, J = 12 Hz, $PC\mathbf{H_3}$), 7.50-7.74 (5H, m, PPh**H**).

cis-$PtCl_2(PEt_3)(PEtCl_2)$ (95)

^{1}**H** (300 MHz, $CDCl_3$): δ 1.19 (9H, dt, J = 7.6 Hz, $P(CH_2C\mathbf{H_3})_3$, 1.40 (3H, dt, J = 9 Hz, $P(CH_2C\mathbf{H_3})Cl_2$, 2.20 (6H, m, $PC\mathbf{H_2}CH_3$), 3.18 (2H, m, $P(C\mathbf{H_2}CH_3)Cl_2$).

cis-$PtCl_2(PEt_3)(P^nPrCl_2)$ (96)

^{1}**H** (400 MHz, $CDCl_3$): 1.11 (3H, bm, $P(CH_2CH_2C\mathbf{H_3})$, 1.18 (9H, dt, J = 18 Hz, $P(CH_2C\mathbf{H_3})_3$, 1.87 (2H, bm, $P(CH_2\mathbf{CH_2}CH_3)$, 2.18 (6H, m, $PC\mathbf{H_2}CH_3$), 3.11 (2H, bm, $P(\mathbf{CH_2}CH_2CH_3)$,

^{13}**C** {^{1}**H**} (101 MHz, $CDCl_3$): δ 8.1 (d, $^2J_{CP}$ = 3.6 Hz ($P(CH_2C\mathbf{H_3})_3$), 14.2 (d, $^3J_{CP}$ = 22.5 Hz ($PCH_2CH_2C\mathbf{H_3}$), 8.1 (d, $^1J_{CP}$ = 38.9 Hz ($P(\mathbf{CH_2}CH_3)_3$), 17.4 (s ($PCH_2\mathbf{CH_2}CH_3$), 46.3 (d, $^1J_{CP}$ = 32.0 Hz ($P\mathbf{CH_2}CH_2CH_3$),

cis-$PtCl_2(PEt_3)(P^iPrCl_2)$ (97)

^{1}**H** (300 MHz, $CDCl_3$): 1.19 (9H, dt, J = 18 Hz, $P(CH_2C\mathbf{H_3})_3$, 1.38 (3H, d, J = 6.7 Hz, $PCH(C\mathbf{H_3})(CH_3)$, 1.45 (3H, d, J = 6.7 Hz, $PCH(CH_3)(C\mathbf{H_3})$, 2.18 (6H, m, $PC\mathbf{H_2}CH_3$), 3.95 (1H, m, $PC\mathbf{H}(CH_3)_2$).

^{13}C {^{1}H} (101 MHz, $CDCl_3$): δ 8.2 $P(CH_2\mathbf{C}H_3)_3$, 15.7 $P(CH_2\mathbf{C}H_3)_3$ J= 39.5 Hz , 16.4 $PCH(\mathbf{C}H_3)_2$, 40.6 $P\mathbf{C}H(CH_3)_2$ J= 27.9 Hz

cis-$PtCl_2(PEt_3)(PPhCl_2)$ (98)

^{1}H (400 MHz, $CDCl_3$): δ 1.15 (9H, dt, J = 18 Hz, $P(CH_2C\mathbf{H}_3)_3$, 2.09 (6H, m, $PC\mathbf{H}_2CH_3$), 7.52-7.64 (3H, m, aromatic protons), 8.06-8.17 (2H, m, aromatic protons)

^{13}C {^{1}H} (175.9 MHz, $CDCl_3$): δ 8.6 (d, $^{2}J_{CP}$ = 3.3 Hz ($P(CH_2\mathbf{C}H_3)_3$), 15.9 (d, $^{1}J_{CP}$ = 38.9 Hz ($P(CH_2\mathbf{C}H_3)_3$), 129.1 (d, $^{2}J_{CP}$ = 15.8 Hz, *o*-Ph<u>C</u>), 134.3 (s, *p*-Ph<u>C</u>), 131.1 (d, $^{3}J_{CP}$ = 18.5, *m*-Ph<u>C</u>), 137.5 (d, $^{1}J_{CP}$ = 62.5 Hz, *i*-Ph<u>C</u>)

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Chapter 7:

Future Work

7.1 Cyclic triphosphenium ions coordination chemistry

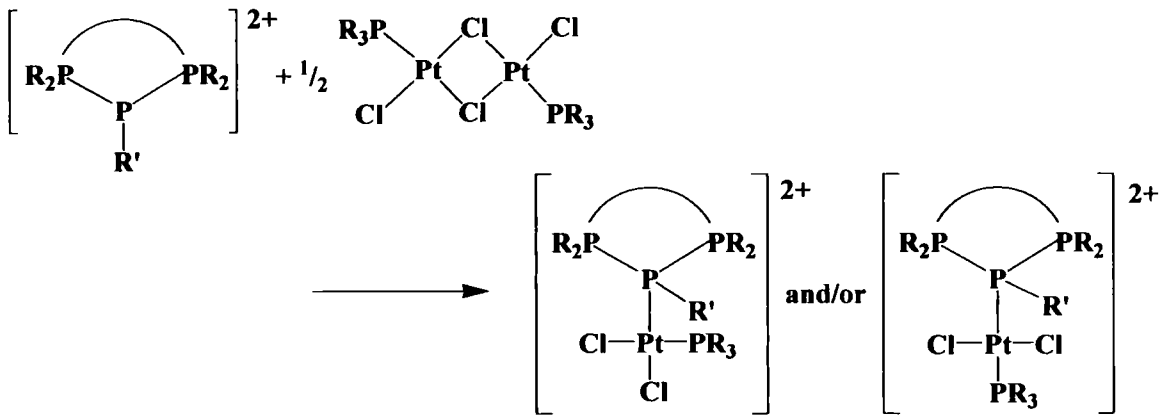
The Pt(II) complexes described in Chapter 6 are some of the first transition metal complexes of cyclic triphosphenium ions. In each complex the $^{1}J_{P\text{-}Pt}$ coupling constant to the phosphenium central P was unusually small for a one-bond phosphorus-platinum coupling. Although no molecular structures were obtained, preliminary theoretical calculations seem to suggest that this is due to a long Pt-phosphenium central P bond,[1] which is not surprising due to the ligand being cationic. However further investigation is needed to confirm this.

Isolation of the complexes is essential. X-ray diffraction studies (where possible) and additional calculations are necessary to investigate further the bonding within these

heterocycles and their metal complexes. Comparisons could be made to the more traditional phosphanes, including the effect of the unusual electron-rich centre in cyclic triphosphenium ions. This will provide invaluable insight into whether a long, weak bond is formed between the cyclic triphosphenium ion and the Pt metal, or whether the unusually small $^{1}J_{Pt\text{-}P}$ is in fact just a function of the ligand. Other possible investigations could involve synthesis of complexes of different transition metals *e.g.* palladium(II) or rhodium(I).

7.2 P-alkyl and P-aryl derivatives

P-alkyl/aryl derivatives can now be synthesised in a one pot reaction with many different substituents on the central P atom (Et, ^{i}Pr, ^{n}Pr, Cy, ^{t}Bu, Ph). However there have been no reported investigations into the coordination of these heterocycles to transition metals. One possibility is to react these P-alkyl/aryl derivatives with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$ in analogous reactions to those described in Chapter 6 using cyclic triphosphenium ions (Scheme 7.1).



Scheme 7.1: Proposed synthesis of Pt(II) complexes with P-alkyl/aryl derivatives of cyclic triphosphenium ions

Comparisons could then be made of the $^{1}J_{P\text{-}Pt}$ coupling constants to the phosphenium central P in these complexes with those obtained when carrying out the reaction with cyclic triphosphenium ions. This would be of interest to see if there was any difference in the Pt-P bond strengths when using a trivalent, P(III) ligand (P-alkyl/P-aryl derivative) compared to a divalent, P(I) ligand (cyclic triphosphenium ion). Although both P-alkyl/P-aryl derivatives and cyclic triphosphenium ions are positively charged donors, cyclic triphosphenium ions are monocations whereas P-alkyl/P-aryl derivatives are dications. This may also affect the Pt-P bond strength within the complex.

7.3 Tetraphosphonium ions

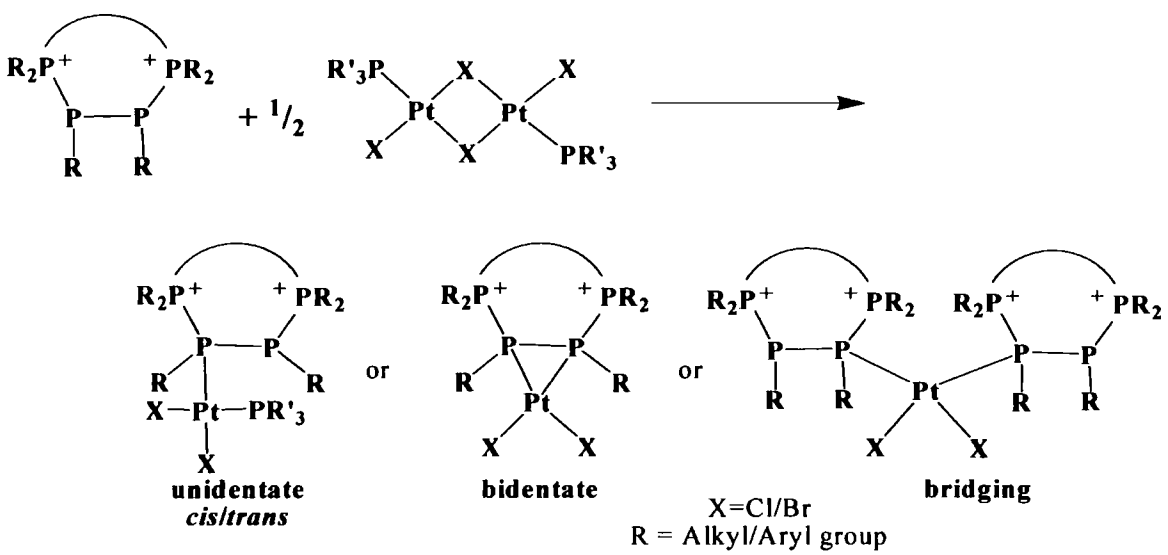
In the synthesis of many cyclic tetraphosphonium ions a mixture of tetraphosphonium ions and P-alkyl/aryl derivatives is obtained. It would be advantageous to synthesise the tetraphosphonium ions without the simultaneous formation of the P-alkyl/aryl derivative. Possible investigations could involve:

- addition of excess $SnCl_2$, which should favour the formation of the tetraphosphonium ion;
- using bulky chlorophosphanes, e.g. $^{t}BuPCl_2$, which should hinder ring closure at the 3P (P-alkyl/aryl derivative) stage.

Other possible investigations could include the formation of new families of unsymmetrical tetraphosphonium ions by adapting the known synthetic route. Investigation into the formation of a 'mixed' tetraphosphonium ion through the addition of two different chlorophosphanes rather than two equivalents of one chlorophosphane could be explored further (Scheme 5.8). One possible route could be using bulky R groups on the chlorophosphanes or the diphosphane to hinder cyclisation and so slow the reaction. Another possibility is to use an unsymmetrical diphosphane (*i.e.* $R_2P\text{^}PR'_2$) as a starting material.

There have been no reported investigations into the coordination of tetraphosphonium ions to transition metals. One possibility is the reaction of a tetraphosphonium ion with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$, although potentially there are a number of possible products (Scheme 7.2). This highlights the difference between these systems and classical phosphanes. Similar to the P-alkyl/ P-aryl derivatives, the tetraphosphonium ions are dications and are trivalent, P(III) ligands. Although there is the potential for coodination to occur through both P atoms to form a three-membered (-P-P-C-) ring. It is expected that only one P atom will donate due to geometric reasons.

Investigations into the coordination of tetraphosphonium ions to platinum through reactions with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$ would again allow a comparison of $^{1}J_{Pt\text{-}P}$ values to be made with those obtained for Pt(II)-cyclic triphosphenium ion complexes previously described in Chapter 6. This would help to establish the effect (if any) of changing from a divalent, P(I) donor atom to a trivalent, P(III) donor atom on the Pt-P bond strength within the complex.



Scheme 7.2: Possible products from the reaction of cyclic tetraphosphonium ions with *trans*-$[Pt(PR_3)Cl(\mu\text{-}Cl)]_2$

Further investigation into the mechanism of formation of these novel heterocycles, for example using variable temperature NMR studies, would help confirm the three stage mechanism.

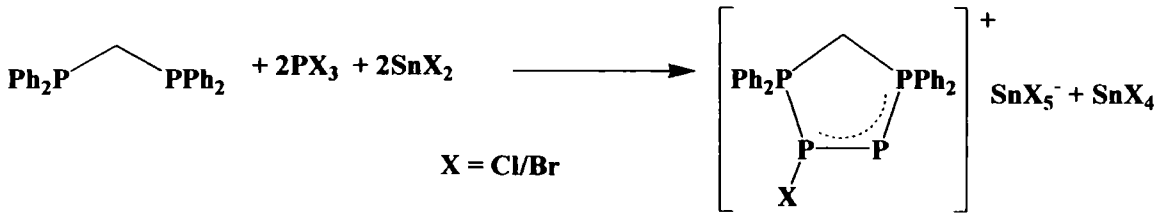
7.4 Tetraphosphenium ions

Preliminary work has shown that the synthesis of a tetraphosphenium ion is possible when using the diphosphane dtbpf which has bulky ^{t}Bu substituents on the phosphorus atoms.[2, 3] Several important to things to note are:

- using dtbpf, the corresponding cyclic triphosphenium ion cannot be synthesised;
- using the diphosphane dpdtbpf, containing ^{t}Bu groups on one phosphorus atom and Ph on the other, the tetraphosphenium ion cannot be synthesised, and only the cyclic triphosphenium ion forms.

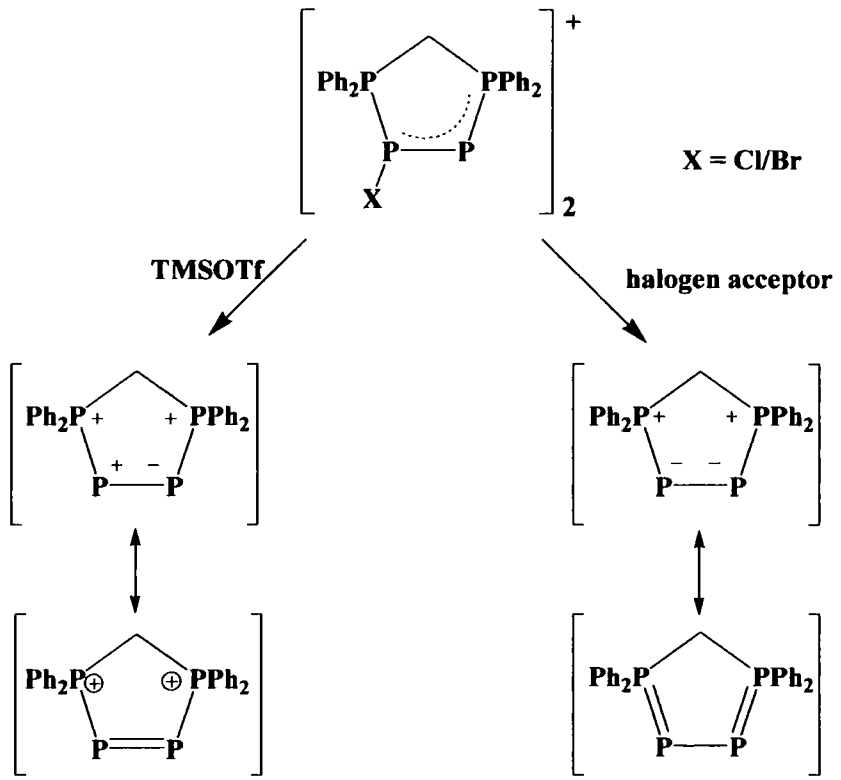
This suggests that along with steric bulk, for the formation of cyclic tetraphosphenium ion to take place it is essential that formation of the cyclic triphosphenium ion is less favourable.

The prime candidate for further studies is the diphosphane dppm. Previous investigations have shown that the formation of the cyclic triphosphenium ion from dppm is not possible.[4] However, using dppm, the synthesis of cyclic tetraphosphonium ion is possible.[5] This was attributed to the five-membered tetraphosphonium ion being more stable than a four-membered cyclic triphosphenium ion. This all suggests that dppm could be an ideal starting material for the formation of a new cyclic tetraphosphenium ion (Scheme 7.3).



Scheme 7.3: Proposed synthesis of a cyclic tetraphosphenium ion from dppm

If stabilisation and/or isolation of a cyclic tetraphosphenium ion were achieved, possible further investigations could involve the removal of the halogen. Two possible investigations are shown in Scheme 7.4.



Scheme 7.4: Possible outcomes from the removal of X from a cyclic tetraphosphenium ion

7.5 Potential applications in catalysis

Well-defined phosphane complexes are vital components in many catalytic systems. Metal-mediated catalysis (especially homogeneous catalysis) lies at the heart of many of the most successful strategies for the preparation of essential 'tailored' materials and molecules and for the production of key chemical intermediates for industry. Further advances in this technologically important and challenging area rely on the development of finely honed catalysts through rational design of the ligands.

The preliminary work on cyclic triphosphenium ion coordination chemistry has highlighted that their overall positive charge may favour an unusually long metal-P interaction, something that will facilitate exchange reactions, while rendering the complex unusual electronic properties. This could be very significant in a number of catalytic systems, with those for the synthetically important hydroamination (direct addition of an NH bond across an unsaturated C–C bond) being particularly relevant, where platinum complexes are known to be active catalysts, but where substrate binding is inefficient due to the low electrophilicity of the Pt complex, something that would be enhanced using cyclic triphosphenium ions as ligands.[6] Additionally, the structure of cyclic triphosphenium ions differs from those of traditional phosphanes, with their steric bulk being located one atom further away from the donor centre, something that is likely to induce unusual reactivity/behaviour of the cyclic triphosphenium ion complexes.

In the field of pharmaceuticals it is very important to be able to synthesise one enantiomer rather than another because different enantiomers of a molecule often exhibit different biological activity. In industry it is also important to be able to produce products as pure as possible in large quantities. For this reason the use of catalysts is very important.[7] The use of small amounts of chiral, enantiomerically pure catalysts can lead to the formation of large amounts of enantiomerically pure or enriched products. One method is to form complexes derived from chiral ligands.[7] Synthesis of chiral derivatives of P-alkyl or P-aryl derivatives of cyclic triphosphenium ions and cyclic tetraphosphonium ions is possible given suitable starting materials. This could lead to further applications in asymmetric synthesis.

7.6 Hydrolysis reactions

Further investigation into the use of 2-aminobenzyl alcohol in hydrolysis reactions is required. In the reactions discussed in Chapter 7, there seems to be a degree of selectivity when using 2-aminobenzyl alcohol to hydrolyse Pt(II) complexes containing chlorophosphane ligands. Isolation of the product of hydrolysis is necessary to confirm assignments to a salt or a non-salt. Perhaps alkylation of the amino group would help solubility problems and increase the yield of hydrolysed product.

7.7 References

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