

W476

FORMATION AND ISOMERISATION PROCESSES
OF SIX-CO-ORDINATE PHOSPHORUS ANIONS

by

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A Thesis presented for the degree of Doctor
of Philosophy in the Faculty of Science of
the University of Leicester

1981

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Summary

A series of spirophosphoranes was prepared in order to study different aspects of nucleophilic substitution at five-co-ordinate phosphorus. The phosphoranes were treated with nucleophiles under temperature controlled conditions and the reactions were monitored by ^{19}F and ^{31}P NMR spectroscopy.

The half-lives of the resulting phosphorides could be extended by increasing the electron withdrawing properties of the ligands and by introducing ligands with low lying empty orbitals.

Wherever possible nucleophilic attack was assisted by the greatest number of antiperiplanar lone pair interactions from the donor atoms (stereoelectronic effects). This led to the kinetically controlled formation of the trans-isomer of some six-co-ordinate bis(bidentate) phosphorus anions, which under thermodynamic conditions produced the more stable cis-isomer(s).

In some cases the trans-cis isomerisation proceeded via a dissociative mechanism, this involving a unidentate ligand. Some cis-phosphorides underwent intramolecular isomerisation processes, possibly via trigonal prismatic intermediates.

Six-co-ordinate phosphorus anions containing a phosphorinane ring or non-equivalent bidentate/unidentate ligand donor atoms were short-lived. Increasing steric hindrance by introduction of substituents onto a donor atom disfavoured the formation of phosphorides.

Only one equilibrium between a phosphorane and a

phosphoride became rapid on the NMR timescale on increasing the temperature; all other equilibria were slow on the NMR timescale.

Introduction of an oxazaphospholane ring into a phosphorane decreased the half-life of the generated phosphoride and introduced in some cases a rigidity at the nitrogen centre.

A review of ^{19}F and ^{31}P NMR data of chemical shifts and coupling constants of phosphorides is given.

Parts of this work have been described in the following publications:

Kinetic Control in the Formation of Six-co-ordinate Phosphorus Anions

J.J.H.M. Font Freide and S. Trippett,
J.C.S. Chem.Comm. 1980, 157.

Intramolecular Isomerisation in Six-co-ordinate Bis(bidentate) Phosphorus Anions

J.J.H.M. Font Freide and S. Trippett,
J.C.S. Chem.Comm. 1980, 934.

Abbreviations and Symbols

a	hyperfine splitting constant (Gauss)
J	nuclear spin-spin coupling constant (Herz)
L	unidentate ligand
MeCN	acetonitrile
NaOPhF	sodium p-fluorophenoxide
P(3)	tervalent phosphorus compound
P(5)	phosphorane
P(6)	six-co-ordinate phosphorus species; phosphoride
TBAF	tetrabutylammonium fluoride
T_c	coalescence temperature for an NMR spectrum
THF	tetrahydrofuran
$w_{\frac{1}{2}}$	width of NMR absorption at half-height (Hz)
δ	chemical shift, positive when the sample resonates to high frequency of the reference
δ_F	fluorine chemical shift, relative to PhCF_3
δ_P	phosphorus chemical shift, relative to 85% H_3PO_4
ΔG^X	free energy of activation (kcalmol^{-1})
$\Delta\nu$	frequency separation between two NMR signals (Hz)
σ	shielding constant of nucleus (ppm)

Phosphorane and phosphoride species can be referred to as $\text{P}(\text{bid})(\text{bid}')(\text{uni})$ and $\text{P}(\text{bid})(\text{bid}')(\text{uni})(\text{uni}')^-$ respectively, with (bid) standing for bidentate ligand and (uni) standing for unidentate ligand. The following ligands have been used:

(uni) unidentate ligand derived from

Cl	chloride
F	fluoride
NMe ₂	N,N-dimethylamine
NPr ⁱ ₂	N,N-di-isopropylamine
OEt	ethanol
OPh	phenol
OPhF	p-fluorophenol

(bid) bidentate ligand derived from

but	2,3-dimethylbuta-1,3-diene
chl	tetrachloro-1,2-benzoquinone (<u>o</u> -chloranil)
eth	ethan-1,2-diol
hfb	hexafluorobiacetyl
Meet	propan-1,2-diol
Net	2-N-methylaminoethanol
Npr	2-N-isopropylaminoethanol
pent	3-benzylidenepenta-2,4-dione
pfp	perfluoropinacol
phen	1,2-dihydroxybenzene (catechol)
pin	2,3-dimethylbutan-2,3-diol (pinacol)
prop	2,2-dimethylpropan-1,3-diol
Set	2-mercaptoethanol

CHAPTER 1

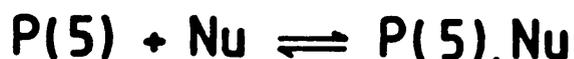
Aspects of Six-co-ordination1.1 Introduction

Six-co-ordinate phosphorus species probably play a much more important role in the chemistry of phosphorus than hitherto appreciated.

The alcoholysis of aminophospholans (1) and the formation of spirophosphoranes from tervalent phosphorus compounds (2) are suggested to proceed via six-co-ordinate transition states. Furthermore, in any substitution reaction involving the formation of five-co-ordinate intermediates there is always the possibility that six-co-ordinate phosphorus species will be present, either as intermediates or as transition states (3, 4).

Hydrolysis of pentaaryloxyphosphoranes (5), base-catalysed exchange of alkoxy ligands in oxyphosphoranes (6) and methanolysis of spirophosphoranes (7) can all involve six-co-ordinate phosphorus species.

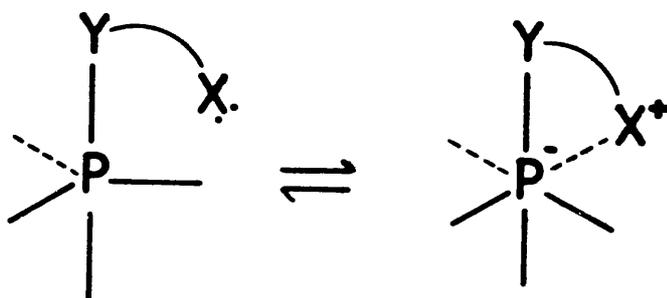
In general, equilibria of the type



lie very much on the right-hand side in the absence of large steric effects (8). Treatment of a phosphorane, P(5), with a base, Nu, may produce six-co-ordinate phosphorus species. Several P(6) adducts are known to be made in this manner (9, 10, 11, 12). Nucleophilic substitution on spirophosphoranes

results in either retention and/or inversion of configuration at the phosphorus and can be understood in terms of six-co-ordinate intermediates (13).

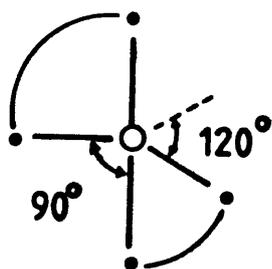
When a basic function X is located at the end of a branched ligand of a five-co-ordinate phosphorus compound,



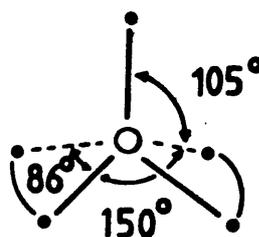
an equilibrium is possible between the five- and six-co-ordinate phosphorus species (14, 15). Reports in the literature concerning stable six-co-ordinate phosphorus compounds have been increased in recent years (16).

1.2 Structure of Phosphoranes

Calculations on AL_5 -structures (A=central atom, L=ligand) with fixed AL bonds of equal lengths, minimizing electrostatic and non-Coulombic repulsive forces, show that the trigonal bipyramid, TB, is slightly favoured over the tetragonal pyramid, TP (17).



ideal TB



ideal TP

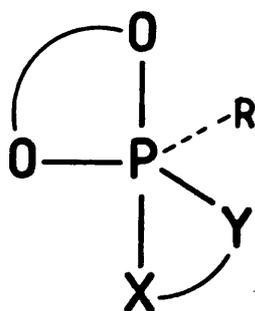
X-ray analyses of spirophosphoranes with two five-membered rings, containing combinations of oxygen, sulphur and carbon as donor atoms, show that the skeletal geometry of these phosphoranes can be described in terms of mixes of TB and TP (18, 19, 20, 21, 22). A calculation model indicates that the energy difference between TB and TP is small in the case of spirophosphoranes with donor heteroatoms (23).

In both TB and TP the possibilities of direction of nucleophilic attack are identical, i.e. either opposite the two bidentate ligands or opposite the unidentate ligand. In this work phosphoranes will be depicted as TB, although this does not represent their exact structure.

1.3 Nucleophilic Attack on P(5)

1.3.1 General

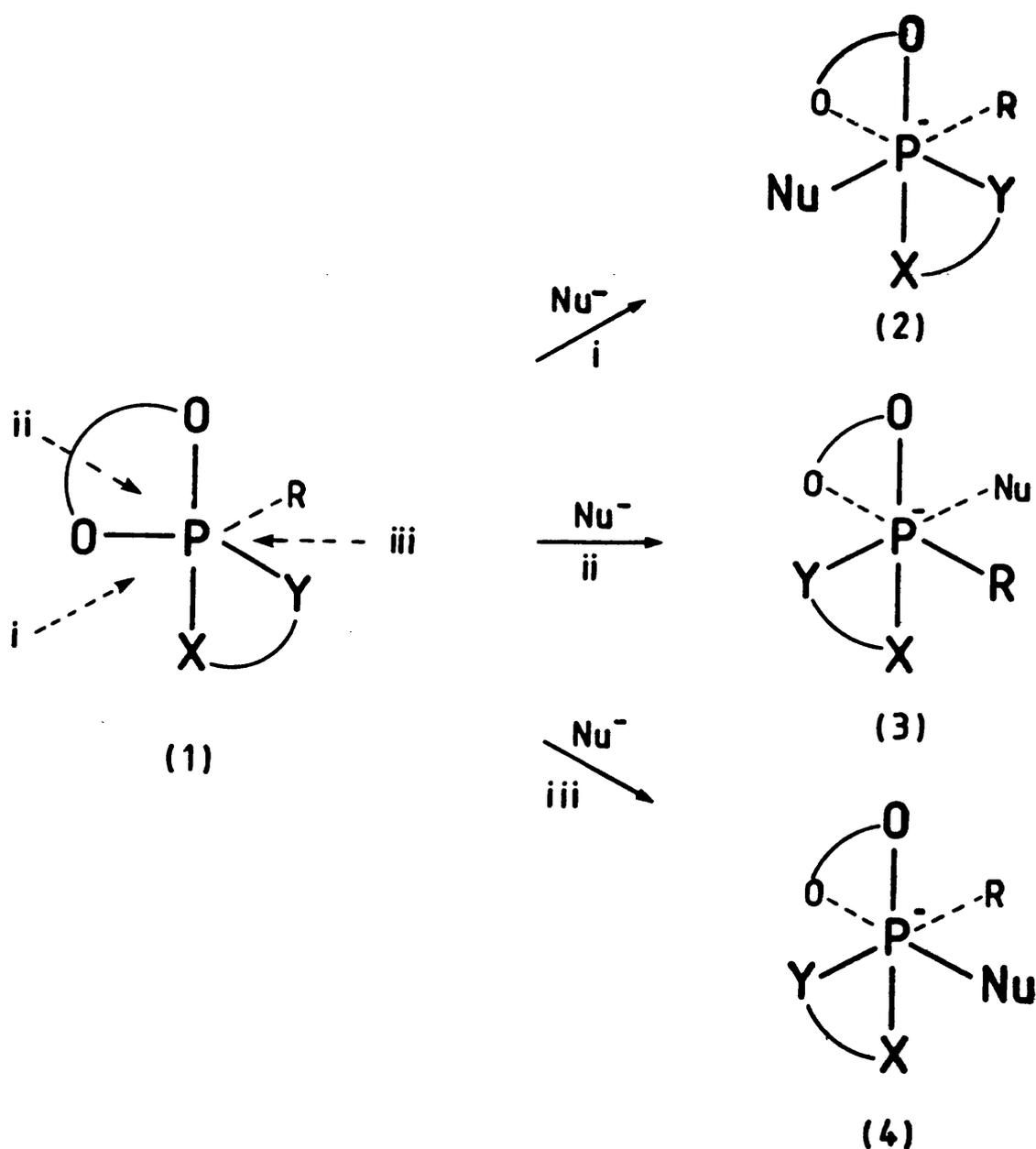
Spirophosphoranes of the general formula (1; X,Y=O, S, N or C; R=OPhF, OPh, F, NMe₂ or OEt) have been treated with nucleophiles (Nu⁻=FPhO⁻ or F⁻).



(1)

An increase in the electronegativity of the donor atoms (F > O > N > C, S) will produce a more electron deficient phosphorus atom, resulting in an easier and faster attack of a

nucleophile (14). If the attacking nucleophile is a π -donor (FPhO^- , F^-) the attack will be facilitated if the approached cis-ligands are able to accept π -electrons (14). When the central phosphorus atom is shielded from attack by neighbouring groups, attack on that side will be slow (24, 25, 26).



Nucleophilic attack on phosphorane 1 opposite unidentate ligand R (pathway i) will produce the six-co-ordinate phosphorus anion 2, with unidentate ligands Nu and R in a trans-relationship. Attack opposite a bidentate ligand (via ii or iii) produces the six-co-ordinate phosphorus anions 3 and 4, in which two unidentate ligands have a cis-relationship.

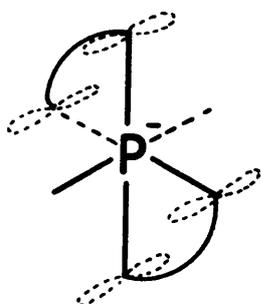
1.3.2 Stereoelectronic Factors

Stereoelectronic effects are those effects which result from the interaction of the σ^* -orbital with the anti-periplanar, app, lone pair(s) of the β -atom(s) (27, 28, 29). The interaction of the doubly occupied app lone pair with the empty σ^* -orbital yields a stabilisation energy.

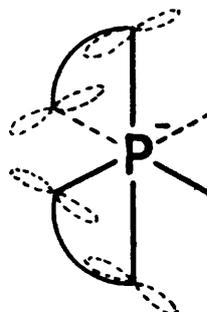
Due to this interaction the bond directly linked to the lone pair carrying atom is strengthened while the app-bond is weakened (30, 31). The lower the σ^* -energy the greater the stabilisation energy, while a decrease in app lone pair population will result in a decrease of the stabilisation effect (32). Also, an increase in the p-character of the lone pair electrons raises their energy and hence increases the stereoelectronic effect of stabilisation (33, 34)

Nucleophilic attack at phosphorus, having up to five donor heteroatoms, can be assisted by stereoelectronic lone pair effects, i.e. overlap of the app p-type lone pair electrons on the donor atoms with the σ^* -orbital of the forming phosphorus-nucleophile bond. The more favourably oriented the lone pairs present, the greater the weakening effect on

the app-bond will be, this resulting in an easier nucleophilic attack/displacement (30, 31).



trans
(6)



cis
(7)

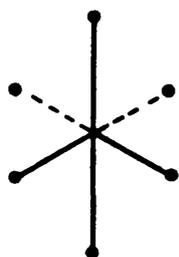
trans-Attack on bicyclic phosphoranes produces trans-phosphoride 6. In trans-phosphoride 6 the app phosphorus-nucleophile bond can be weakened by the effect of lone pairs on four donor heteroatoms. In cis-phosphoride 7, produced by cis-attack, the app-bond is weakened by stereoelectronic effects from lone pairs of only two bidentate donor heteroatoms, plus any effect from lone pairs on the unidentate donor atom.

1.4 Stability of Six-co-ordinate Species

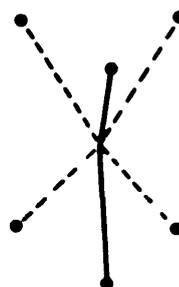
The stability of either the cis- or trans-isomer of a six-co-ordinate species $A(\text{bid})_2(\text{uni})_2$ depends on the σ - and the π -bonding characteristics of the donor atoms, the inductive effects of the groups appended to the donor atoms of the ligands and the steric requirements of the attached ligands as a whole (35, 36). In terms of minimising the mutual repulsion between the ligand donor atoms, where all A-ligand bonds are equal, then only for a specified distance

between two donor atoms of a bidentate ligand (bite) are the cis- and trans-isomers of equal energy (36). Otherwise the cis-isomer is always favoured, even in the case of shortening A-ligand bonds when trans-favouring is to be expected for larger bites (36).

Stereoelectronic factors are operational in both cis- and trans-isomers. Experimentally it has been found that for six-co-ordinate phosphorus species the most stable configuration is cis (9, 37, 42)



(8)



(9)

Most six-co-ordinate species have an octahedral structure 8 (39, 40, 41). and only when large distortions are to be accommodated (bond length, bite) will the octahedron be distorted towards a trigonal prismatic structure 9 (36, 38, 43).

Derivatives of P(6) with aromatic carbons as ligands have been known for some time (16, 44, 45, 46). Trischelates with six oxygen donor atoms have been isolated (47, 48) and trischelates with mixed oxygen and nitrogen donor atoms are also reported (16, 49).

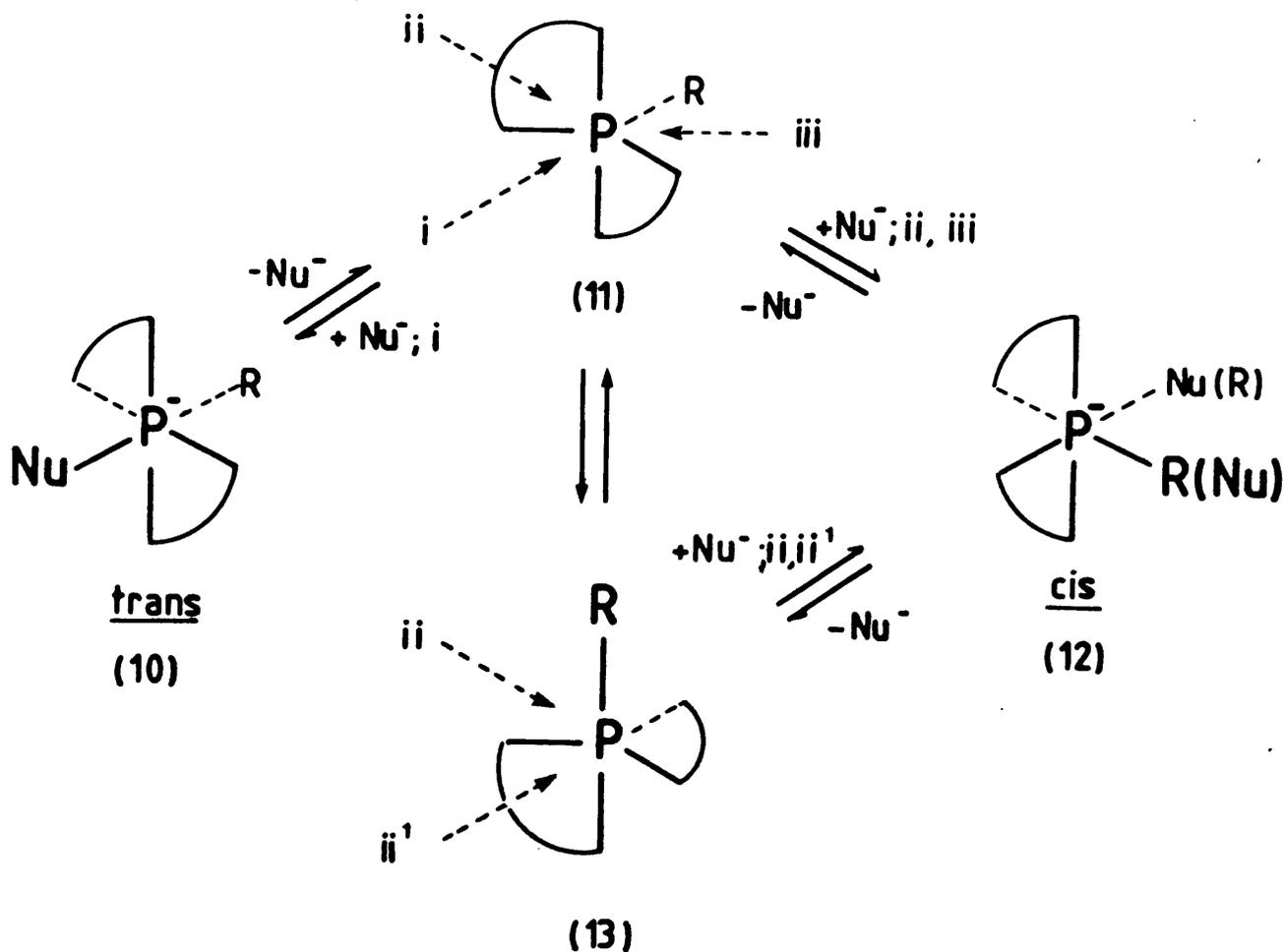
For bischelate P(6) the pyridine adducts (37) and the phenol adduct (42) have been isolated, all with the two

unidentate ligands in cis-relationship.

1.5 Isomerisation Processes

Both diastereomerisation and enantiomerisation in six-co-ordinate species are well known in inorganic chemistry. These isomerisation processes can proceed via intramolecular (regular or irregular) and intermolecular mechanisms (36, 50, 51, 52). Previous work on the isomerisation of tris-(bidentate) phosphorus species indicates an irregular acid-catalysed mechanism (49, 53).

1.5.1 Intermolecular Mechanisms



Unidentate ligand Nu^- dissociates from the phosphoride 10 or 12 forming a spirophosphorane 11 with R in an equatorial position. Renewed attack of Nu^- on the phosphorane via i, ii or iii produces respectively trans- 10 and both cis-isomers 12. Where pseudorotation of phosphorane 11 produces phosphorane 13, with the R-group apical, (54) nucleophilic attack via ii or ii' produces again the cis-isomers 12.

trans-cis Isomerisation as well as cis-cis isomerisation are possible via this route.

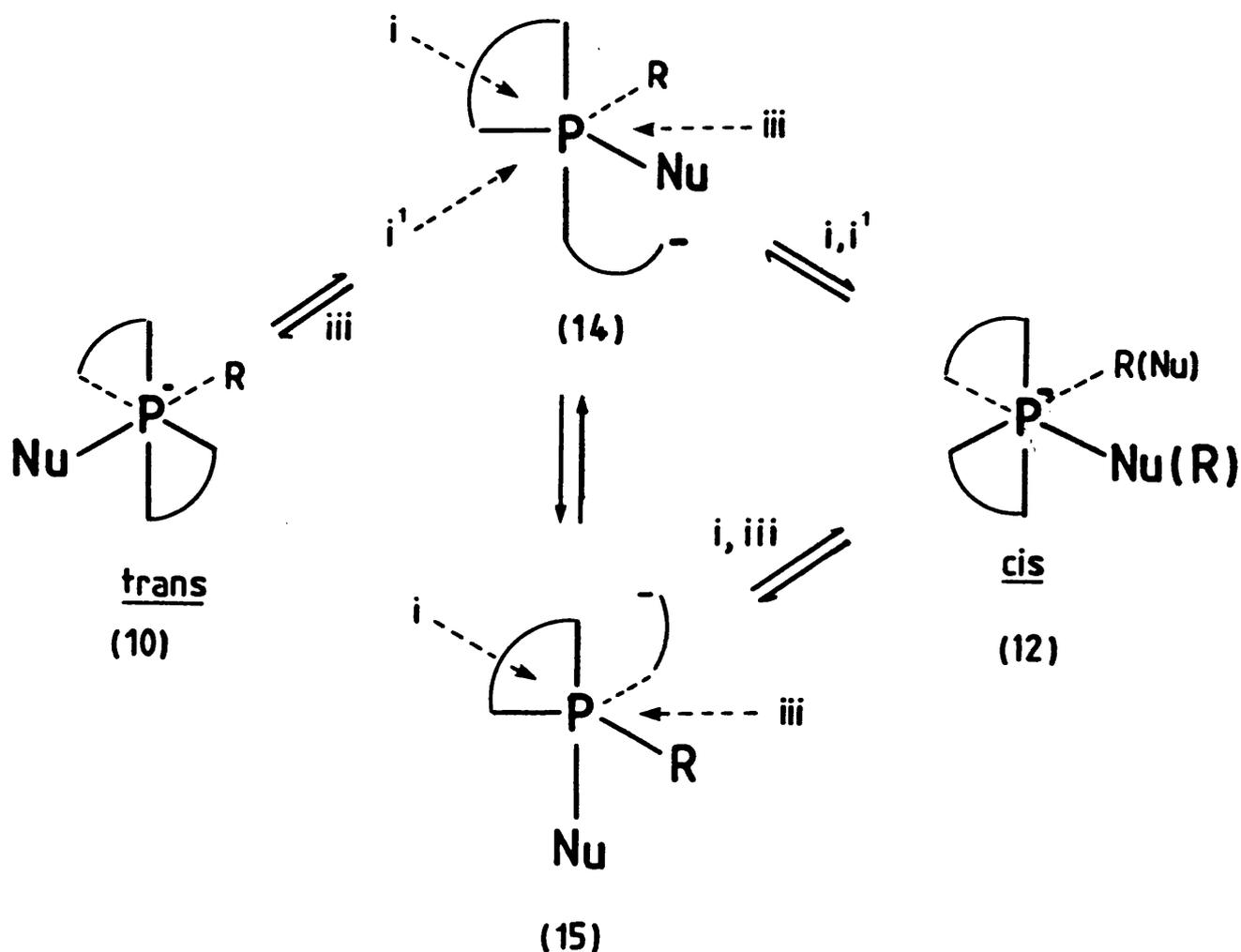
Attack of Nu^- on phosphoride to produce a seven-co-ordinate central atom, followed by dissociation of any one of the unidentate ligands can lead to formation of all the isomers. Although seven-co-ordination is well known in inorganic chemistry (48, 55, 56) species of its kind have not been reported in phosphorus chemistry.

1.5.2 Intramolecular Mechanisms

1.5.2.1 Irregular

Dissociation of one P-heteroatom bond of a bidentate ligand will produce a phosphorane with a dangling ligand. Where the dangling ligand occupies an apical position, 14, recombination via iii, i or i' will produce respectively the trans- 10 and both cis-isomers 12. Where pseudorotation forces the dangling ligand to occupy an equatorial position, 15, recombination via i or iii produces the cis-isomers 12.

Both irregular mechanisms described in 1.5.1 and above can account for identical diastereomerisation and



enantiomerisation processes.

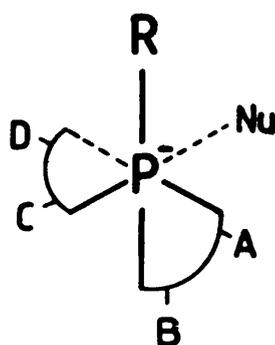
1.5.2.2 Regular

An octahedron can be converted into a trigonal prism by 60° rotation of one end of the structure relative to the other end. When this internal rotation is repeated an octahedron is again formed (36, 39).

Several twist processes are known which enable an octahedron to rearrange its ligands, e.g. rhombic twist, trigonal twist, etc. (51, 57, 58). The differences between the twisting mechanisms appear to arise from differences in

chelate ring bond angles. Thus there is only one basic type of twisting mechanism (58, 59, 60), which when carried out gives rise to a trigonal prismatic transition state which may vary slightly in symmetry (52).

cis-Phosphoride 16, cis-P(ABbid)(Cdbid)R Nu^- , contains four imaginary threefold axes $i\text{-C}_3$, each going through the centre of a triangular face of the octahedron and through the central phosphorus atom. The four imaginary C_3 -axes are



(16)

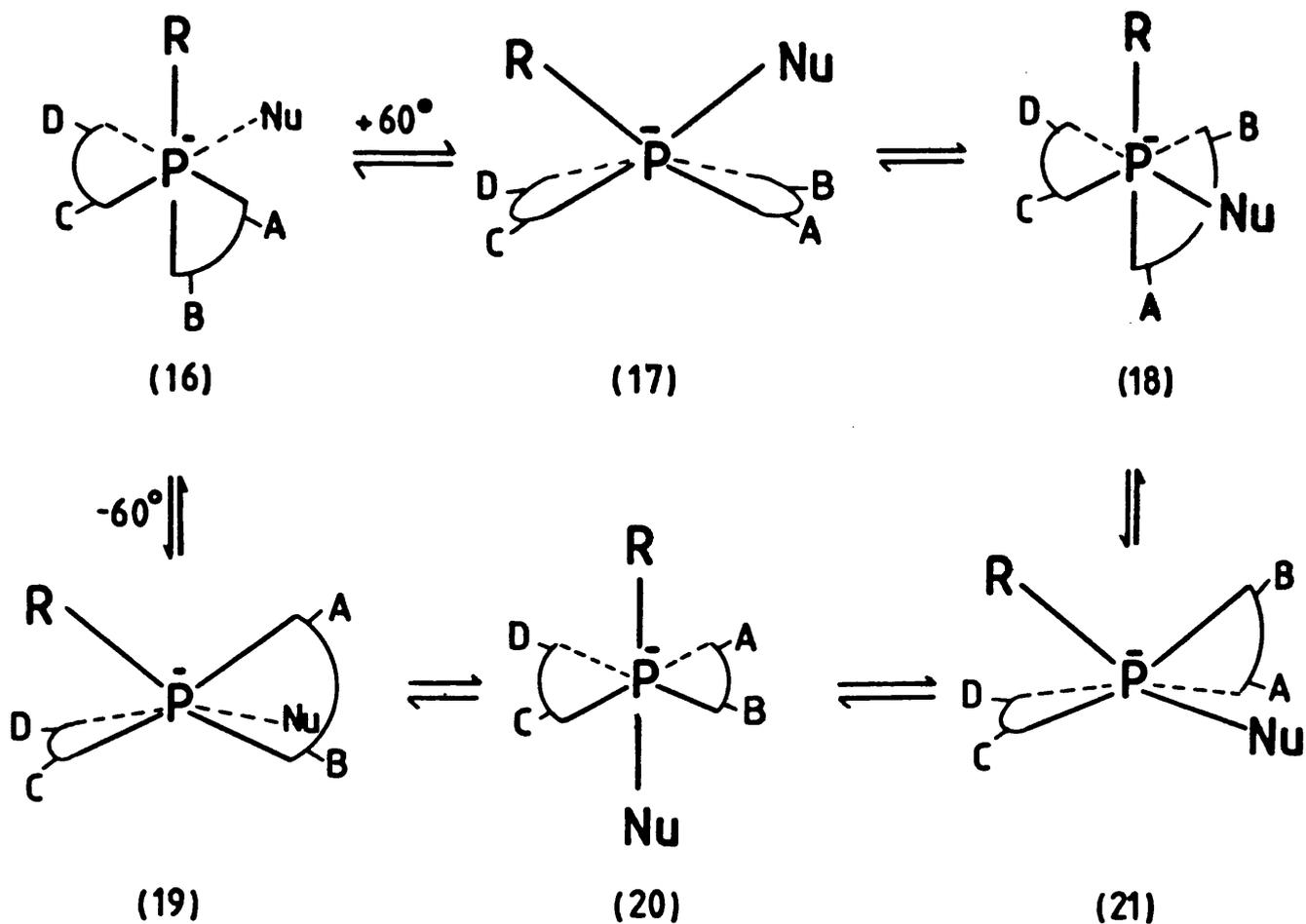
labelled as indicated in Table A.

Table A

axis	through centre of triangle
$i\text{-C}_3$ (a)	R C D
$i\text{-C}_3$ (b)	R D Nu
$i\text{-C}_3$ (c)	R Nu A
$i\text{-C}_3$ (d)	R A C

Rotations of 60° about these axes produce trigonal prismatic intermediates (41) via which a regular isomerisation can occur.

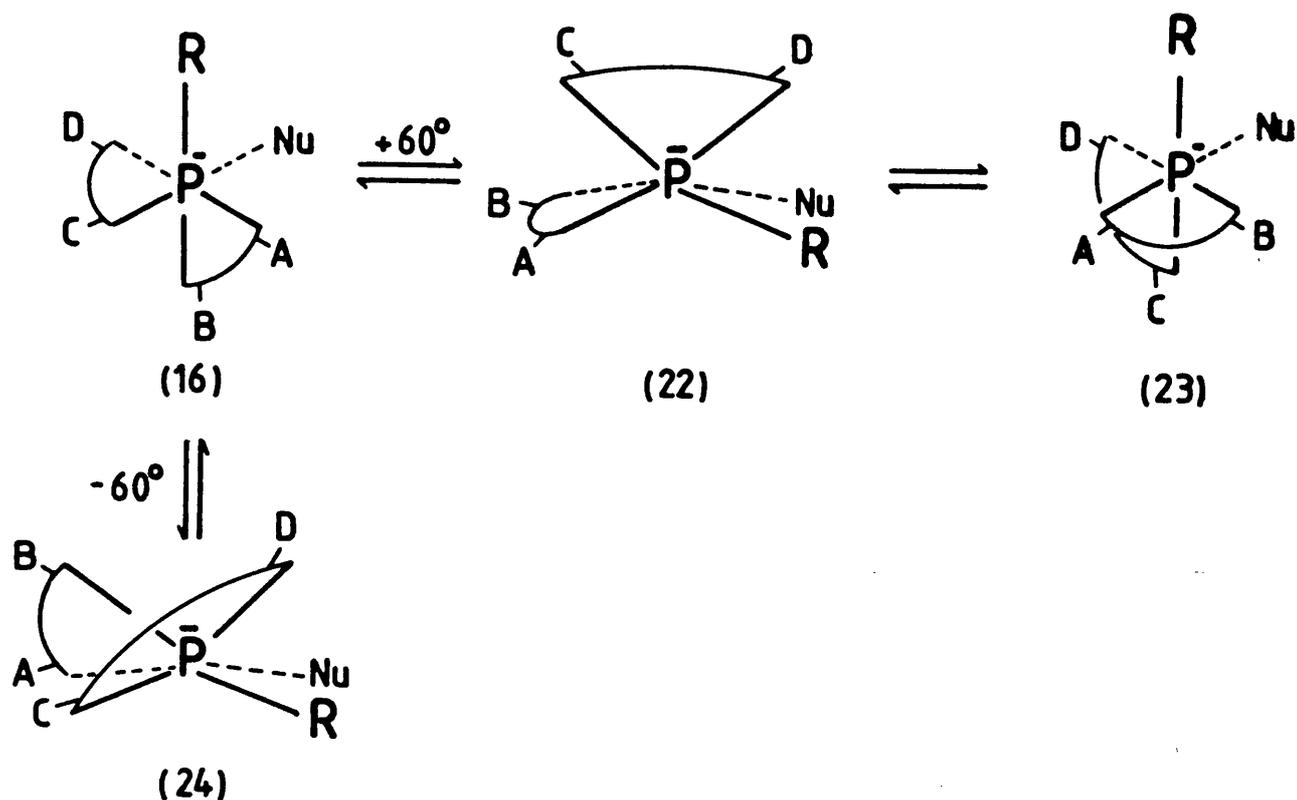
Rotation about $i-C_3(a)$



Rotation of trio (NuBA) through 60° anticlockwise* about $i-C_3(a)$ relative to trio (RCD) transforms 16 via 17 into the cis-isomer 18. Rotation of the same trio (NuBA) this time through 60° clockwise will eventually lead via 19 to the trans-isomer 20. Hence this twist process can provide a path for cis-trans isomerisation as well as isomerisation of cis-isomers.

*Looking towards phosphorus from the centre of the trio.

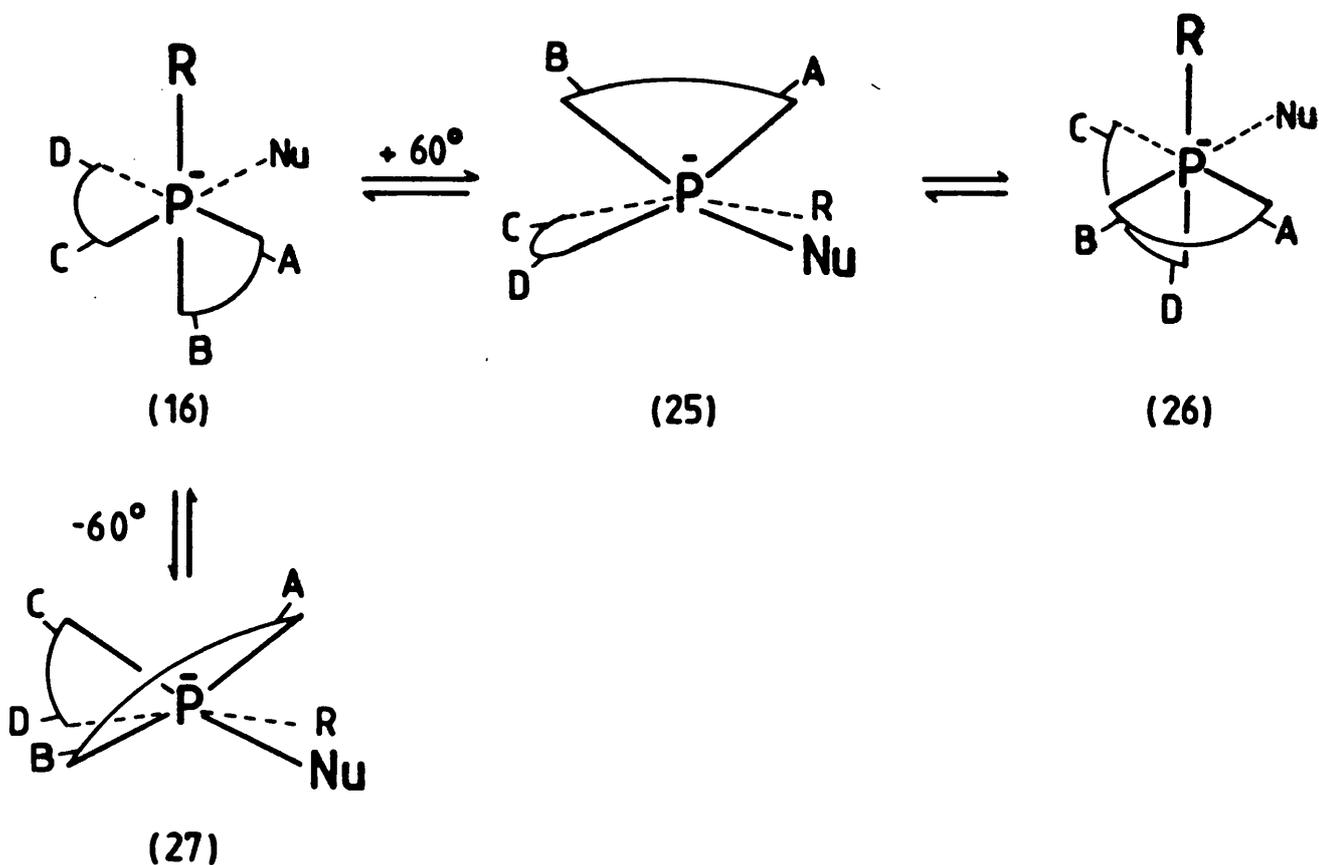
Rotation about $i-C_3(b)$



Rotation of trio (ABC) through 60° anticlockwise about $i-C_3(b)$ relative to trio (RDNu) produces cis-isomer 23 via trigonal prismatic intermediate 22, in which bidentate ligand CD is spanning across the two triangular faces.

Trigonal prism 24 is obtained by a 60° clockwise rotation of trio (ABC). Further rotation in the same direction will lead to a structure with a bidentate ligand angle $\hat{C}P\hat{D}$ approaching 180° .

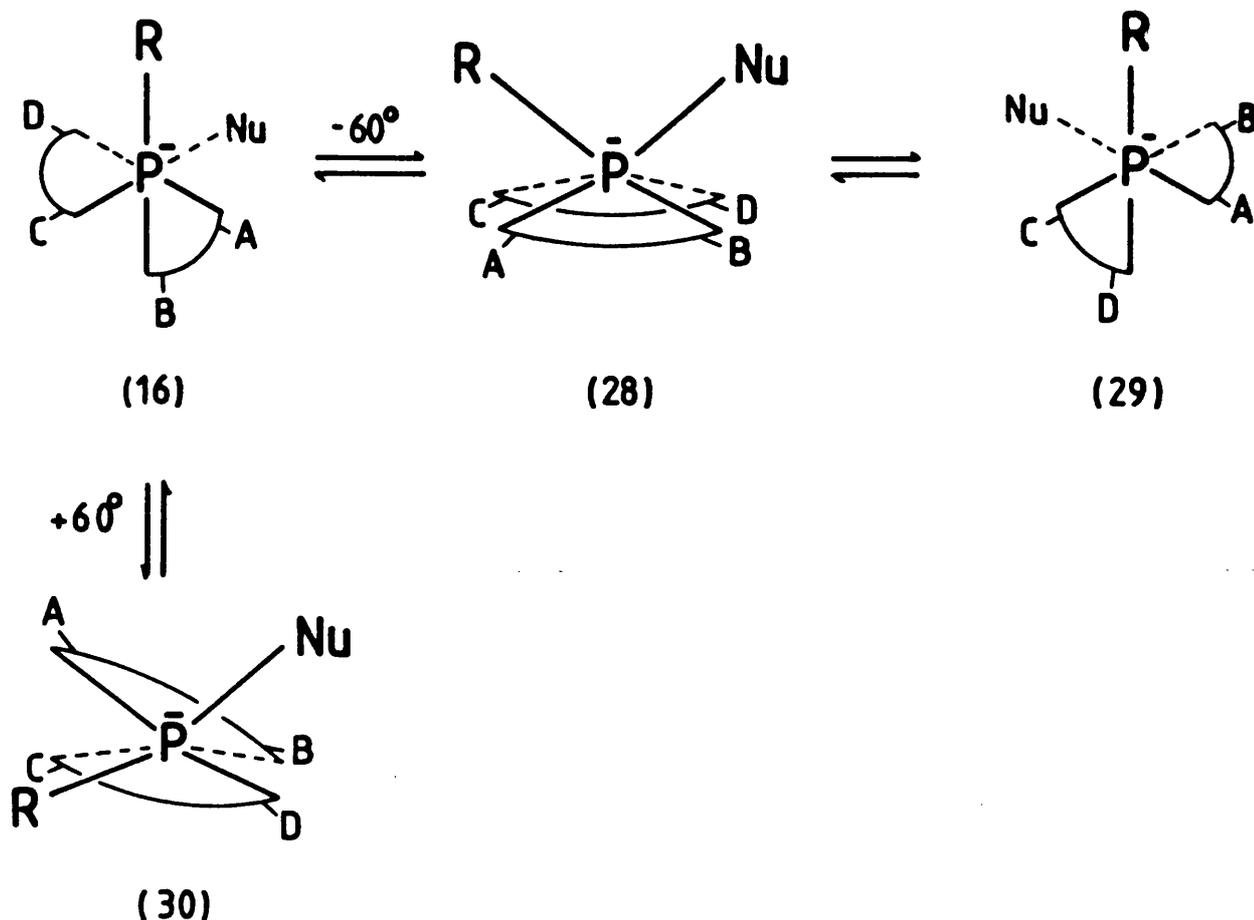
Rotation about $i-C_3(c)$



Rotation of trio (BDC) through 60° anticlockwise about $i-C_3(c)$ relative to trio (RNuA) produces cis-isomer 26 via trigonal prismatic intermediate 25, in which bidentate ligand AB spans across the two triangular faces.

Clockwise rotation of the same trio (BDC) leads to 27, which upon further rotation produces a high energy species with bidentate ligand angle \hat{BPA} approaching 180° .

Rotation about $i-C_3(d)$



Rotation of trio (BNuD) through 60° clockwise about $i-C_3(d)$ relative to trio (RAC) produces cis-isomer 29 via the trigonal prismatic intermediate 28, in which both bidentate ligands are spanning across the two triangular faces. Anticlockwise rotation of trio (BNuD) produces 30 which on further rotation will produce a structure with two bidentate ligand angles approaching 180° .

Geometrical cis-trans isomerisation only occurs

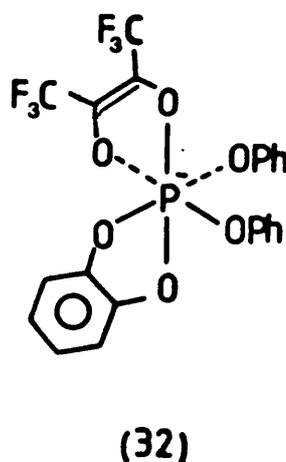
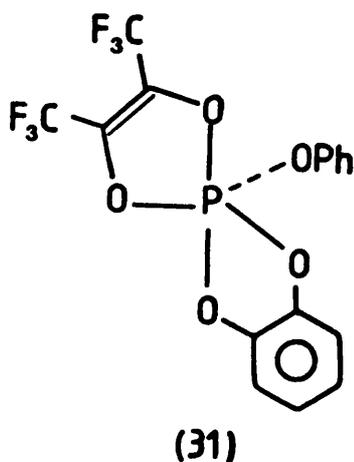
using the rotation about $i-C_3(a)$. Rotations about all other threefold axes lead to isomerisation of cis-bis-(bidentate) phosphorus species.

Twist processes are well known in inorganic chemistry where it is possible for more than one twist to occur consecutively (52, 60, 61, 62).

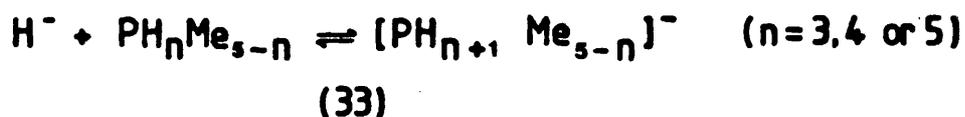
CHAPTER 2

Nucleophilic Attack on P(5)

Previous work (42) has concluded that associative nucleophilic substitution at five-co-ordinate phosphorus takes place via cis-attack, this requiring the least amount of ligand rearrangement in the phosphorane. Evidence is provided by a comparison of X-ray analyses of phosphorane 31 and the related six-co-ordinate phosphorus anion 32.

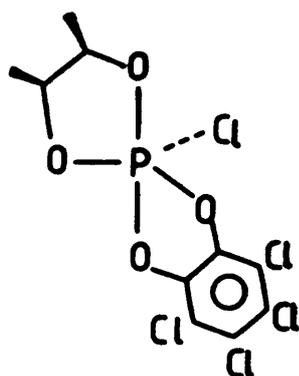


Semi-empirical calculations of attack by the hydride ion on model TB phosphoranes, 33, show a preference for cis-attack (63).



It has also been reported that associative nucleophilic substitutions at spirophosphorane 34 proceed with inversion

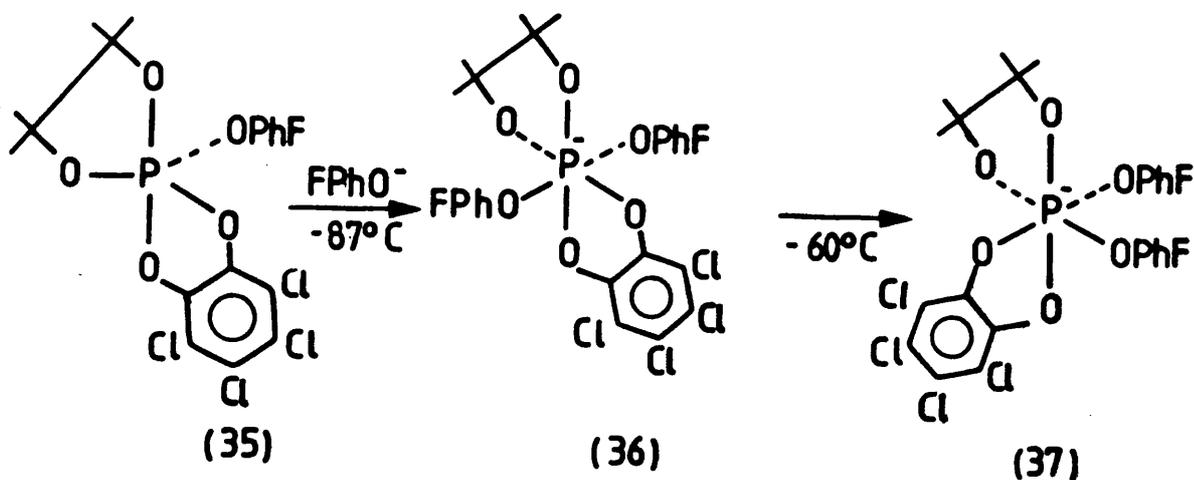
and/or retention of configuration at phosphorus. Inversion implies a trans-attack by the nucleophile, whilst retention implies a cis-attack (13).



(34)

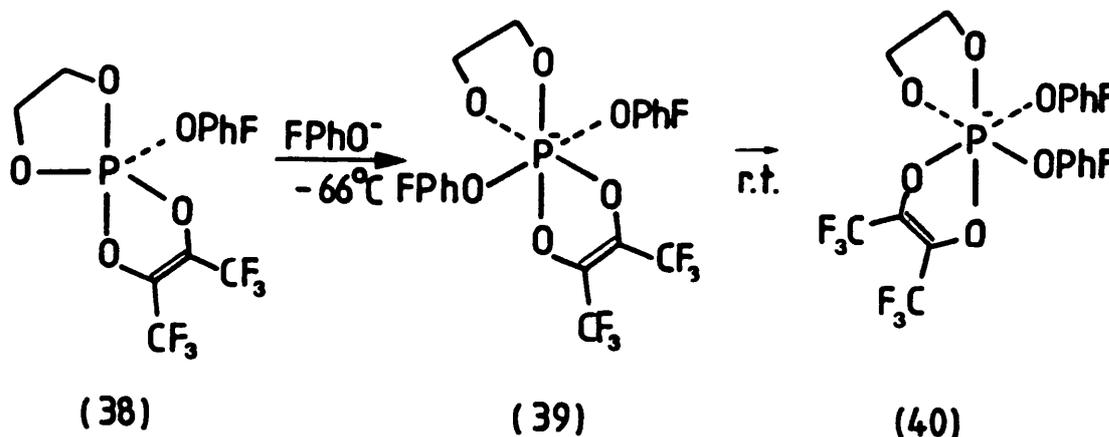
In the present work spirophosporanes are treated with one equivalent of sodium *p*-fluorophenoxide, NaOPhF, or two equivalents of tetrabutylammonium fluoride, TBAF, in tetrahydrofuran, THF, unless otherwise stated. For experimental details see CHAPTER 5.3.

2.1 Bidentate Donor Atoms: Oxygen



The ^{19}F and ^{31}P NMR spectra of the reaction of phosphorane

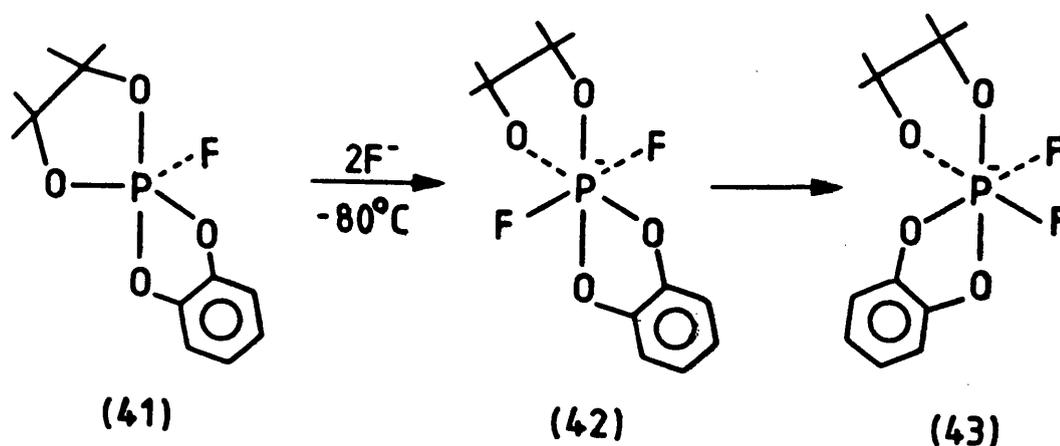
35, δP -35.9, δF -54.3 ppm^{*}, with NaOPhF at -87°C showed the presence of 35 and the trans-phosphoride 36, δP -103.7, δF -63.0 ppm. On warming to -60°C the trans-anion was slowly replaced by the cis-anion 37, δP -107.1, δF -59.9 (1F,s) and -61.3 ppm (1F,s). Warming the mixture to room temperature produced no further change in the ^{19}F and ^{31}P NMR spectra, with 90% of the phosphorane converted into phosphoride.



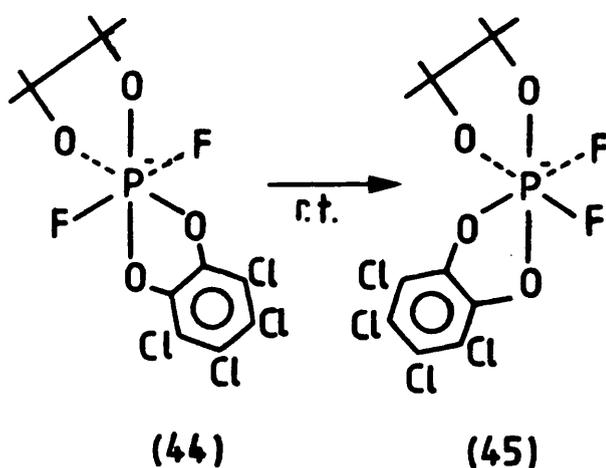
Treating phosphorane 38, δP -29.0, δF -2.4 (6F,s) and -54.9 ppm (1F,s), with sodium *p*-fluorophenoxide at -66°C produced the trans-phosphoride 39, δP -105.1, δF -1.0 ppm (2CF₃,s), which was replaced upon warming by the cis-phosphoride 40, δP -105.5, δF -0.6 (3F,q, $^5J_{FF}$ 10.5 Hz), -1.4 (3F,q, $^5J_{FF}$ 10.5 Hz) and -61.3 ppm (2F). At room temperature 66% of the phosphorane had been converted into phosphoride.

Treatment of fluorophosphorane 41, δP -30.6 (d, $^1J_{PF}$ 981 Hz), δF -0.39 ppm (d, $^1J_{PF}$ 982 Hz), with tetrabutyl-

^{*}Positive chemical shifts are to high frequency of the external standards, 85% H₃PO₄ and PhCF₃ (64).

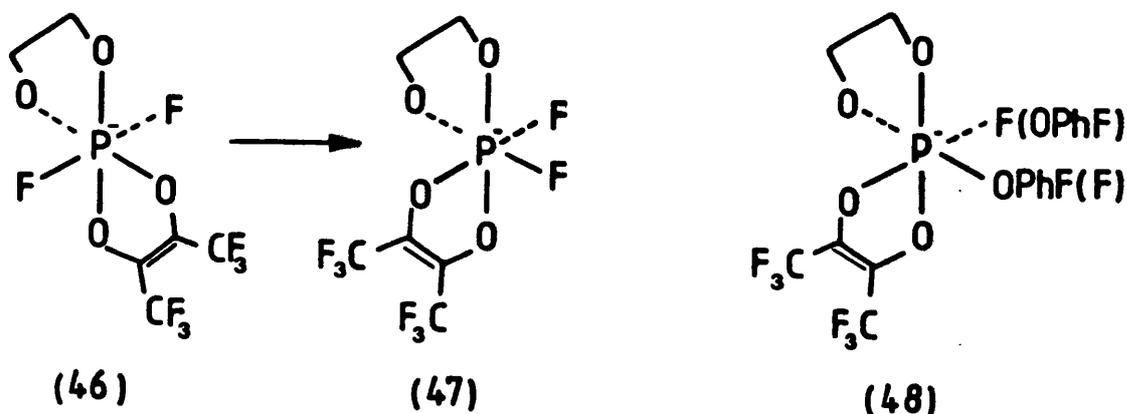


ammonium fluoride at $-80^\circ C$ resulted initially in the formation of trans-phosphoride 42, δP -101.9 (t, $^1J_{PF}$ 757 Hz), δF $+31.6$ ppm (d, $^1J_{PF}$ 745 Hz). On maintaining this temperature anion 42 was slowly replaced by the cis-phosphoride 43, δP -105.9 (dd, $^1J_{PF}$ 723.5 and 726.5 Hz), δF $+21.4$ (1F, dd, $^1J_{PF}$ 715 and $^2J_{FF}$ 34 Hz) and $+16.3$ ppm (1F, dd, $^1J_{PF}$ 715 and $^2J_{FF}$ 34 Hz).



The addition of two equivalents of caesium fluoride to phosphorane 35, $P(chl)(pin)OPhF$, in THF-MeCN (1:1) at $-60^\circ C$ produced the trans-six-co-ordinate phosphorus anion 44,

δP -99.6 (t, $^1J_{PF}$ 768.0 Hz), δF +33.1 ppm (d, $^1J_{PF}$ 768 Hz), which at room temperature was replaced by the cis-isomer 45, δP -102.3 (dd, $^1J_{PF}$ 735.5 and 738.0 Hz), δF +23.0 (1F, dd, $^1J_{PF}$ 738 and $^2J_{FF}$ 33 Hz) and +12.3 ppm (1F, dd, $^1J_{PF}$ 733 and $^2J_{FF}$ 33 Hz).



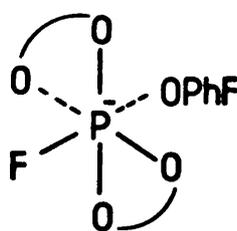
Addition of two equivalents of caesium fluoride to phosphorane 38, P(eth)(hfb)OPhF, at -60°C in THF-MeCN (1:1) produced the trans-anion 46, δP -98.8 (t, $^1J_{PF}$ 756.0 Hz), δF +22.3 (2F, d, $^1J_{PF}$ 746 Hz) and -1.2 ppm (6F, s). At room temperature this trans-anion was replaced by the cis-phosphoride 47, δP -101.0 (dd, $^1J_{PF}$ 728 and 738 Hz), δF +21.5 (1F, dd, $^1J_{PF}$ 717, $^2J_{FF}$ 32 Hz), +3.2 (1F, dd, $^1J_{PF}$ 726, $^2J_{FF}$ 32 Hz) and -1.2 ppm (6F, s), with the transient appearance of the, probably cis, anions 48, δP -102.5 (d, $^1J_{PF}$ 762 Hz), δF +23.0 (F, d, $^1J_{PF}$ 748 Hz), -1.2 (6F, s) and -60.7 ppm (F, s); and δP -102.7 (d, $^1J_{PF}$ 767 Hz), δF +5.7 (F, d, $^1J_{PF}$ 767 Hz), -1.2 (6F, s) and -60.7 ppm (F, s), in the ratio 2:1 respectively.

Discussion

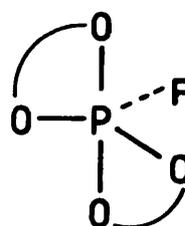
Nucleophilic attack at phosphorus with up to five donor

heteroatoms each having lone pairs of electrons, produces the kinetically controlled trans-six-co-ordinate phosphorus anion, which upon warming is replaced by the thermodynamically more stable cis-anion. This reaction sequence can be ascribed to stereoelectronic control, i.e. overlap of the p-type lone pair electrons of the donor atoms with the σ^* -orbital of the forming phosphorus-nucleophile bond.

trans-Attack on bicyclic phosphoranes is assisted by p-type lone pairs on four donor atoms, whereas cis-attack is assisted by p-type lone pairs on only two donor atoms of a bidentate ligand, plus any effect from the lone pairs on the unidentate donor atom.

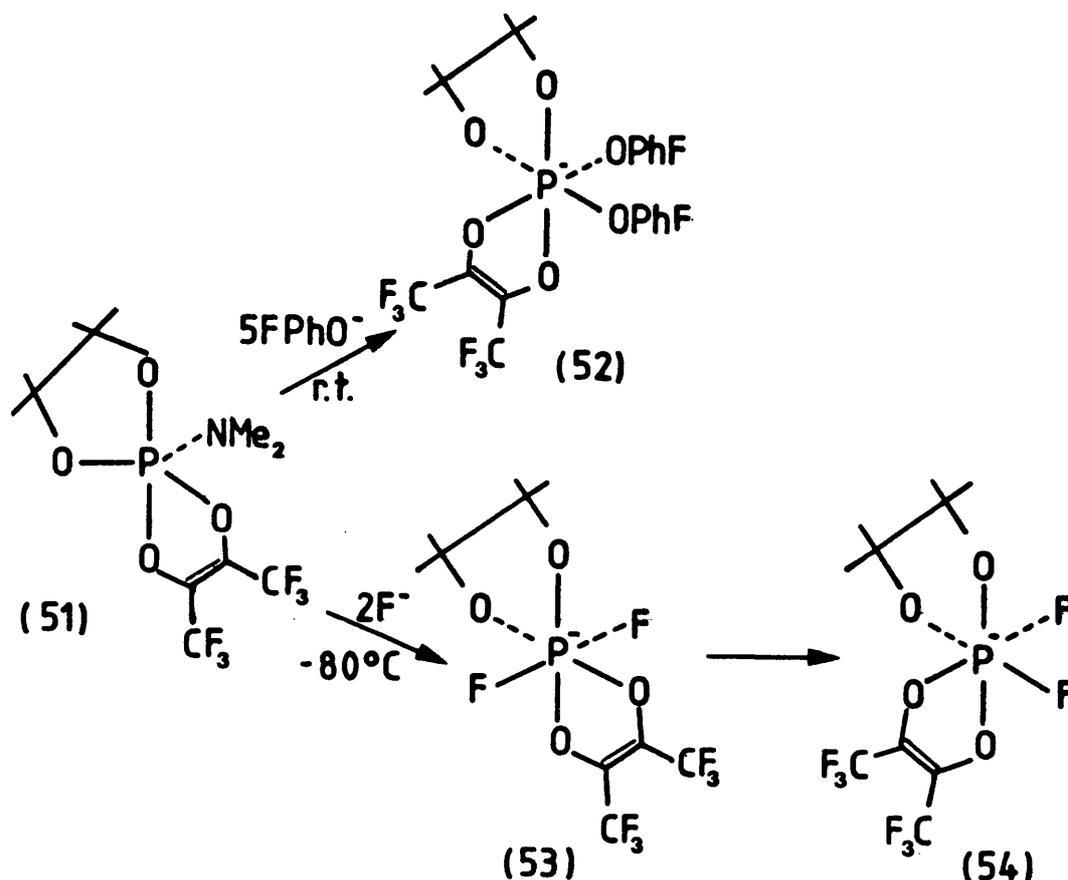


(49)



(50)

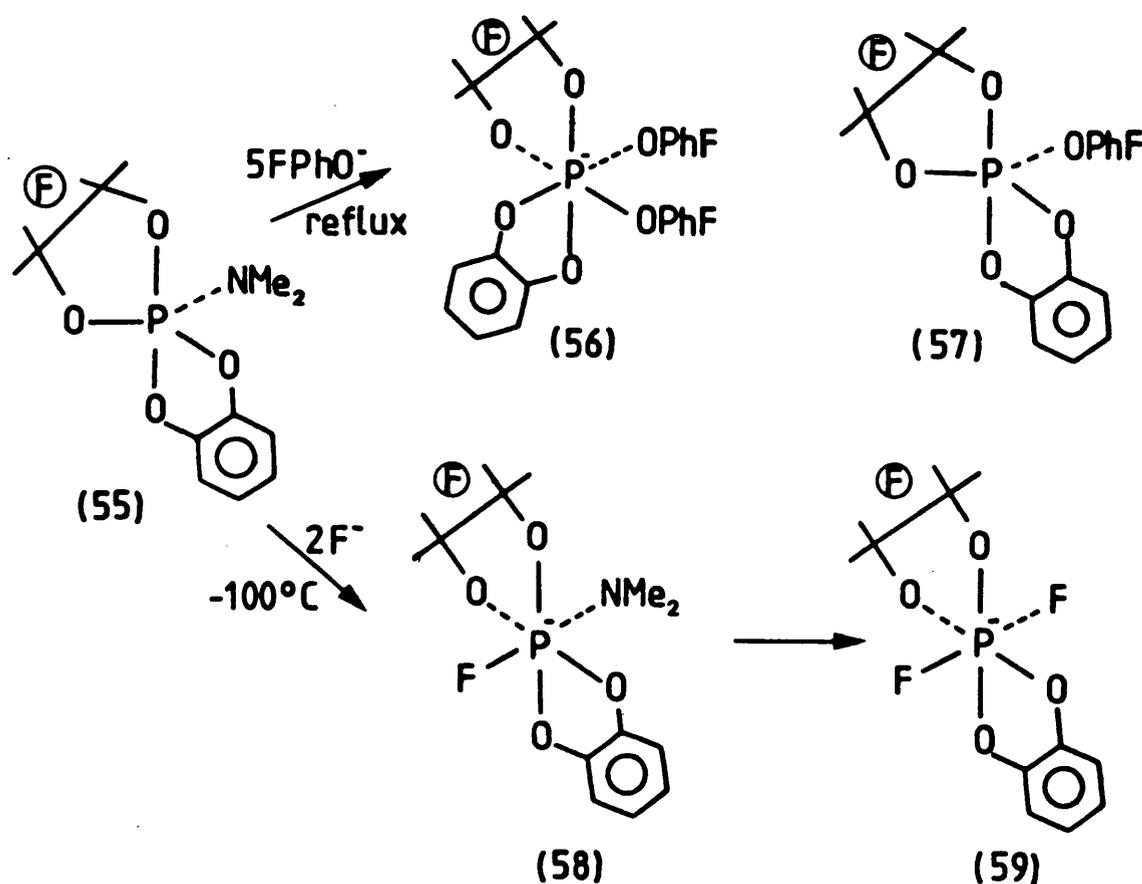
Nucleophilic attack of F^- on phosphoranes of the general formula $P(\text{bid})_2\text{OPhF}$, e.g. 35 and 38, may proceed via species of the general structure 49 and 50, although they have not been observed. The half-lives of mixed unidentate ligand phosphorides, e.g. 48 and 49, and of fluorophosphoranes, e.g. 41 and 50, are probably extremely short under the prevailing conditions.

2.2 Unidentate Ligand: NMe₂

The reaction of spirophosphorane 51, δP -30.7, δF -0.6 ppm, with NaOPhF produced no observable amount of P(6), even after a period of three hours at room temperature. Addition of five equivalents of NaOPhF at -100°C followed by careful warming produced the cis-phosphoride 52, δP -109.9, δF -0.49 (CF₃), -0.75 (CF₃), -60.2 (1F,s) and -61.7 ppm (1F,s).

Treatment of phosphorane 51 with TBAF at -80°C resulted in the formation of trans-anion 53, δP -102.3 (t, $^1J_{PF}$ 766 Hz), δF +32.5 (2F,d, $^1J_{PF}$ 752 Hz) and -0.76 ppm (6F,s). Upon warming this was replaced by cis-anion 54, δP -105.2 (dd, $^1J_{PF}$ 718 and 732 Hz), δF +25.2 (1F,dd, $^1J_{PF}$ 710 and $^2J_{FF}$ 31 Hz),

+14.3 (1F,dd, $^1J_{PF}$ 738 and $^2J_{FF}$ 31 Hz), -0.7 (3F,m, $^5J_{FF}$ 11 Hz) and -1.1 ppm (3F,m, $^5J_{FF}$ 11 Hz). On repeating the reaction with caesium fluoride in THF-MeCN (7:3) the cis-phosphoride 54 was observed only after heating to reflux of the reaction mixture.



No reaction was observed between phosphorane 55 (65), δP -26.6, δF -4.8 (6F) and -5.6 ppm (6F), and NaOPhF even at room temperature. On heating to reflux for thirty seconds with five equivalents of NaOPhF NMR spectral data indicated the formation of cis-phosphoride 56, δP -107.1, δF -5.06, -5.14, -5.66, -5.74 (four CF_3), -59.1 (1F,s) and -61.0 ppm

(1F,s). Upon further heating phosphoride 56 disappeared, leaving phosphorane 55 and a new phosphorane, probably 57, δP -32.9 ppm (66).

Treatment of phosphorane 55 with TBAF at -100°C produced a monofluorophosphoride 58, δP -93.6 (d, $^1J_{PF}$ 708 Hz), δF +47.0 (d, $^1J_{PF}$ 704 Hz) with the CF_3 -signals as a broad absorption from -9.2 to +2.8 ppm. On maintaining this temperature the anion 58 was slowly replaced by the trans-anion 59, δP -99.8 (t, $^1J_{PF}$ 800.0 Hz), δF +26.2 (2F,d, $^1J_{PF}$ 790 Hz) and -3.3 ppm (12F,s). The trans-anion remained after heating to reflux for thirty minutes and after twelve days at room temperature.

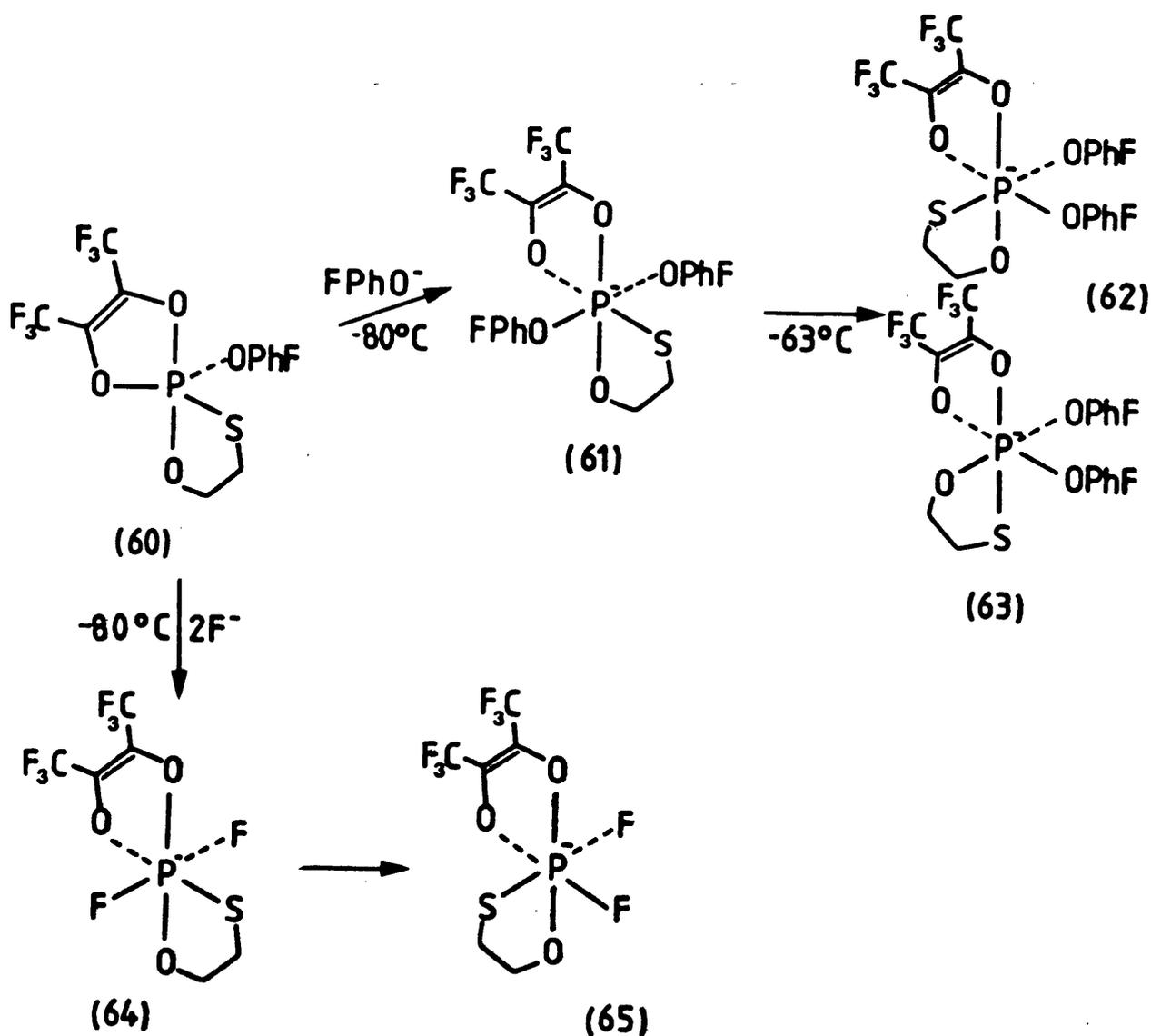
Discussion

The introduction of an NMe_2 -group as the unidentate ligand in bicyclic phosphoranes diminishes the ease of associative nucleophilic substitution. This observation may be ascribed to an inductive effect which results in the phosphorus centre having less Lewis acid character, nitrogen being less electronegative than oxygen and fluorine. Also possible p - d interaction between nitrogen and phosphorus which favours a planar N-configuration (67, 68, 69), can introduce double bond character in the P-N bond (70).

The reaction of FPhO^- with phosphoranes 51 and 52 occurs under conditions such that only the cis-phosphorides can be observed. Decomposition of phosphoride 56 produces eventually phosphorane 57, a species which could well have been formed initially.

The anion 58 is assigned to be of a trans-configuration because of the high frequency ^{19}F and ^{31}P chemical shifts observed (cf. CHAPTER 4.1.2.5 and 4.3.6). Hence in the case of the reactions of TBAF the formation of trans-anions 54 and 58 indicates kinetically controlled reactions, which upon warming can produce the more stable cis-isomers (trans-anion 59 has probably a comparatively long half-life).

2.3 Bidentate Donor Atoms: Oxygen, Sulphur and Nitrogen

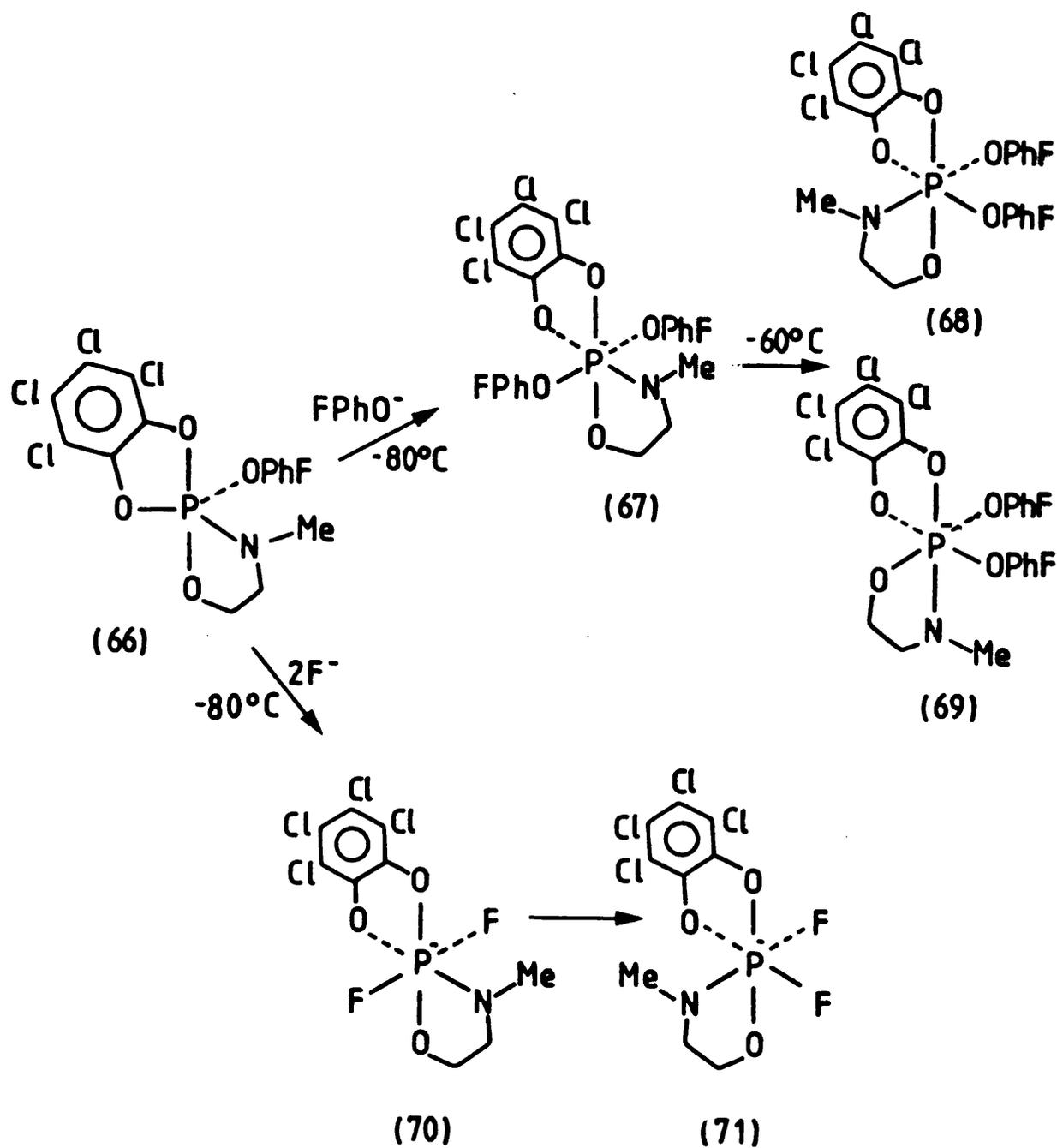


Treatment of phosphorane 60, $\delta P +1.6$, $\delta F -1.43$ (3F), -3.16 (3F) and -54.9 ppm (1F), at -80°C with sodium *p*-fluorophenoxide produced the trans-phosphoride 61, $\delta P -91.8$, $\delta F -0.17$ (6F,s) and -61.7 ppm (2F,s), which upon warming to -60°C was replaced by the cis-phosphoride 62, $\delta P -96.8$, $\delta F +0.61$ (3F,q, $^5J_{\text{FF}}$ 11Hz), -0.64 (3F,q, $^5J_{\text{FF}}$ 11 Hz) and -60.8 ppm (2F,s), and then by cis-anion 63, $\delta P -96.0$, $\delta F +0.13$ (3F,q, $^5J_{\text{FF}}$ 11 Hz), -0.87 (3F,q, $^5J_{\text{FF}}$ 11 Hz) and -60.8 ppm (2F,s). Upon further warming the cis-isomers were present in ratio 1:1.

Repeating the experiment with TBAF produced at -80°C the trans-anion 64, $\delta P -88.1$ (t, $^1J_{\text{PF}}$ 882.5 Hz), $\delta F +60.0$ (2F,d, $^1J_{\text{PF}}$ 870 Hz) and -0.24 ppm (6F,s), which upon warming was replaced by one cis-isomer 65, $\delta P -89.5$ (dd, $^1J_{\text{PF}}$ 864 and 882 Hz), $\delta F +12.2$ (1F,dd, $^1J_{\text{PF}}$ 788 and $^2J_{\text{FF}}$ 48 Hz), $+0.18$ (2CF₃) and -8.81 (1F,dd, $^1J_{\text{PF}}$ 839 and $^2J_{\text{FF}}$ 48 Hz).

Treatment of spirophosphorane 66, $\delta P -38.9$, $\delta F -56.2$ ppm, with NaOPhF at -80°C produced trans-phosphoride 67, $\delta P -102.7$, $\delta F -62.2$ ppm, which upon warming to -60°C was replaced by cis-phosphoride 68, $\delta P -104.3$, $\delta F -60.6$ ppm, and then by cis-phosphoride 69, $\delta P -103.3$, $\delta F -59.9$ (1F) and -61.4 ppm (1F). Eventually the cis-isomers were present in ratio 1:1. At -80°C the P(5)-P(6) equilibrium was 40% on the P(6)-side, while at room temperature the equilibrium was predominantly on the P(5)-side.

Treatment of phosphorane 66 with TBAF at -80°C gave the trans-anion 70, $\delta P -99.4$ (t, $^1J_{\text{PF}}$ 789.0 Hz), $\delta F +20.0$ ppm (d, $^1J_{\text{PF}}$ 775 Hz), which upon warming was replaced by cis-anion



71, δP -100.3 (dd, $^1\text{J}_{\text{PF}}$ 747 and 811 Hz), δF +14.4 (1F, dd, $^1\text{J}_{\text{PF}}$ 775 and $^2\text{J}_{\text{FF}}$ 35 Hz) and 2.81 ppm (1F, dd, $^1\text{J}_{\text{PF}}$ 712 and $^2\text{J}_{\text{FF}}$ 35 Hz). The cis-anion survived heating to reflux for twenty seconds and no other cis-isomers were observed. The P(5)-P(6) equilibrium showed no dependency upon temperature.

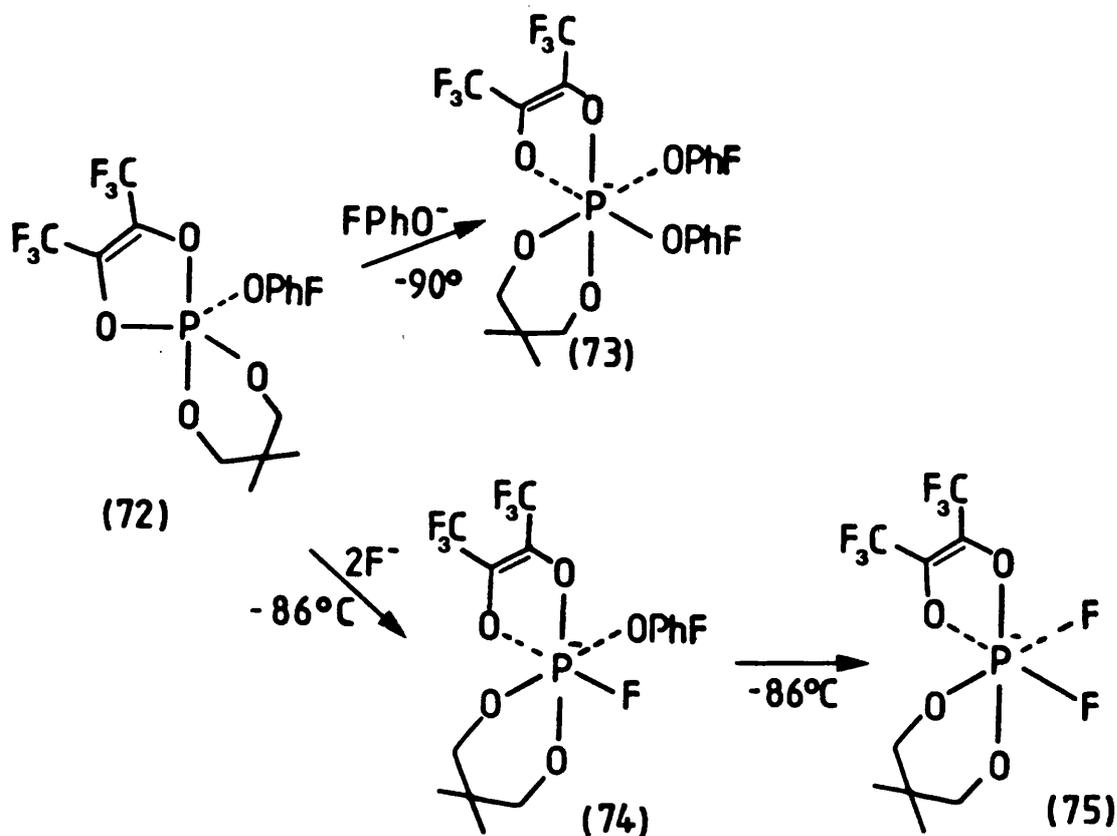
Discussion

The introduction of sulphur or nitrogen as a donor atom of a bidentate ligand in a phosphorane does not alter the reaction sequence so far established, i.e. kinetically controlled trans-attack of the nucleophile, followed by the formation of the thermodynamically more stable cis-phosphoride,

From the observations made it is apparent that one cis-isomer is produced before the formation of the other cis-isomer is observed. An explanation for this can be found in the different apicophilicities of the donor atoms. Although it is reported that oxygen and sulphur have identical apicophilicities (70) the preferential position of a sulphur donor atom (like a nitrogen donor atom) in a spirophosphorane is in the equatorial plane of the TB structure (69). Hence initial cis-attack by a nucleophile Nu will produce a six-co-ordinate phosphorus anion with a co-linear Nu-P-X (X=S or N) configuration; the other cis-isomer will not have such a configuration.

For further information about the formation of cis-phosphorides see CHAPTER 3.1.

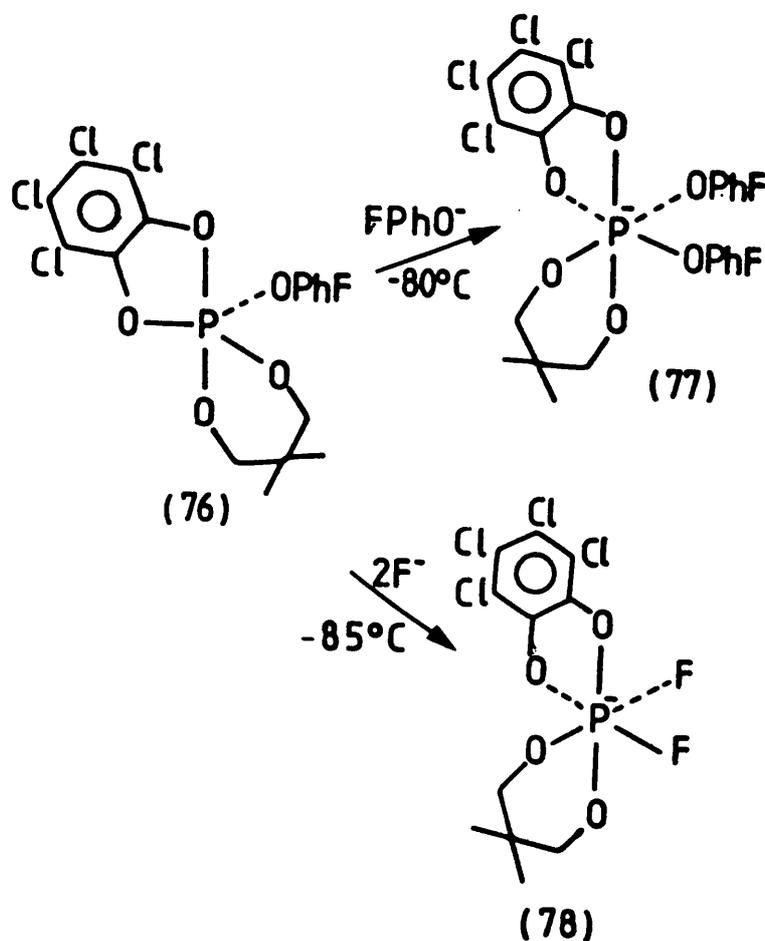
The temperature dependency of the P(5)-P(6) equilibrium in the case of phosphorane 66 with NaOPhF will be discussed in CHAPTER 3.3.

2.4 Increase in Chelate Size

Addition of sodium *p*-fluorophenoxide to phosphorane 72, δP -51.0, δF -1.27 (6F,s) and -55.6 ppm (1F,s), at -90°C produced immediately *cis*-phosphoride 73, δF +0.52 (3F,q, $^5\text{J}_{\text{FF}}$ 10 Hz), -0.69 (3F,q, $^5\text{J}_{\text{FF}}$ 10 Hz), -59.0 (1F,s) and -61.4 ppm (1F,s). The ^{31}P NMR spectrum of the same reaction mixture showed that initially two six-co-ordinate phosphorus species were formed, δP -129.3 and -130.9 ppm (ratio 1:1), which upon warming gave only the isomer at lower frequency.

Treatment of phosphorane 72 with tetrabutylammonium fluoride at -86°C produced a six-co-ordinate phosphorus anion, containing one fluorine unidentate ligand, with the possible structure 74, δP -127.1 (d, $^1\text{J}_{\text{PF}}$ 762 Hz), δF 0.0

(CF₃), -0.45 (CF₃), -7.97 (F,d, $^1J_{PF}$ 791 Hz) and -61.2 ppm (OPhF). On maintaining this temperature the cis-phosphoride 74 was slowly replaced by cis-phosphoride 75, δP -124.6 (dd, $^1J_{PF}$ 728 and 747 Hz), δF +11.7 (F,dd, $^1J_{PF}$ 764 and $^2J_{PF}$ 42 Hz), -0.78 (2CF₃,s) and -8.31 ppm (F,dd, $^1J_{PF}$ 764 and $^2J_{FF}$ 42 Hz).



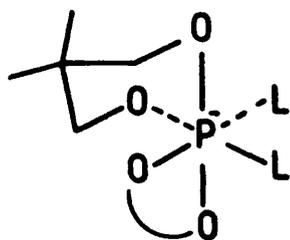
Addition of NaOPhF at -80°C to spirophosphorane 76, δP -50.3, δF -55.2 ppm, produced immediately the six-co-ordinate phosphorus anion 77, δF -59.4 (1F) and -62.0 ppm (1F), of which two isomers were formed with absorptions at δP -125.4 and -127.5 ppm. Upon warming the isomer absorption at higher ^{31}P frequency disappeared, while the ^{19}F -spectrum remained the same.

Treatment of phosphorane 76 with TBAF at -85°C produced a monofluorophosphoride, $\delta\text{P} -121.3$ (d, $^1\text{J}_{\text{PF}}$ 737 Hz), whose structure could not be determined. This phosphoride was replaced by cis-phosphoride 78, $\delta\text{F} +18.5$ (1F, dd, $^1\text{J}_{\text{PF}}$ 757 and $^2\text{J}_{\text{FF}}$ 37 Hz) and -9.37 ppm (1F, dd, $^1\text{J}_{\text{PF}}$ 749 and $^2\text{J}_{\text{FF}}$ 37 Hz) followed by a second cis-isomer, $\delta\text{F} +10.5$ (1F, dd, $^1\text{J}_{\text{PF}}$ 737 and $^2\text{J}_{\text{FF}}$ 37 Hz) and also -9.37 ppm, which after warming to room temperature were present in ratio 1:1. The ^{31}P -spectrum showed P(6)-absorptions of $\delta\text{P} -121.3$ (dd, $^1\text{J}_{\text{PF}}$ 737 and 752 Hz) and -120.9 ppm (dd, $^1\text{J}_{\text{PF}}$ 737 and 771 Hz).

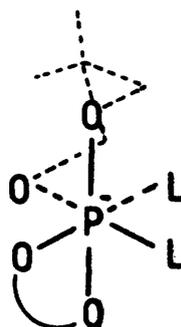
Discussion

From the ^{19}F NMR data it can be deduced that in all cases (FPhO⁻ and F⁻ attack) no trans-phosphorides are observed, but only the more stable cis-phosphorides. It is possible that the steric requirements of a phosphorinane ring inhibit trans-attack or result in the formation of a trans-phosphoride with a very short half-life. Alternatively the 1,3-repulsive and other steric interactions in the phosphorinane ring may be such that they do not enable the p-type lone pairs of the oxygen donor atoms to align themselves properly for app-interaction with the σ^* -orbital of the developing phosphorus-nucleophile bond (71).

Phosphorinane ring containing phosphoranes have the six-membered ring twisted in the unusual boat-form (69, 72). It is possible that upon formation of a six-co-ordinate phosphorus anion the boat-preference is lost and a more chair-like ring is formed (73, 74), which can have different orientations in the six-co-ordinate anion, e.g. 79 and 80.

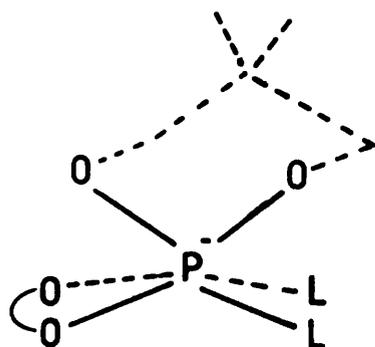


(79)

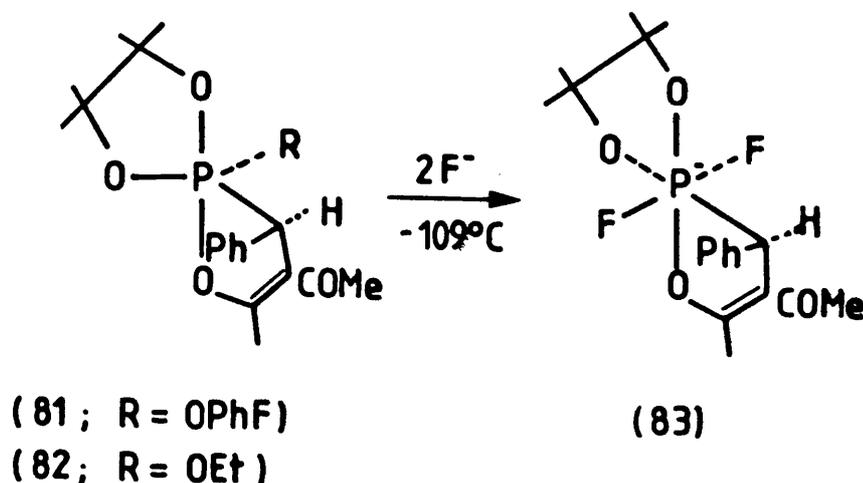


(80)

Due to steric interactions one of these cis-isomers will be more stable and this will be the final product. The conversion can take place via a bond rupture mechanism for a bidentate ligand; an intramolecular rearrangement of only the six-membered ring via a boat-intermediate; or via a trigonal twist mechanism, this involving rotation about $i-C_3(c)$ with (ABbid) being the phosphorinane ring in 25, as shown below.



All these processes are slow on the NMR timescale, the phosphorides containing fluorine as unidentate ligand L having a greater half-life than the FPhO-analogues.

2.5 Increase in Steric Hindrance

On treatment of phosphoranes 81, δP -17.8, δF -56.1 ppm, and 82, δP -15.3 ppm, with one or more equivalents of NaOPhF no change occurred in the ^{19}F - and ^{31}P -NMR spectra.

Treatment of phosphorane 32 with one equivalent of TBAF at $-100^{\circ}C$ produced a small amount of a monofluorine species (probably a trans-phosphoride) absorbing at δF +38.6 ppm (d, $^1J_{PF}$ 763 Hz) which was replaced by trans-phosphoride 83, δP -102.5 (t, $^1J_{PF}$ 800 Hz), δF +31.3 (1F, d, $^1J_{PF}$ 785 Hz) and +26.2 ppm (1F, dd, $^1J_{PF}$ 799 and $^3J_{FH}$ 14 Hz). The trans-phosphoride was also produced when phosphorane 81 was treated with TBAF. No cis-phosphoride could be observed.

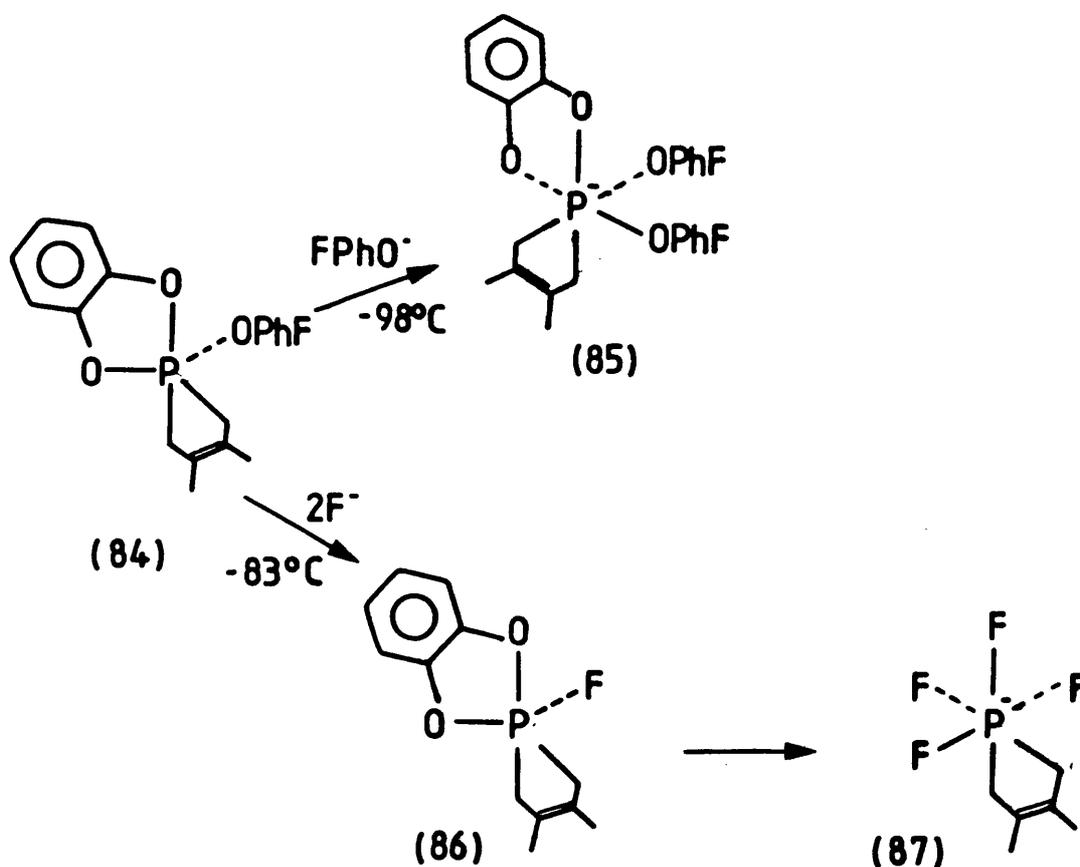
Discussion

The NaOPhF-reaction produces no phosphorides either due to increased steric crowding and/or because of lack of electron-acceptor properties of the bidentate ligands.

The observed six-co-ordinate phosphorus anion lacks the expected value of a coupling between two cis fluorine ligands (30 - 60 Hz) and shows no observable trans-fluorine coupling (75, 76). The lower frequency fluorine is coupled

to the proton of the 1,2-oxaphospholene ring (77). Hence the introduction of a bulky phenyl-group next to the central phosphorus atom still enables the formation of a trans-phosphoride.

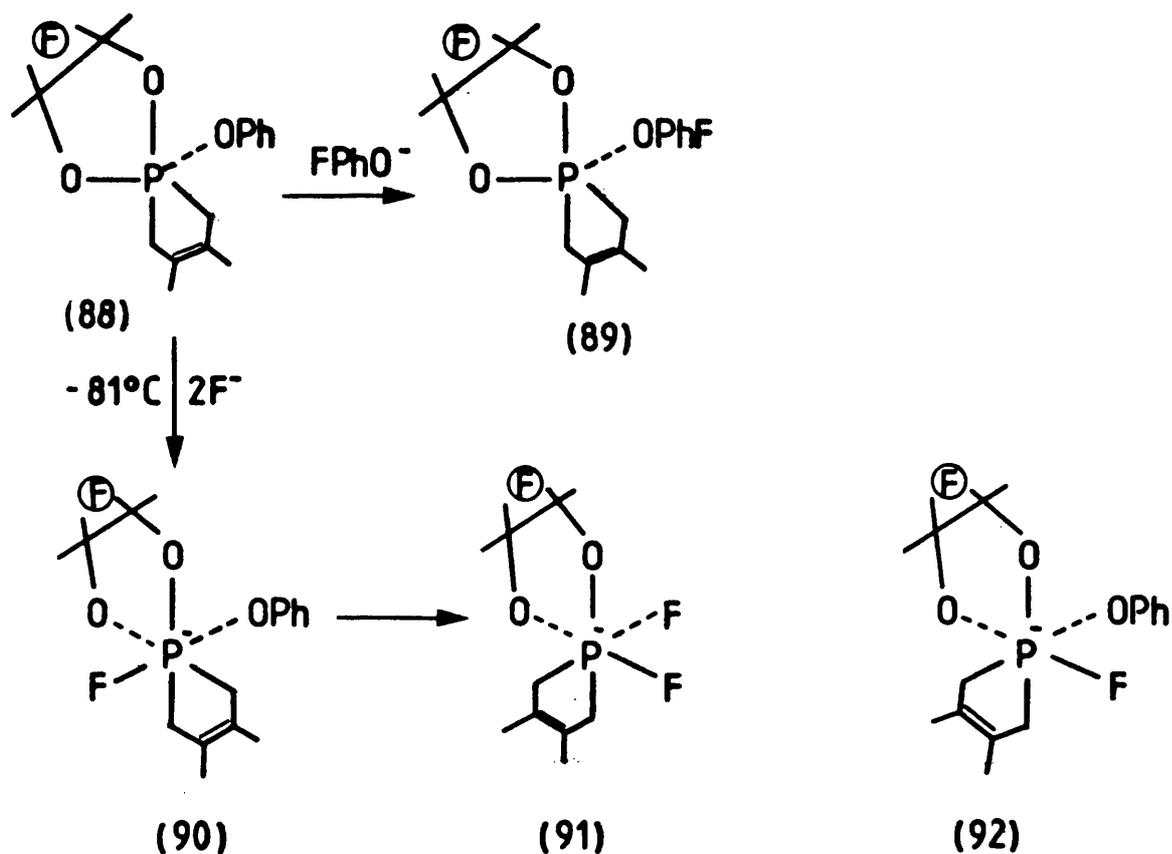
2.6 Bidentate Donor Atoms: Carbon and Oxygen



Treatment of phosphorane 84, $\delta\text{P} +13.3$, $\delta\text{F} -57.5$ ppm, with NaOPhF at -98°C gave immediately cis-phosphoride 85, $\delta\text{P} -100.6$, $\delta\text{F} -60.0$ (1F) and -61.5 ppm (1F). In this case the P(5)-P(6) equilibrium became fast on the NMR timescale on increasing the temperature (cf. CHAPTER 3.3).

Treatment of phosphorane 84 with TBAF at -83°C produced

fluorophosphorane 86, $\delta P +18.8$ (d, $^1J_{PF}$ 791 Hz), $\delta F +37.4$ (d, $^1J_{PF}$ 783 Hz), which underwent dechelation to produce tetrafluorophosphoride 87, $\delta P -109.9$ (quint, $^1J_{PF}$ 754 Hz), $\delta F +16.9$ (2F, dt, $^1J_{PF}$ 753 and $^2J_{FF}$ 37 Hz) and + 15.5 ppm (2F, d, $^1J_{PF}$ 746 Hz).



Treatment of phosphorane 88, $\delta P +19.60$, $\delta F -5.81$ ppm (78), with NaOPhF gave besides phosphorane 88 only the fluoro-substituted phosphorane 89, $\delta P +19.46$, $\delta F -5.61$ (12F, s) and -56.9 ppm (1F, s). No associative products were observed at any one temperature, $-83^\circ C$ to room temperature.

When phosphorane 88 was treated with TBAF at $-81^\circ C$ a monofluorophosphoride 90, $\delta P -90.2$ (d, $^1J_{PF}$ 713 Hz),

$\delta F +35.7$ (F,d, $^1J_{PF}$ 742 Hz) and -2.25 ppm ($4CF_3$,s), was formed which upon warming was replaced by cis-phosphoride 91, $\delta P -88.6$ (dd, $^1J_{PF}$ 771 and 786Hz), $\delta F +27.2$ (2F,d, $^1J_{PF}$ 771 Hz), -3.00 (3F), -3.07 (6F) and -3.14 ppm (3F), with the transient appearance of a cis-phosphoride, possibly 92, $\delta P -94.4$ (d, $^1J_{PF}$ 802 Hz), $\delta F +12.4$ (F,d, $^1J_{PF}$ 777 Hz) and -2.80 ppm ($4CF_3$).

Discussion

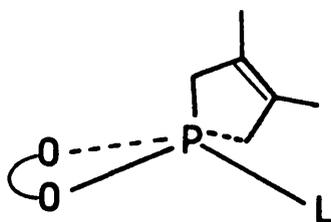
Spirophosphoranes containing a bidentate ligand with two carbon donor atoms are very close to the TP structure (23) with the phospholene ring occupying a basal and an apical position. This is more extreme where fluorine is the unidentate ligand.

Even so cis-attack of $FPhO^-$ on phosphoranes 84 and 88 can be assisted by the greatest number of app lone pairs. In the case of phosphorane 88 the predicted cis-phosphoride is possibly too short-lived because of the lack of electron acceptor characteristics if the cis-bidentate ligands (cf. CHAPTER 2.5 and 2.7).

When phosphorane 84 is treated with TBAF direct substitution takes place to produce a fluorophosphorane with fluorine in a more basal-like position (79, 80). Continued attack of TBAF probably produces the phosphoride $P(\text{but})(\text{phen})F_2^-$, this having a very short half-life possibly due to the presence of the excellent leaving group catechol, loss of which results eventually in the formation of a dechelated phosphoride.

Phosphoride 90 is depicted as the trans-isomer because

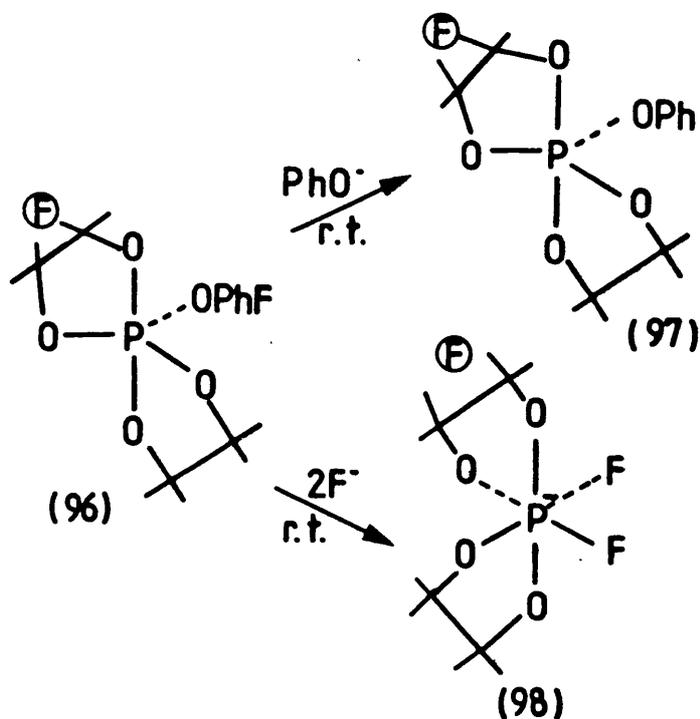
of the high frequency absorptions shown, these being characteristic of trans-phosphorides (cf. CHAPTER 4.1.2.3 and 4.3.6). No conclusive data have been obtained because at -81°C it is slowly converted into the other reaction products. When the first observed product, 90, is formed by F^- attack on phosphorane 88 a cis-phosphoride can be expected (cf. FPhO^- with phosphorane 84) because of the possible assistance of three lone pair centres. Since the substitution of OPh/OPhF in $\text{P}(5)$ can be very rapid (cf. phosphoranes 84/86 and 88/89) it may well be that the first observed product is formed from PhO^- attack on the fluorophosphorane of the general structure 93.



(88; L = OPh)

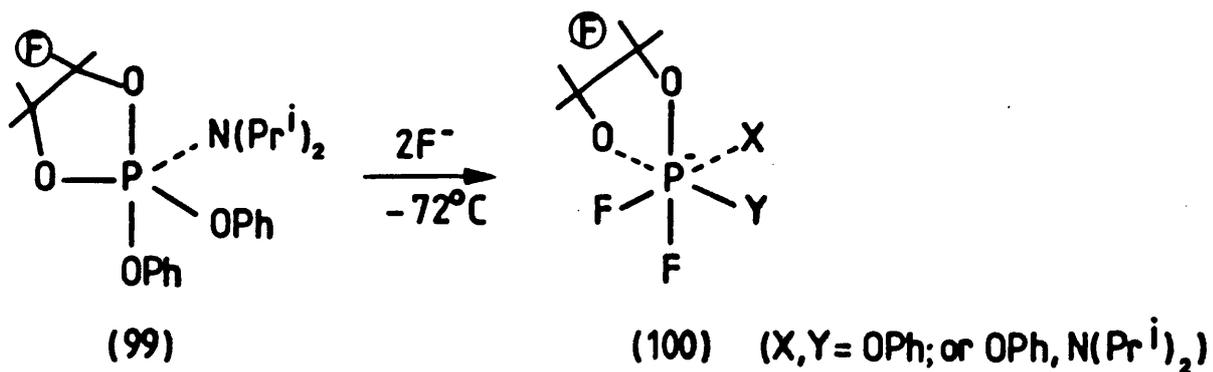
(93; L = F)

trans-Attack is possible with app lone pair assistance of the oxygen donor atoms, the lone pairs interacting more effectively with the lowest σ^* -orbital (cf. co-linear PhO-P-F with PhO-P-C). When thermodynamic conditions prevail the more stable cis-phosphoride is formed, e.g. 92.

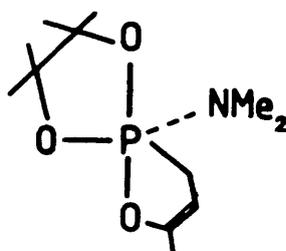


temperature cis-phosphoride 98, $\delta\text{P} -103.9$ (t, $^1\text{J}_{\text{PF}}$ 725.0 Hz), $\delta\text{F} +21.7$ (1F,d, $^1\text{J}_{\text{PF}}$ 723 Hz), $+16.3$ (1F,dd, $^1\text{J}_{\text{PF}}$ 725 and $^2\text{J}_{\text{FF}}$ 28 Hz) and -2.72 ppm (12F,m), was formed.

As previously described, CHAPTER 2.6, the reaction of phosphorane 88, $\text{P}(\text{but})(\text{pfp})\text{OPh}$ with FPhO^- gave phosphorane 89, $\text{P}(\text{but})(\text{pfp})\text{OPhF}$, whilst the reaction with TBAF produced six-co-ordinate phosphorus anions.



Treatment of phosphorane 99, δP -51.0, δF -1.22 (3F), -2.44 (3F) and -5.02 (6F), (105) with NaOPhF at -80°C produced, even after heating to reflux, no apparent reaction. Treatment with TBAF at -72°C produced a cis-phosphoride 100, containing two fluorine unidentate ligands, δP -126.1 (dd, $^1J_{PF}$ 772 and 786 Hz), δF +20.3 (1F,d, $^1J_{PF}$ 758 Hz), +1.9 (1F,dd, $^1J_{PF}$ 781 and $^2J_{FF}$ 36 Hz) and -2.5 ppm (12F,s).



(101)

Treatment of phosphorane 101, δP -14.5, with NaOPhF gave no observable reaction, while treatment with TBAF produced after ten seconds heating to reflux a phosphorane, most likely of the general type P(bid)LL'F, δP -36.9 (d, $^1J_{PF}$ 713 Hz), δF +29.0 ppm (d, $^1J_{PF}$ 714 Hz), with the fluorine atom occupying an apical position (75).

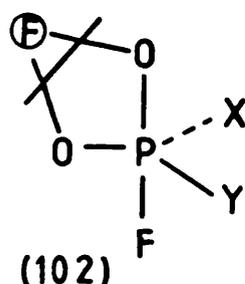
Discussion

The formation of P(6) from the reaction of NaOPhF with P(5) requires a more acidic phosphorane than in the case of TBAF with P(5). The phosphorane has to be able to delocalise the extra negative charge over the ligands. Substitution is possible, as for phosphoranes 88 and 96, but the P(6)-species

involved have an extremely short half-life, probably due to lack of π -acceptor bidentate ligands.

Even so for the formation of $P(\text{bid})_2\text{F}_2^-$ it requires an increase in Lewis acidity of the phosphorus centre, caused by inductive effects (cf. examples 94/95 and 96/98).

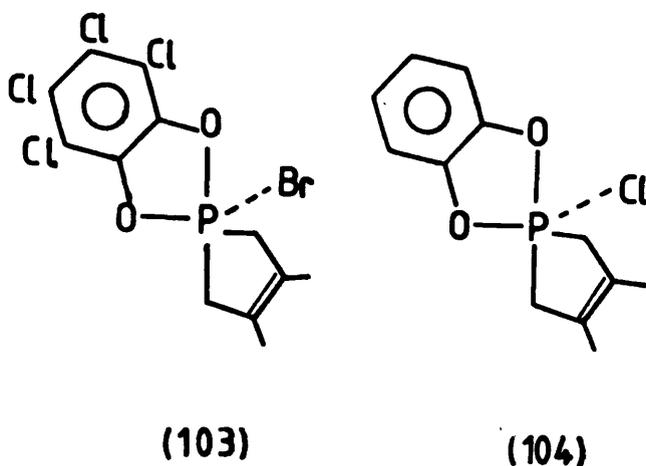
When the formation of phosphoride 100 proceeds via a monofluorophosphorane, the fluorine will occupy an apical position, as in phosphorane 102, because of its greater apicophilicity (54).



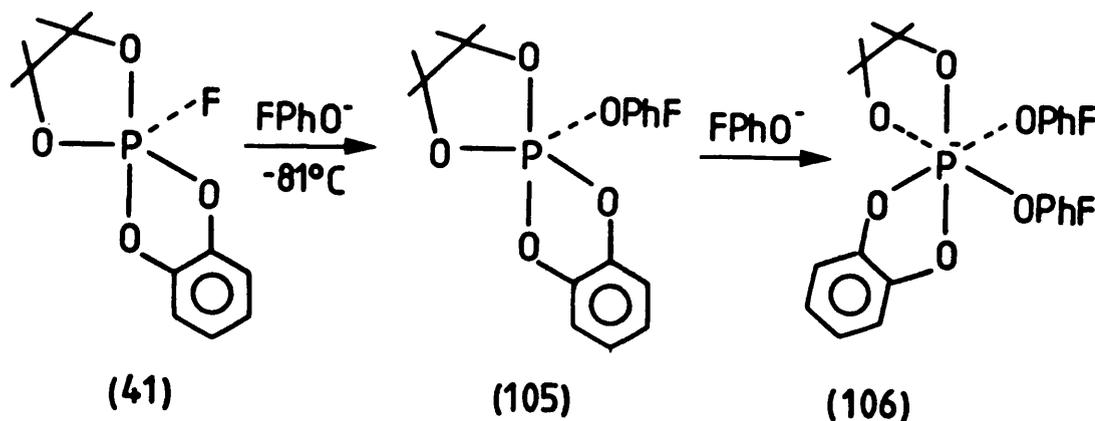
Hence the introduction of a second fluorine ligand will only result in the formation of a cis-phosphoride, assisted by the p -type lone pairs on the donor atoms of the bidentate ligand and any lone pair interaction from X (Y).

2.8 Unidentate Ligand: Halogen

Treatment of phosphorane 103 with two equivalents of caesium fluoride in THF-MeCN (1:1) at -73°C resulted in the formation of a monofluorine species, $\delta\text{F} +32.5$ ppm (d, $^1J_{\text{PF}}$ 829 Hz), this being similar to phosphorane 86, $P(\text{but})(\text{phen})\text{F}$. Upon gentle warming many products were formed and no analysis could be made of the structures.



Treatment of phosphorane 104, $\delta P +21.4$ ppm, with NaOPhF or TBAF produced immediately phosphoranes 94, P(but)(phen)OPhF, and 96, P(but)(phen)F, respectively, which upon further reaction produced similar reaction sequences as described under CHAPTER 2.6.



Addition of NaOPhF at -81°C to phosphorane 41 gave phosphorane 105, $\delta P -37.9$ ppm (81) with transient appearances of cis-phosphorides $\text{P}(\text{phen})(\text{pin})\text{X}_2^-$ (43; X=F, $\delta P -105.5$ ppm; 106; X=OPhF, $\delta P -110.1$ ppm). An additional quantity of NaOPhF produced six-co-ordinate phosphorus anion 106 solely, $\delta F -60.0$ (1F,s) and -61.4 ppm (1F,s).

Treatment of phosphorane 41 with tetrabutylammonium *p*-fluorophenoxide at -80°C produced first trans-phosphoride 42, $\text{P}(\text{phen})(\text{pin})\text{F}_2^-$, $\delta\text{P} -101.9$ ppm (t), which was then replaced by cis-isomer 43, $\delta\text{P} -105.5$ ppm (dd).

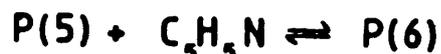
Discussion

From the results obtained it can be deduced that the half-life is very short for a phosphoride of the general formula $\text{P}(\text{bid})(\text{bid}')\text{LL}'^-$, having two different unidentate ligands L and L' of which at least one is halogen. Since halogen groups are good leaving groups nucleophilic attack of Nu^- ($\text{Nu} \neq \text{L}$) on phosphorane $\text{P}(\text{bid})(\text{bid}')\text{L}$ (L=halogen) will produce substitution only and produce $\text{P}(\text{bid})(\text{bid}')\text{Nu}$.

The reaction performed with tetrabutylammonium *p*-fluorophenoxide had possibly *p*fluorophenol present. Hence part of the phosphorane will decompose, releasing F^- which then can attack the original phosphorane, producing the described phosphorides.

2.9 Nucleophile: Pyridine

It has been reported in the literature that addition of pyridine to certain phosphoranes can produce an equilibrium,

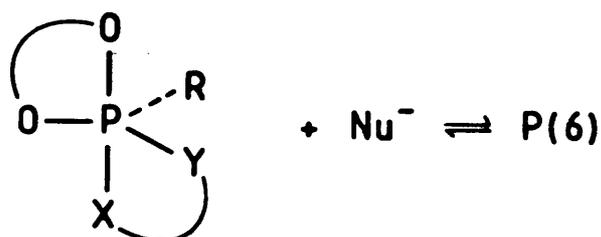


which is either fast or slow on the NMR timescale (37, 70, 82).

Treatment of phosphoranes $\text{P}(\text{chl})(\text{pin})\text{OPhF}$, $\text{P}(\text{Meet})(\text{chl})\text{-OPhF}$ and $\text{P}(\text{eth})(\text{hfb})\text{OPhF}$ with pyridine, either ratio 1:1 or

neat, produced no significant change in the chemical shifts of the respective phosphoranes, nor were characteristic low frequency P(6) chemical shifts observed. The Lewis acidity of these phosphoranes is probably too weak to produce a significant amount of pyridine adduct and stronger bases, e.g. NaOPhF and TBAF, are required in order to produce stable six-co-ordinate phosphorus anions.

2.10 Summary



Substitution reactions at five-co-ordinate phosphorus can take place via six-co-ordinate phosphorus species. The half-life of the phosphorides can be extended by increasing the electron withdrawal effect of the ligands (e.g. pfp > pin; F > OPhF > NMe₂) and introducing ligands with low lying empty orbitals (e.g. phen, chl > pin).

The formation of some six-co-ordinate phosphorus anions can be understood in terms of app interactions of p-type lone pair electrons of donor atoms with the σ^* -orbital of the phosphorus-nucleophile bond. Attack of the nucleophile will take place in such a way that it can be assisted by the greatest number of app lone pair interactions. This

is observed in the kinetically controlled formation of trans-phosphorides (X=O; Y=O,C,S and N) and in direct formation of the thermodynamically more stable cis-phosphoride (X,Y=C).

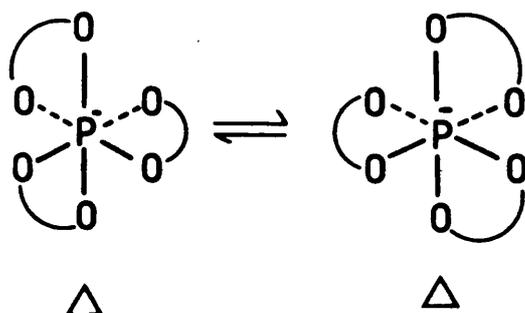
Where a six-membered ring is present the results can be explained when the trans-isomer is very short-lived or when the p-type lone pairs of the donor atoms of this ring are unable to align themselves due to steric requirements of the ring.

Phosphorides containing a six-membered ring or an asymmetric arrangement of donor atoms (e.g. X=O and Y=C, S or N; R \neq Nu) have a short half-life under the reaction conditions.

CHAPTER 3

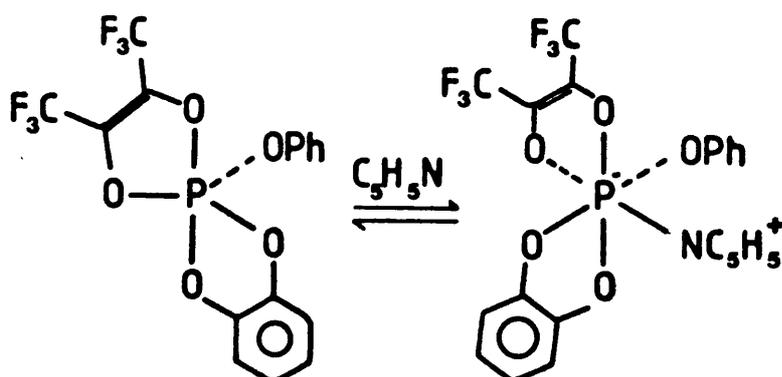
Variable Temperature NMR Observation of P(6)

Intramolecular cis-trans isomerisation in octahedral species is well known in transition metal chemistry (36, 52). Previous work (53, 70) on the racemisation of optically active tris(bidentate) phosphorus anions has shown that the



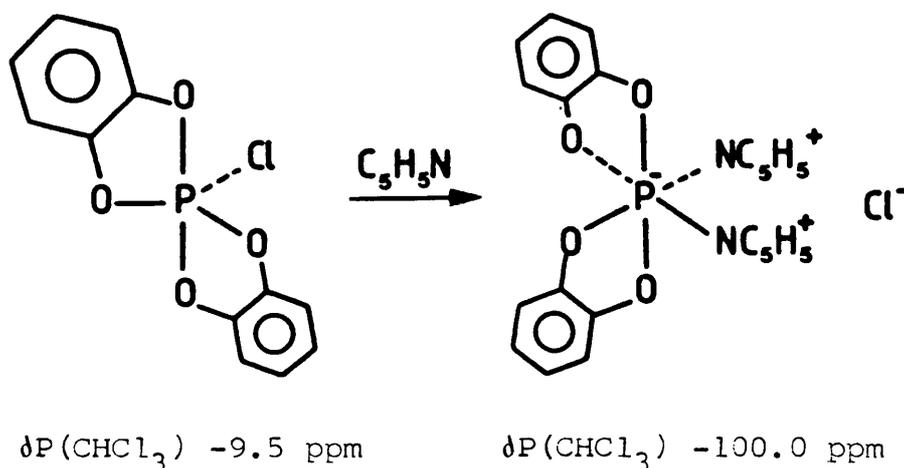
isomerisation processes are acid-catalysed and involve P-O bond fission. Permutational isomerisation in six-coordinate phosphorus species may take place via trigonal prismatic intermediates which are derived from octahedral structures with possibly the smallest energy requirement (41).

An equilibrium can be established between certain spiro-phosphoranes and pyridine, which can either be fast (70, 82), e.g.



mol equivalent pyridine	$\delta P(CH_2Cl_2)/$ ppm
0	-31.5
1.0	-60.0
2.0	-69.0
neat	-82.0

or slow on the NMR timescale (37), e.g.



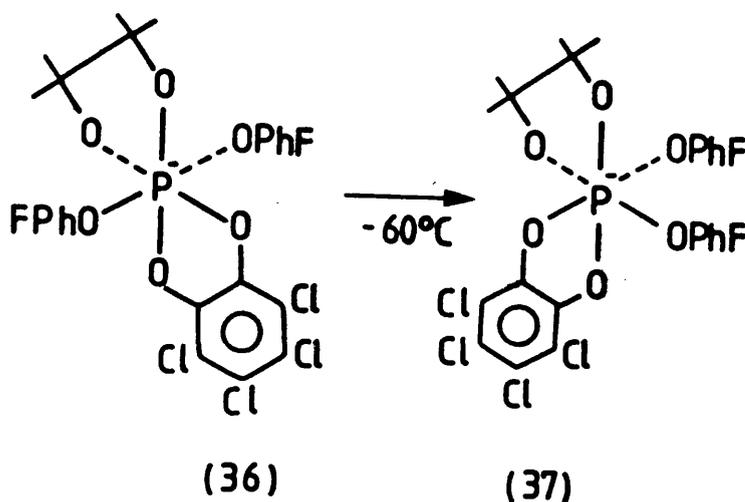
In this chapter the six-co-ordinate phosphorus species under consideration are prepared by treatment of the appropriate phosphorane with sodium *p*-fluorophenoxide or tetrabutylammonium fluoride, as described in CHAPTER 2 and 5.3. For reaction temperatures above 70°C THF is replaced by *N,N*-dimethylformamide, DMF, as the solvent used.

The different processes described are proposed to account for observations made from variable temperature fluorine and phosphorus NMR spectra.

3.1 cis-trans Isomerisation

All trans-isomers were initially generated from the phosphoranes and FPhO^- (F^-) below -80°C (cf. CHAPTER 2.1, 2.3 and 5.3).

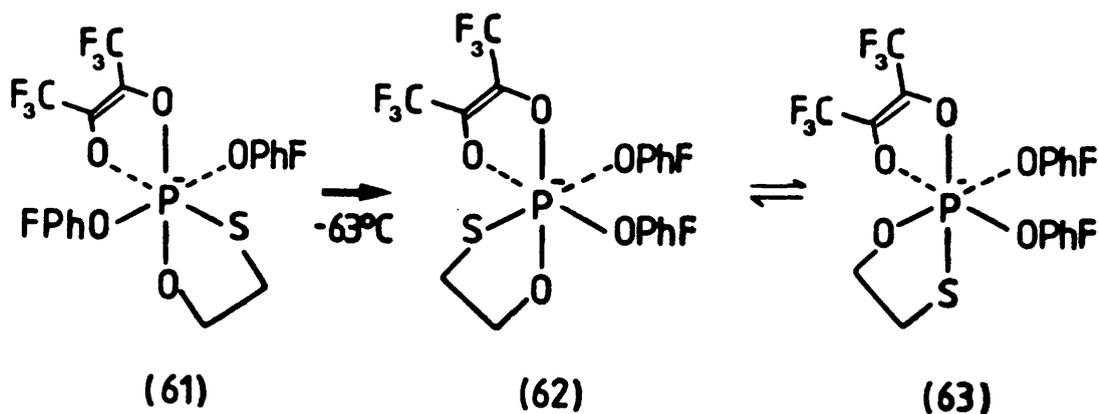
Table 1



$\delta\text{P} -103.7$ ($w_{\frac{1}{2}}$ 6.3 Hz)

$\delta\text{P} -107.1$ ($w_{\frac{1}{2}}$ 6.6 Hz; dd,

${}^6J_{\text{PF}}$ 1.7 and 3.7 Hz)



$\delta\text{P} -91.2$

$\delta\text{P} -96.8$

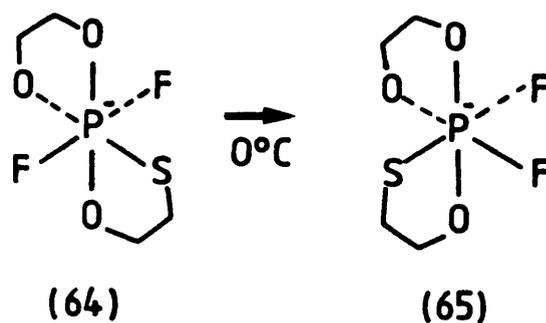
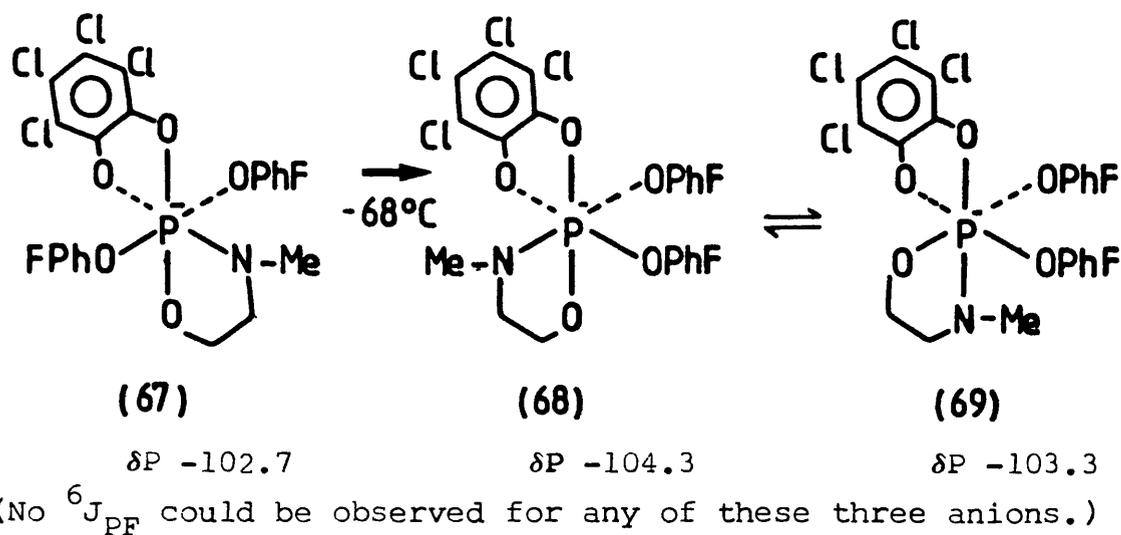
$\delta\text{P} -96.0$ (t)

($w_{\frac{1}{2}}$ 13 Hz)

($w_{\frac{1}{2}}$ 11 Hz;

t, ${}^6J_{\text{PF}}$ 4.0 Hz)

Table 1 (cont'd)



(Only careful warming to around $0^\circ C$ produced the cis-isomer 65 from the trans-isomer 64.)

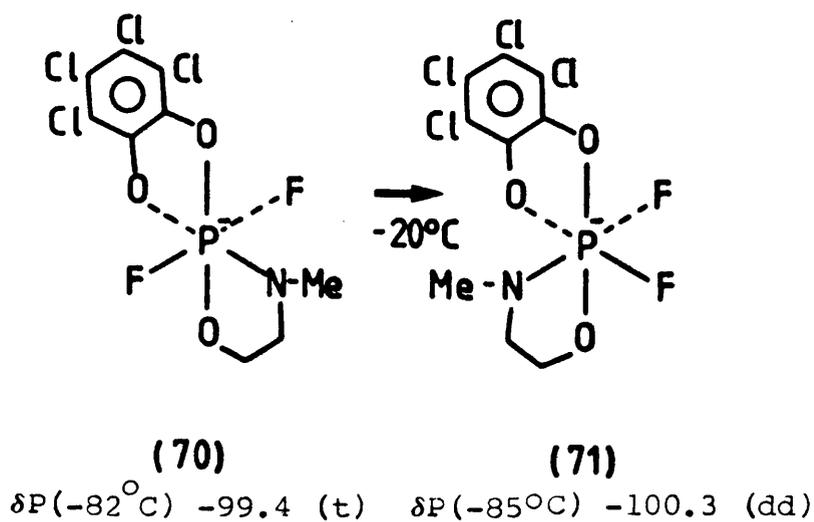
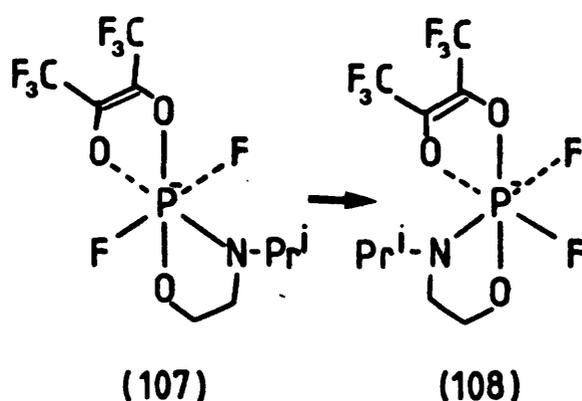


Table 1 (cont'd)

(Careful warming of the reaction mixture containing trans-anion 70, to below room temperature, produced cis-anion 71.)



$\delta P(-82^{\circ}\text{C}) -99.4$ (t) $\delta P(-82^{\circ}\text{C}) -104.3$ (dd)

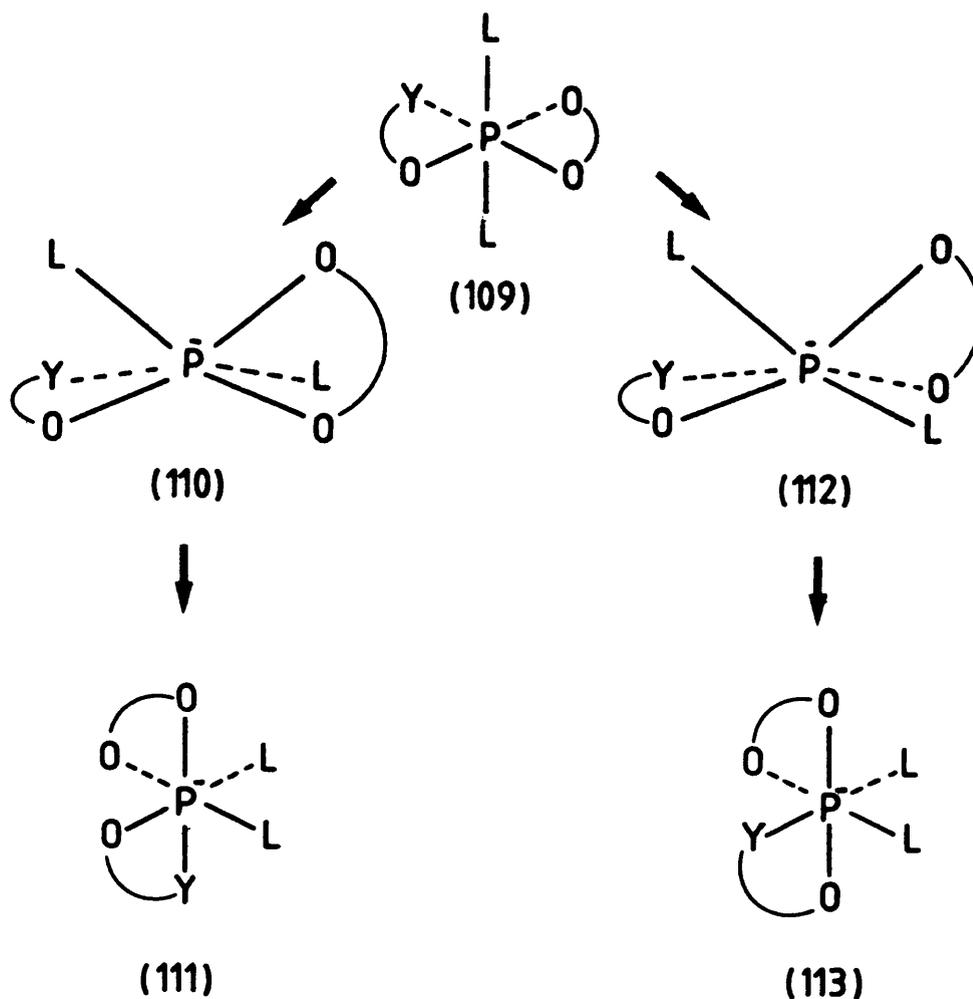
(Warming the mixture containing trans-isomer 107 to room temperature produced the cis-isomer 108.)

Discussion

The regular intramolecular rearrangement of the trans-isomer of a species of the general type 109, via the trigonal prismatic intermediates 110 and 112 (cf. CHAPTER 1.5.2.2, Rotation about $i\text{-C}_3(a)$), will produce two cis-isomers 111 and 113 where $Y \neq O$.

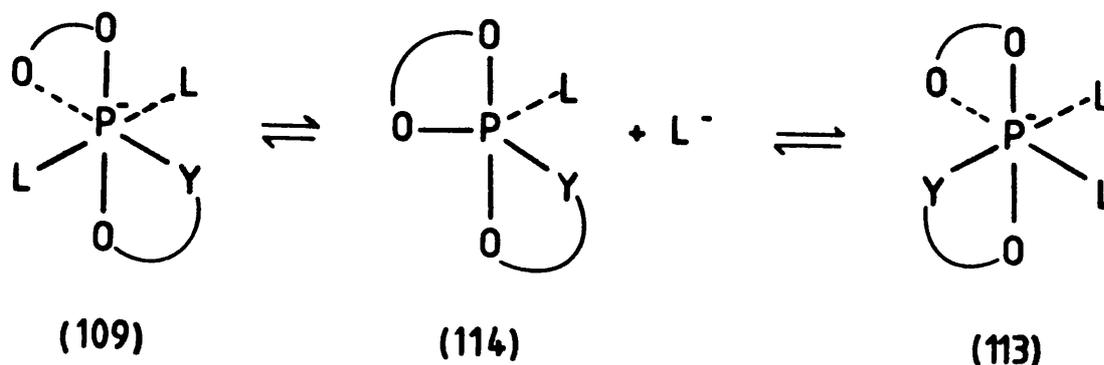
The energy difference between trigonal prisms is mainly attributed to the ring strain of the bidentate ligands present (36, 38, 52). Since the trigonal prismatic intermediates 110 and 112 contain identical bidentate and unidentate ligands in an almost similar configuration, the difference in energy barriers to the two possible twists is expected to be minimal or zero. Formation of the two cis-isomers 111 and 113 in about equal amounts is expected

to occur simultaneously.



From the data given in Table 1 (cf. CHAPTER 2.3) it can be deduced that a trans-isomer is converted initially into only one cis-isomer ($L=F, OPhF$; $Y=S, NMe, NPr^i$) and when thermodynamic conditions prevail an equal amount of the second cis-isomer is formed (cf. phosphorides 62/63 and 68/69). In the case ($L=F$) the conversion of trans- into cis-isomer takes place at a higher temperature than where ($L=OPhF$), this indicating a higher energy barrier to isomerisation. That only one cis-phosphoride is observed where ($L=F$) is probably a consequence of the longer half-life of fluorophosphorides.

Hence the conversion of trans- into cis-phosphorides in the species discussed can not proceed via a regular intramolecular rearrangement of the ligands but may possibly proceed via an irregular mechanism, this involving either the bidentate or unidentate ligands.



Dissociation of a bidentate ligand is not expected to take place under the given conditions (70, 82; cf. CHAPTER 3.2), while dissociation of unidentate ligand L would produce spirophosphorane 114 with (Y=S, NMe, NPrⁱ) in an equatorial position (54, 69; cf. CHAPTER 2.3). Renewed cis-attack by L⁻ would then initially produce one cis-isomer with the co-linear L-P-Y configuration. Under thermodynamic conditions the other cis-isomer with two co-linear L-P-O configurations may be formed.

The described dissociative mechanism also accounts for the absence of ${}^6J_{PF}$ coupling in trans-phosphorides 36 and 61 while ${}^6J_{PF}$ coupling is present in the cis-isomers. The $w_{\frac{1}{2}}$ of the respective absorptions are comparable, indicating a possible life-time broadening of the trans-phosphoride signal due to the PF coupling.

3.2 Intramolecular Isomerisation in P(6)

Table 2

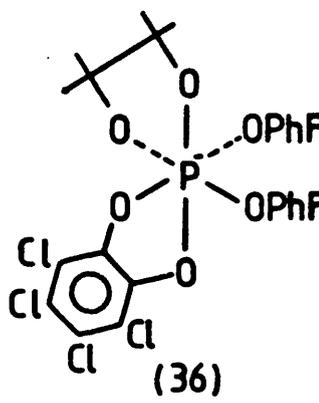
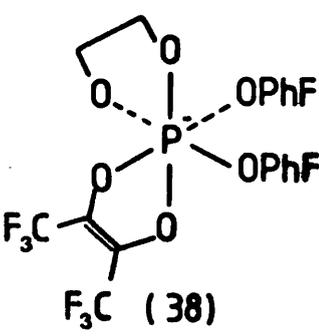
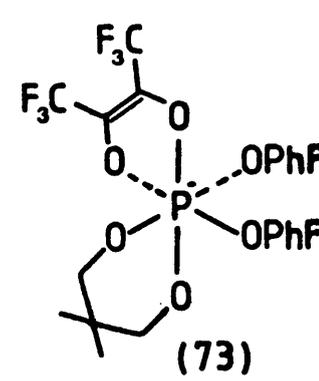
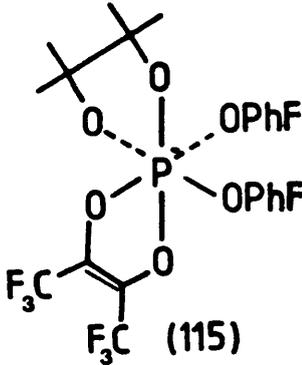
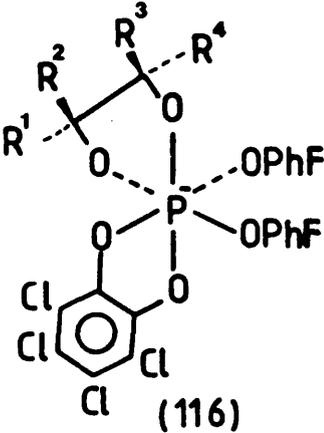
Phosphoride	Observations
 <p>(36)</p>	<p>Me: $T_c < -41^\circ\text{C}$, $\Delta G^x < 11 \text{ kcalmol}^{-1}$.</p> <p>OPhF: $T_c 53^\circ\text{C}$, $\Delta\nu 113 \text{ Hz}$, $\Delta G^x 15.5 \text{ kcalmol}^{-1}$.</p> <p>Retention of PF coupling at 60°C (t, ${}^6J_{\text{PF}}$ 2.9 Hz.)</p>
 <p>(38)</p>	<p>CF_3: $T_c 80^\circ\text{C}$, $\Delta\nu 73 \text{ Hz}$, $\Delta G^x 17.2 \text{ kcalmol}^{-1}$.</p> <p>OPhF: $T_c 50^\circ\text{C}$, $\Delta\nu 21 \text{ Hz}$, $\Delta G^x 16.5 \text{ kcalmol}^{-1}$.</p> <p>Separate signals were present for the trifluoromethyl groups of phosphorane 37 and anion 38 at 151°C ($\Delta\nu 73 \text{ Hz}$).</p>
 <p>(73)</p>	<p>CF_3: $T_c 3^\circ\text{C}$, $\Delta\nu 111 \text{ Hz}$, $\Delta G^x 13.1 \text{ kcalmol}^{-1}$.</p> <p>OPhF: $T_c > 66^\circ\text{C}$, $\Delta\nu 216 \text{ Hz}$, $\Delta G^x > 15.8 \text{ kcalmol}^{-1}$.</p> <p>The trifluoromethyl groups of phosphorane 72 and anion 73 had separate signals at 100°C ($\Delta\nu 51 \text{ Hz}$).</p>

Table 2 (cont'd)

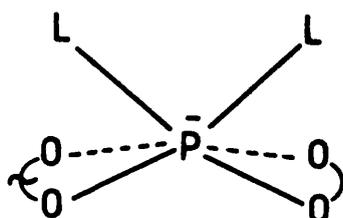
Phosphoride	Observations
 <p>(115)</p>	<p>CF₃: T_c -77°C, Δν 30 Hz, ΔG^x 9.7 kcalmol⁻¹. OPPhF: T_c 34°C, Δν 145 Hz, ΔG^x 14.5 kcalmol⁻¹.</p> <p>The trifluoromethyl groups of phosphorane P(hfb)(pin)OPhF and anion 115 showed separate signals at 72°C (Δν 95 Hz).</p>
 <p>(116)</p>	<p>OPPhF: T_c 58.5°C, Δν 67 Hz, ΔG^x 16.2 kcalmol⁻¹.</p> <p>The ³¹P NMR spectrum at 48°C showed all possible isomers present with ⁶J_{P,F} 3.8 Hz.</p> <p>(R^{1,2,3,4} = H, H, H, Me)</p>

Discussion

For the phosphorides in Table 2 both the retention of PF couplings, and the presence of separate ¹⁹F NMR signals for trifluoromethyl groups of phosphorane and phosphoride at a given temperature, show that the dissociation of phosphoride to give a phosphorane is slow on the NMR timescale compared with the equilibration processes involving the ligands of P(6). Intramolecular isomerisation with different energy barriers to the different trigonal twists is consistent

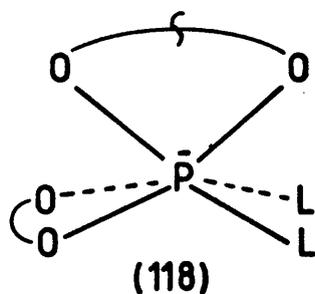
with the data obtained.

Rotation about the $i-C_3$ (a) axis via the trigonal prismatic intermediate 117 introduces equivalency in the bidentate ligands of phosphorides 36, 73 and 115, leaving the unidentate ligands ($L=OPhF$) non-equivalent.

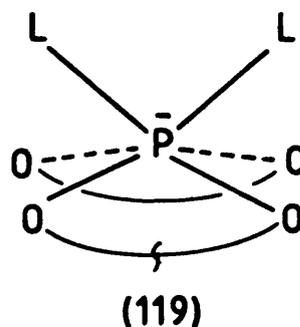


(117)

The unidentate ligands may become equivalent via rotation about any of the three remaining $i-C_3$ axes, producing the trigonal prismatic intermediates 118 or 119.



(118)



(119)

In anion 38 it may be that the barrier to the formation of intermediate 118 (i.e. rotation about $i-C_3$ (b) or $i-C_3$ (c)) is lower in energy than the barrier to formation of intermediate 117.

A combination of trigonal twists will produce equilibration of all four possible isomers in the case of anion 116.

Table 3

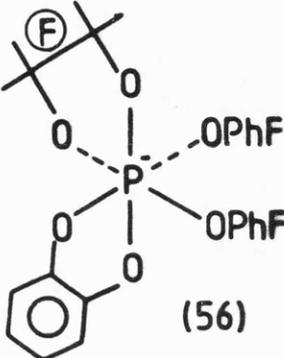
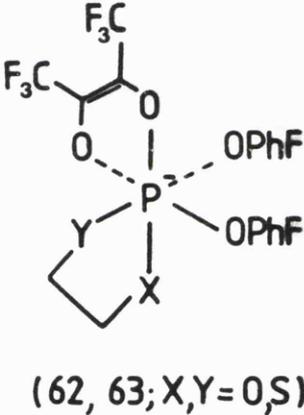
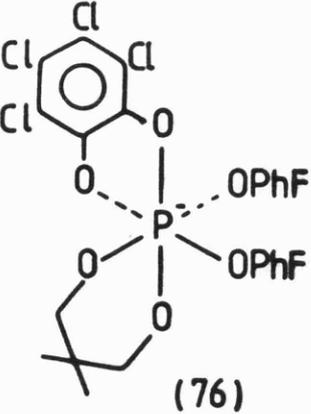
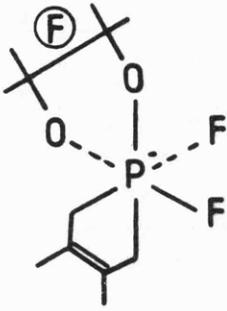
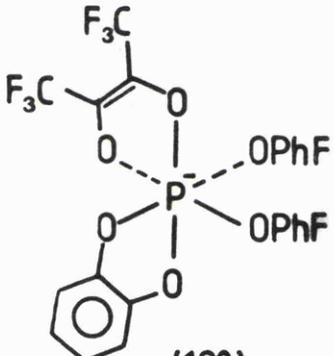
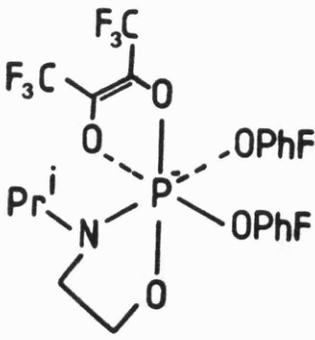
Phosphoride	Observations
 <p>(56)</p>	<p>CF_3: T_C 70°C, $\Delta\nu$ 7 Hz, ΔG^X $13.3 \text{ kcalmol}^{-1}$. OPhF: T_C $> 70^\circ\text{C}$, $\Delta\nu$ 163 Hz, ΔG^X $> 16.1 \text{ kcalmol}^{-1}$.</p> <p>At 70°C the four different signals of the trifluoromethyl groups had collapsed to two separate signals ($\Delta\nu$ 35 Hz, ΔG^X $> 17.2 \text{ kcalmol}^{-1}$).</p>
 <p>(62, 63; X, Y = O, S)</p>	<p>CF_3: T_C $> 51^\circ\text{C}$, $\Delta\nu$ 100 Hz, ΔG^X $> 15.5 \text{ kcalmol}^{-1}$. $\delta P(62, 63)$: $\Delta\nu$ 20.5 Hz, T_C $> 27^\circ\text{C}$, ΔG^X $> 15.3 \text{ kcalmol}^{-1}$.</p> <p>At 51°C rapid decomposition took place.</p>
 <p>(76)</p>	<p>OPhF: T_C $> 31^\circ\text{C}$, $\Delta\nu$ 143 Hz, ΔG^X $> 16.3 \text{ kcalmol}^{-1}$.</p> <p>Above 31°C rapid decomposition occurred (cf. phosphoride 73).</p>

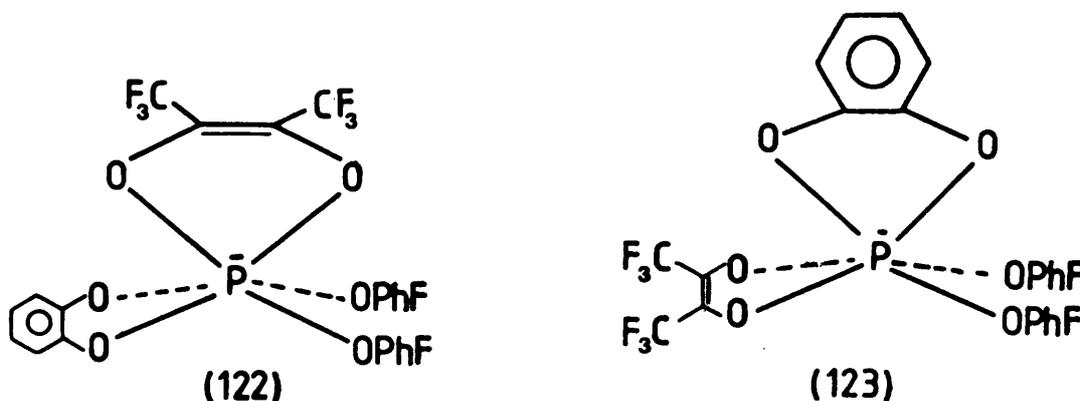
Table 3 (cont'd)

Phosphoride	Observations
 <p data-bbox="391 789 459 825">(92)</p>	<p data-bbox="580 449 1428 591">CF_3: T_C 63°C, $\Delta\nu$ 14 Hz, ΔG^X 17.4 kcalmol$^{-1}$. Collapse of three signals, present in ratio 1:2:1, to one signal.</p> <p data-bbox="580 637 1428 802">The two unidentate ligands show identical chemical shifts between -80 and 43°C, with retention of PF coupling ($^1J_{PF}$ 771 Hz).</p>
 <p data-bbox="379 1299 459 1333">(120)</p>	<p data-bbox="580 920 1428 1000">CF_3: T_C $> 159^\circ\text{C}$, $\Delta\nu$ 67 Hz, ΔG^X > 21.3 kcalmol$^{-1}$.</p> <p data-bbox="580 1034 1428 1136">OPhF: equivalent between -92 and 159°C. δP -109.0 ppm (t, $^6J_{PF}$ 4.1 Hz).</p> <p data-bbox="580 1181 1428 1401">Phosphoride 120 and anion PPhO^- show separate signals at 159°C ($\Delta\nu$ 242 Hz), while the CF_3 signals became a singlet at -92°C.</p>
 <p data-bbox="309 1866 395 1900">(121)</p>	<p data-bbox="580 1442 1428 1499">CF_3: T_C -63°C, $\Delta\nu$ 25 Hz, ΔG^X 10.5 kcalmol$^{-1}$.</p> <p data-bbox="580 1510 1428 1589">OPhF: T_C $> -42^\circ\text{C}$, $\Delta\nu$ 100 Hz, ΔG^X > 10.9 kcalmol$^{-1}$.</p> <p data-bbox="580 1635 1428 1930">Due to interference from ^{19}F absorptions of decomposition products and the temperature dependence of the P(5)-P(6) equilibrium no clear observations could be made above -42°C.</p>

Discussion

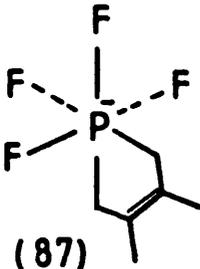
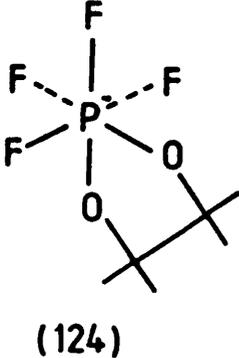
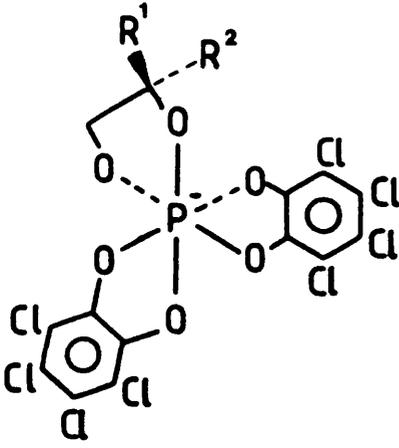
For none of the anions described in Table 3 has the nature of the observed processes been established, i.e. irregular or regular mechanism. Different energy barriers to the eight possible twists or to bond breaking processes may account for the data obtained.

The appearance of one single resonance for different ligand groups can either be caused by processes which are rapid on the NMR timescale or because the chemical shifts are coincident (e.g. phosphoride 92). In phosphoride 120 the energy barrier to the twist leading to trigonal prismatic intermediate 122 may be low while the energy barrier to intermediate 123 is high ($\Delta G^{\ddagger} > 21.3 \text{ kcal mol}^{-1}$).



Phosphorides 87 and 124, cf. Table 4, were produced in the reactions of tetrabutylammonium fluoride with phosphoranes 84 and 41 respectively; while phosphoride 125 was produced in the reaction involving sodium *p*-fluorophenoxide and P(chl)(Meet)OPhF.

Table 4

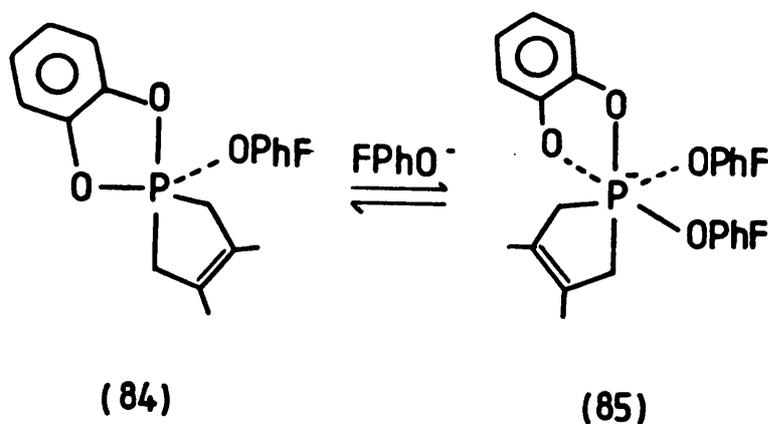
Phosphoride	Observations
 <p>(87)</p>	<p>F: T_c -10°C, $\Delta\nu$ 104 Hz, ΔG^x 12 kcalmol$^{-1}$.</p> <p>Retention of PF coupling at 40°C in ^{31}P signal (quint, $^1J_{\text{PF}}$ 754 Hz).</p>
 <p>(124)</p>	<p>F: T_c 58°C, $\Delta\nu$ 64 Hz, ΔG^x 16.1 kcalmol$^{-1}$ (loss of triplet fine structure due to $^2J_{\text{FF}}$).</p> <p>δP -125.4 ppm (tt, $^1J_{\text{PF}}$ 684, 723 Hz).</p>
 <p>(125; $R^1, R^2 = \text{H, Me}$)</p>	<p>δP -78.85 and -79.15 ppm (ratio 1:1).</p> <p>$\Delta\nu(\text{DMF})$ 2.9 Hz, T_c 152°C, ΔG^x 23.6 kcalmol$^{-1}$.</p>

Discussion

The intramolecular nature of the isomerisation in phosphoride 87 is shown by the retention of the PF coupling at 40°C. The isomerisation process in phosphoride 124 may be either regular or irregular, although comparison with phosphoride 87 favours a regular mechanism.

The isomerisation barrier of the trischelate phosphorus anions 125 is comparable with values reported in the literature (53, 70) for cases which involve an acid-catalysed irregular mechanism.

3.3 Mobile P(5)-P(6) Equilibria

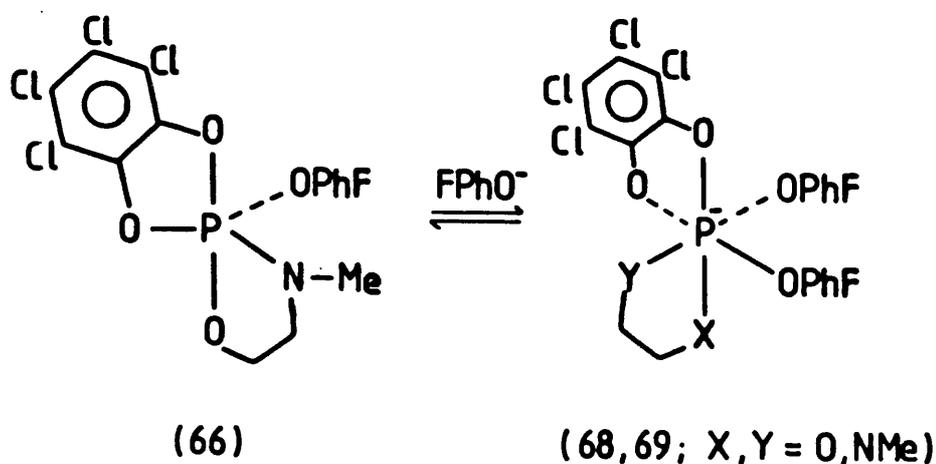


Treatment of spirophosphorane 84, δF -57.2 ppm, with one equivalent of sodium *p*-fluorophenoxide^{*}, δF -66.8 ppm, at -93°C produced immediately *cis*-phosphoride 85, δF -60.0 (1F) and -61.5 ppm (1F). At -60°C the phosphoride ¹⁹F absorptions disappeared while those of the phosphorane and NaOPhF ($\Delta\nu$ 920 Hz) broadened and coalesced reversibly at 0°C to a broad signal, δF -62.2 ppm.

The equilibrium mixture showed separate ³¹P absorptions

* Observation of radicals, cf. CHAPTER 5.3 NaOPhF.

at -80°C for the phosphorane and phosphoride ($\Delta\nu$ 2740 Hz), both broadening at -60°C with subsequent disappearance at about -50°C . A new signal appeared at -30°C , δP $-0,80$ ppm. The ^{19}F and ^{31}P NMR observations were both reversible processes.

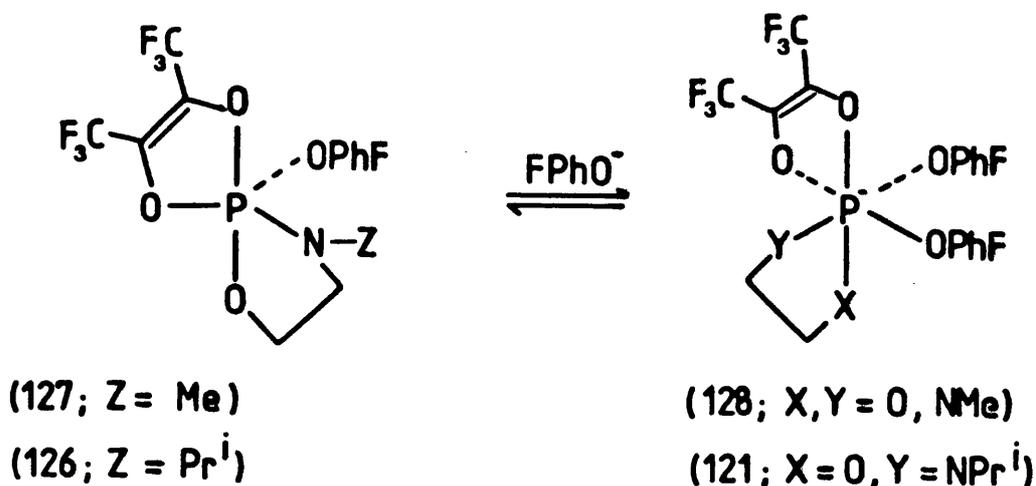


Treatment of spirophosphorane 66 with one equivalent of sodium *p*-fluorophenoxide produced 33%* conversion to the phosphorides 68, 69 at -31°C . Repetition of the reaction with two equivalents of NaOPhF produced 100% P(6) formation at -36°C . Upon increasing the temperature the amount of phosphoride slowly diminished (-18°C : 80% P(6); $+2^{\circ}\text{C}$: 25% P(6)). The ^{31}P and ^{19}F absorptions of the species involved maintained their respective chemical shifts with change in temperature

On treatment of phosphorane 127 with one equivalent of sodium *p*-fluorophenoxide the equilibrium was established

* ^{31}P NMR signal intensity, with the sum of P(5) and P(6) intensities to be 100%.

and at -85°C only 7% phosphoride was formed.



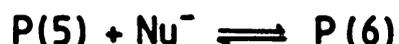
In the case where three equivalents of NaOPhF were used 81% phosphoride formation was observed at -85°C . Upon increasing the temperature to -25 and $+27^{\circ}\text{C}$ the amount of phosphoride diminished to 48% and 23% respectively, while the phosphorane intensity increased. The species involved showed distinct absorptions in the ^{31}P and ^{19}F NMR spectra, maintaining their chemical shifts within experimental error, on changing the temperature.

In the case of phosphorane 126 twenty equivalents of sodium *p*-fluorophenoxide were used in order to produce 17% of phosphoride 121 at -86°C . At room temperature no NMR signals due to phosphoride 121 could be observed. The chemical shifts of phosphorane and phosphoride remained constant at various temperatures between -86 and -41°C

Discussion

Of all P(5)-P(6) equilibria discussed in this work the equilibrium between phosphorane 84 and phosphoride 95 is the

only example where the equilibrium becomes rapid on the NMR timescale on increasing the temperature. The decreased Lewis acidity of the phosphorane due to the two carbon donor atoms may be contributing to this effect.



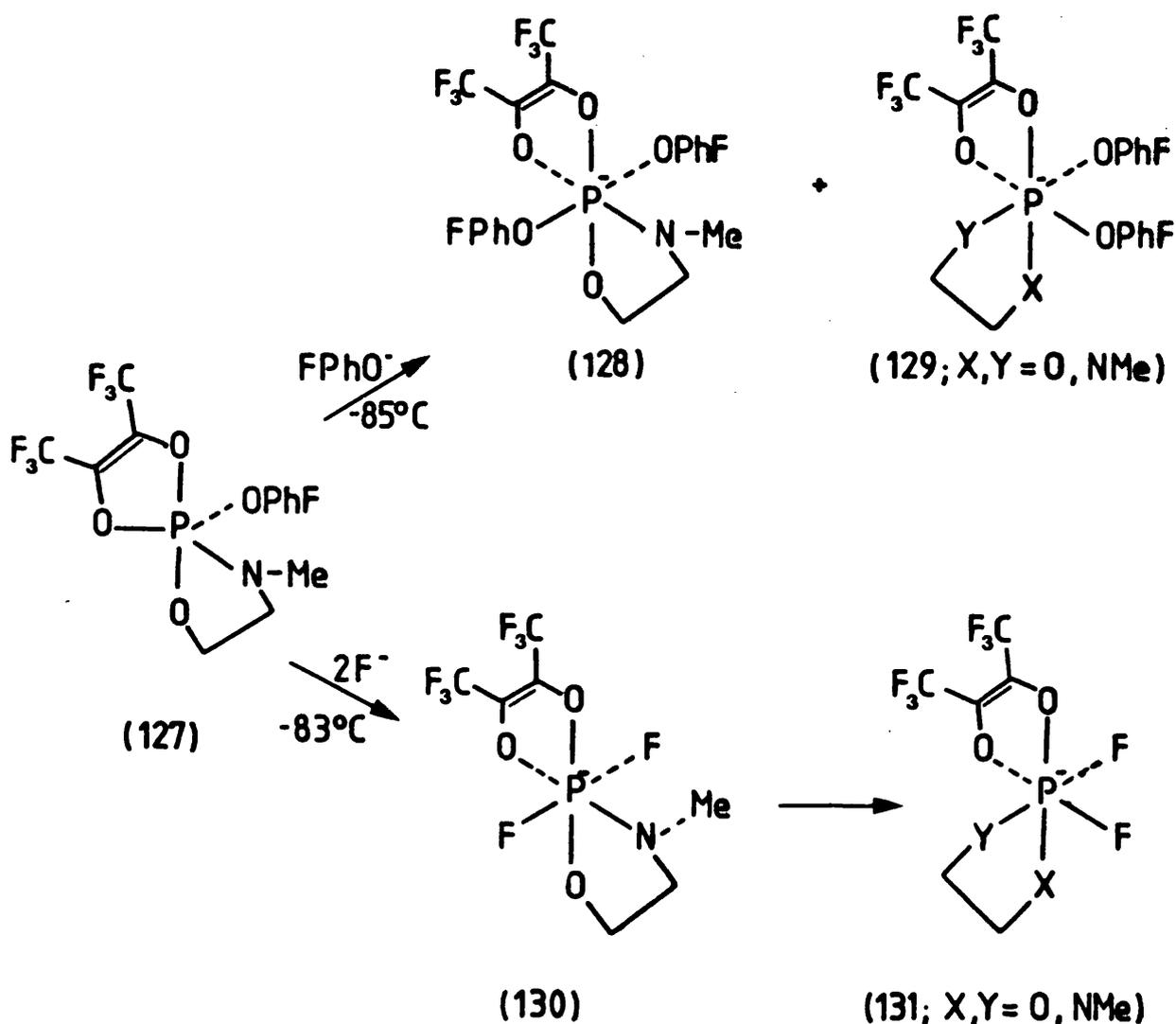
For phosphoranes containing a 1,3,2-oxazaphospholane ring the P(5)-P(6) equilibria are slow on the NMR timescale, although at higher temperatures the equilibria shift to the phosphorane side, this possibly caused by the increased importance of the entropy factor.

An increase in bulkiness of the exocyclic group attached to the nitrogen donor atom (isopropyl vs. methyl) shortens the half-life of the phosphoride, especially where larger unidentate ligands are present (cf. initial trans-formation of phosphoride 107 vs. cis-formation of phosphoride 121).

3.4 Bidentate N-Me Flip

Treatment of spirophosphorane 127, δP -40.1, δF -1.28 (3F,q, $^5J_{FF}$ 10 Hz), -2.87 (3F,q, $^5J_{FF}$ 10 Hz) and -55.6 ppm (1F), with three equivalents of sodium p-fluorophenoxide at -85°C (cf. CHAPTER 3.3) produced in total five phosphoride species. The transient appearance of δP -99.6, δF -0.06 (CF₃,s) and -62.3 ppm (rPhO) may be attributed to the trans-isomer 128, while two isomers 129, δP -103.3 and -105.3 ppm, are formed before two other phosphorides, δP -109.5 and -110.5 ppm. The isomer absorbing at δP -103.3 was initially the major absorption and was eventually replaced by the three isomers at

lower frequency, present in ratio 1:1:2 respectively. At -73°C the three absorptions collapsed reversibly to one signal, $\delta\text{P} -109.7$ ppm. The ^{19}F NMR absorptions of the cis-isomers appeared at $\delta\text{F} -1.35$ (6F,s), -59.8 , -61.0 and -61.9 ppm (total 2F).



On addition of TBAF to phosphorane **127** at -83°C the trans-phosphoride **130**, $\delta\text{P} -108.5$ (t, $^1\text{J}_{\text{PF}}$ 820 Hz), $\delta\text{F} +27.2$ (1F,d, $^1\text{J}_{\text{PF}}$ 811 Hz), $+10.7$ (1F,d, $^1\text{J}_{\text{PF}}$ 825 Hz) and -0.50 ppm (2CF_3 ,s) was produced. The ^{19}F NMR signals due to the

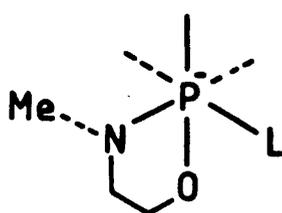
unidentate ligands coalesced reversibly at -57°C ($\Delta\nu$ 1545 Hz, ΔG^{\times} 9.0 kcalmol $^{-1}$) to δF +18.8 ppm, while the triplet structure of ^{31}P signal was retained at -33°C .

Upon warming the reaction mixture to room temperature cis-isomers were formed. Initially at δF +9.1 (dd, $^1J_{\text{PF}}$ 811 Hz and $^2J_{\text{FF}}$ 54 Hz) and +3.7 ppm (dd, $^1J_{\text{PF}}$ 806, $^2J_{\text{FF}}$ 54 Hz); these followed by δF +18.2 (dd, $^1J_{\text{PF}}$ 780, $^2J_{\text{FF}}$ 54 Hz), which were eventually present in ratio 1:2:1 respectively. The signals due to the trifluoromethyl groups, δF +0.74 (q, $^5J_{\text{FF}}$ 9 Hz), -0.33, -0.95 and -1.55 ppm (q, $^5J_{\text{FF}}$ 9 Hz), were equal in intensity and coalesced reversibly at -39°C ($\Delta\nu$ 94 Hz, ΔG^{\times} 11.1 kcalmol $^{-1}$) and -48°C ($\Delta\nu$ 67 Hz, ΔG^{\times} 10.3 kcalmol $^{-1}$) to -0.28 (CF $_3$, q, $^5J_{\text{FF}}$ 11 Hz) and -1.25 ppm (CF $_3$, q, $^5J_{\text{FF}}$ 11 Hz). Two distinct CF $_3$ signals remained at 40°C . Other possible ^{19}F absorptions due to unidentate fluoro ligands could well have been present in the CF $_3$ -region of the NMR spectrum, but were obscured by signals due to CF $_3$ -groups.

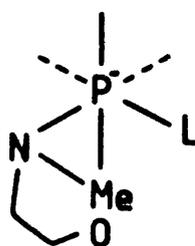
The ^{31}P NMR spectrum showed that trans-isomer 130 was initially replaced by one cis-isomer 131, δP -107.6 ppm (dd, $^1J_{\text{PF}}$ 780 and 304 Hz), this followed by two more cis-isomers, δP -110.4 (dd, $^1J_{\text{PF}}$ 804 and 813 Hz) and -112.8 ppm (dd, $^1J_{\text{PF}}$ 782 and 303 Hz). All three cis-isomers were eventually present in ratio 1:1:2 respectively at -83°C , while at -63°C the two lower frequency absorptions collapsed to δP -111.2 ppm (dd). At 36°C the ^{31}P NMR spectrum showed δP -107.3 (dd) and -110.3 ppm (dd) in ratio 1:3 respectively.

Discussion

The formation of more than three phosphoride isomers can be accounted for if the phosphoride structure becomes rigid on the NMR timescale, with the N-methyl group either trans, 132, or cis, 133, to unidentate ligand L.



(132)



(133)

This rigidity of the N-methyl group may then be lost (Methyl Flip) on increasing the temperature through P-N bond rotation and/or pyramidal nitrogen inversion processes (cf. (86), Goldwhite et al.).

If the nitrogen retains a planar configuration, as in phosphoranes (67, 83), the oxazaphospholane ring will be twisted due to repulsive interactions between P-ligand bonds and the p-type lone pair of nitrogen. As a result of this the nitrogen lone pair will be directed between two neighbouring P-ligand bonds, forcing the methyl group into a fixed position, cis or trans (40). On increasing the temperature the barrier to P-N bond rotation will be overcome (84) and the Methyl Flip become fast on the NMR timescale.

It is also possible that due to the extra negative charge in the six-co-ordinate phosphorus anion there will be less p-d interaction between the nitrogen lone pair and

the d-orbitals of phosphorus (85, 86). This combined with increased repulsive interactions from neighbouring P-ligand bonds and the nitrogen lone pair may result in an sp_3 -type configuration of nitrogen, with two possible orientations of the methyl group, i.e. trans or cis. On increasing the temperature the barrier to the inversion at nitrogen, probably occurring via an identical transition state as for the P-N bond rotation described above, will be overcome and the Methyl Flip become operational.

The presence of the Methyl Flip can clearly be seen in trans-phosphoride 130, in which case the two different unidentate fluoro ligands become equivalent on the NMR timescale on increasing the temperature. The intramolecular nature of the isomerisation is shown by retention of PF coupling at -33°C in the ^{31}P NMR spectrum ($t, {}^1J_{\text{PF}}$ 818 Hz).

3.5 Summary

trans-cis Isomerisation of some phosphorides proceeds via a dissociative mechanism involving a unidentate ligand, while some of the thermodynamically more stable cis-isomers show isomerisation processes which have an intramolecular character, proceeding via trigonal prismatic intermediates.

The introduction of a nitrogen donor atom into a bidentate ligand disfavours the phosphoride formation and may introduce a possible rigidity at the nitrogen centre.

CHAPTER 4

 ^{19}F and ^{31}P Nuclear Magnetic Resonance Spectroscopy4.1 ^{19}F NMR Spectroscopy4.1.1 Introduction

^{19}F NMR Spectroscopy is an attractive tool for the study of kinetics and stereochemistry because of the large range of chemical shifts experienced by the fluorine nuclei.

The shielding constant, σ_{F} , consists of a diamagnetic term, σ^{d} , and a paramagnetic term, σ^{p} , (87):

$$\sigma_{\text{F}} = \sigma^{\text{d}} + \sigma^{\text{p}}$$

The diamagnetic term depends only on the electron distribution in the electronic ground state. The paramagnetic term depends also on the excited states and it is the main factor in the determination of the chemical shift.

The paramagnetic shielding is caused by the interaction of the lone pair electrons, n , of the fluorine atom with the antibonding, σ^* , orbital of the X-F bond (X=another atom). When the X-F bond is highly covalent (e.g. X=F) the electronic excitation energy, ΔE , is low, resulting in a strong $n \rightarrow \sigma^*$ interaction (88). Due to this large paramagnetic shielding F_2 has a negative screening relative to the bare nucleus.

In the case of the spherical F^- ion there is no paramagnetic term and the nucleus is shielded purely through the diamagnetic term.

^{19}F Chemical shifts cover a range of 1000 ppm, including the two extremes given above. Increase in covalent character of the X-F bond will lower the diamagnetic shielding and increase the paramagnetic shielding. The overall result is a deshielding effect since σ^{d} and σ^{p} have opposing signs.

The diamagnetic shielding does not change much from one species to another (88). In the change from F_2 to HF (a difference in chemical shift of about 625 ppm) it is less than 10% (89). For the chemical shifts under consideration in this work presented here (range of 70 ppm) it will be about 1%.

4.1.2 ^{19}F P-F Shielding Constants

4.1.2.1 General

The diamagnetic term of the experimental chemical shift, δF , has to be eliminated in order to establish the paramagnetic term. Because of the small changes in σ^{d} the chemical shift of fluorine atoms will be derived mainly from the paramagnetic term. Hence experimental values, δF , of different octahedral fluorine species may be compared in order to remove the diamagnetic shielding term (90).

Since the value of σ^{p} of SF_6 has been determined as $-(575 \pm 66)$ ppm, other σ^{p} values can be derived (90). In the case of the hexafluorophosphate anion, PF_6^- :

$$\delta(\text{PF}_6^-) - \delta(\text{SF}_6) \approx \sigma_{\text{PF}_6}^{\text{p}} - \sigma_{\text{SF}_6}^{\text{p}}$$

$\delta(\text{PF}_6^-) - \delta(\text{SF}_6)$ has a value of 127 ppm (91),

resulting in a paramagnetic shielding constant of PF_6^- , σ^{P} -448 ppm.

The paramagnetic term, σ^{P} , can be considered as being made up of a ground state term, $\sigma_{\text{G}}^{\text{P}}$, and a term resulting from contributions of the excited wave functions, $\sigma_{\text{EX}}^{\text{P}}$, (90):

$$\sigma^{\text{P}} = \sigma_{\text{G}}^{\text{P}} + \sigma_{\text{EX}}^{\text{P}}$$

$\sigma_{\text{G}}^{\text{P}}$ and $\sigma_{\text{EX}}^{\text{P}}$ are a function of the inverse of the ground state energy and the excitation energy, ΔE , respectively. In the case of SF_6 32% of the paramagnetic shielding constant is a ground state contribution. This ground state contribution increases in heavier species as the charge cloud around the central atom becomes more spherical.

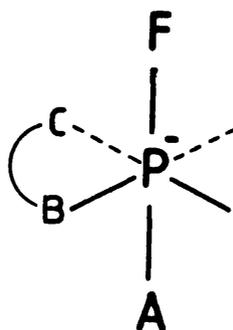
4.1.2.2 Method of Compilation

The experimental ^{19}F NMR chemical shifts of the phosphorides have been converted into paramagnetic shielding constants, using the method shown above for PF_6^- . The resulting shielding constants, σ^{P} , have been compiled using the following considerations.

- I The atom, A, opposite the P-F bond is linked to the central phosphorus atom using the same hypervalent orbital (93, 95). The characteristics of A influence the P-F bond and therefore the ground state term of the paramagnetic shielding constant of the fluorine nucleus. Hence shielding constants of similar arrangements (e.g. co-linear F-P-F, F-P-O)

have been grouped together.

- II Lone pairs on the heteroatoms, B and C, which are antiperiplanar to the P-F bond interact with the σ^* -orbital of the P-F bond and therefore have an influence on the excited term of the paramagnetic shielding constant (92). Shielding constants of fluorine atoms which have an identical cis-arrangement of the atoms B and C are grouped together. In trans-phosphorides two bidentate ligands have to be considered, while in cis-phosphorides only one.



4.1.2.3 trans-Phosphorides

Table 5

co-linear	(bid)(bid')	A	σ^P /ppm
F-P-N	(pfp)(phen)	NMe ₂	-502
F-P-O	(but)(pfp)	OPh	-490
	(pent)(pin)	OEt	-493 (a)
F-P-F	(chl)(pin)	F	-488
	(hfb)(pin)	F	-488
	(pent)(pin)	F	-486

Table 5 (cont'd)

co-linear	(bid)(bid')	A	σ^P /ppm
F-P-F	(phen)(pin)	F	-486 (a)
	(pfp)(phen)	F	-481
	(eth)(hfb)	F	-477
F-P-F	(hfb)(Set)	F	-515
	(hfb)(Net)	F	-473 (b)
	(hfb)(Npr)	F	-482
	(chl)(Net)	F	-475

(a) corrected -5 ppm due to ring current effect from neighbouring phenyl group;

(b) below -57°C : -482 and -465 ppm, due to slowing down of the Me-flip (cf. CHAPTER 3.4);

Comparing similar P(6) of table 5 it can be deduced that the less electronegative the trans-ligand (F > O > N) the larger the paramagnetic shielding. This may be caused by 2nd order hybridisation: the less electronegative trans-atom will require more s-character in its bonding to the central atom, hence forcing the P-F bond to have more p-character, with a lower σ^* -orbital and a greater paramagnetic shielding.

Replacing an oxygen donor atom with carbon, (but), sulphur, (Set), or nitrogen, (Net) and (Npr), will influence the ground state as well as the excited wave functions. A comparison between the shielding constants is difficult to make.

4.1.2.4 cis-Phosphorides

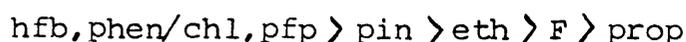
Table 6

co-linear	B,C	A	other ligands	σ^P /ppm
F-P-O	(pfp)	(pin)	F	-477 (a)
		(OPh)	(b)	-475 (a)
F-P-O	(hfb)	(eth)	F	-476
		(eth)	(OPhF)	-478
		(pin)	F	-480
F-P-O	(pin)	(chl)	F	-467
		(hfb)	F	-467
		(pfp)	F	-472
		(phen)	F	-471
F-P-O	(eth)	(hfb)	F	-458
		(hfb)	(OPhF)	-460
F-P-O	(phen)	(pin)	F	-476
	(chl)	(pin)	F	-478
F-P-O	(prop)	(chl)	F	-445
		(hfb)	F	-446
		(hfb)	(OPhF)	-447
F-P-O	F,F	(pin)	F	-456
		(eth)	F	-454
		(pfp)	F	-457
F-P-O	(but)	(pfp)	F	-482
		(pfp)	(OPh)	-467
F-P-O	(Set)	(hfb)	F	-446

(a) identified because ^{19}F signal showed broadening due to neighbouring CF_3 -groups;

(b) trans-ligand is either phenoxy- or di-isopropylamino-group;

Keeping the same co-linear F-P-O and identical B,C in the cis-position the paramagnetic shielding constants can be put in groups which vary only 2-4 ppm within each group (with the exception of the (but) bidentate ligand). The ligands can be arranged according to increased paramagnetic screening:



This may be used as a measure of the effective influence of the anti-periplanar lone pair electrons. Fluorine and the phosphorinane oxygens have the least influence on the σ^* -orbital of the P-F bond. In the case of fluorine this is probably because its lone pairs are too low in energy for any interaction, while in the phosphorinane ring skeleton distortions of the ring can cause the oxygen lone pairs to be less available.

hfb, phen/chl And pfp have the greatest paramagnetic shielding effect probably because of strong lone pair interactions of their donor atoms with the σ^* -orbital.

Table 7

co-linear	B,C	A	other ligands	σ^P /ppm
F-P-F	(pin)	F	F, F	-470
	(eth)	F	F, F	-459
	(but)	F	F, F	-470

The σ^P values, table 7, in the case of $\text{P}(\text{bid})\text{F}_4^-$ resemble closely the values of $\text{P}(\text{bid})(\text{bid}')\text{F}_2^-$, table 6, for the corresponding bidentate ligand, having F-P-O co-linear; this again with the exception where the bidentate

ligand is (but).

Table 8

co-linear	B,C	A	other ligands	σ^P /ppm
F-P-O	(hfb)	(prop)	F	-466
	(chl)	(prop)	F	-473 (a)
	(chl)	(prop)	F	-465 (a)
	(hfb)	(Set)	F	-467
	(chl)	(Net)	F	-469

(a) two isomers, possibly because of different conformations of the phosphorinane ring;

It can be noted that on replacing a dioxaphospholane ring with a dioxaphosphorinane ring the paramagnetic shielding constants under consideration decrease in absolute value by 10 ppm.

Even so when (Set), (Net) or (but) bidentate ligands are part of the phosphoride the σ^P values are difficult to compare with the other phosphorides. Sulphur, nitrogen and carbon directly attached to the central phosphorus atom not only alter the ground state term drastically but also the excited state term. The same applies for the phosphorinane ring.

4.1.2.5 trans/cis-Phosphorides

The thermodynamically more stable cis-phosphoride contains fluorine nuclei which have a smaller paramagnetic screening than in the case of the corresponding trans-phosphoride (cf. Table 9).

Table 9

phosphoride	$\sigma^{\text{P}}/\text{ppm}$		
	trans		cis
P(chl)(pin)F ₂ ⁻	-488	-478	-467
P(eth)(hfb)F ₂ ⁻	-477	-476	-458
P(hfb)(pin)F ₂ ⁻	-488	-480	-467
P(hfb)(Set)F ₂ ⁻	-515	-467	-446
P(chl)(Net)F ₂ ⁻	-475	-469	-458
P(phen)(pin)F ₂ ⁻	-486	-476	-471

The cis-phosphoride, being the more stable, will have a different ground state energy and therefore a change in $\sigma_{\text{G}}^{\text{P}}$ is to be expected. Also in the cis-phosphoride only two heteroatoms can have their lone pair electrons interacting with the σ^* -orbital of the P-F bond. Hence there will be less lone pair interaction than in the trans-phosphoride with its four donor atoms in the right position for interaction. This can lead to a decrease in $\sigma_{\text{EX}}^{\text{P}}$ since in the cis-phosphoride the σ^* -orbital is expected to be higher in energy.

4.1.3 ¹⁹F P-OPhF Chemical Shifts

4.1.3.1 General

When a fluorine atom is linked to an aromatic system (e.g. phenyl group) its chemical shift is determined by inductive, σ^{I} , and resonance interactions, σ^{R} , (96):

$$\delta\text{F} = \sigma^{\text{I}} + \sigma^{\text{R}}$$

Introducing additional substituents into the phenyl

group will cause the σ^I and σ^R to change. The inductive interaction results from the power of the substituent to attract or repel the electrons of the phenyl group, either through space or via the σ -bonds. When this attraction or repulsion of electrons takes place via the π -orbitals a resonance interaction occurs.

The shielding parameters of the attached fluorine atom are more sensitive to the resonance than to the inductive interaction. When the fluorine atom is separated by four or more bonds from a changing substituent, it is the resulting changes in the π -electron density of the phenyl group which account for the changes in chemical shift (96).

Substituents like (O, NH_2 and F) will donate π -electrons to the phenyl ring (97). Increased π -electron density in the phenyl ring will make it more difficult for the fluorine atom to donate its p -electrons. Hence there will be less resonance interaction, resulting in less screening of the fluorine nucleus.

4.1.3.2 Observations

Listed in Table 10 are the experimental ^{19}F chemical shifts for the equilibrium:



The FPhO^- ion, which has been added to the phosphorane, P(5), has the largest electron density on its oxygen atom. This results in an increased π -electron

density of the phenyl group, forcing a smaller resonance interaction with the fluorine lone pairs and therefore a lower resonance frequency.

Table 10

phosphorane	P(5)	$\delta F/\text{ppm}$		
		cis-phosphoride		FPhO ⁻
P(chl)(pin)OPhF	-54.3	-60.0	-61.2	-63.7
P(hfb)(pin)OPhF	-54.9	-60.2	-61.7	-68.1 [*]
P(eth)(hfb)OPhF	-54.9	-61.2	-61.4	-63.7
P(hfb)(phen)OPhF	-58.1	-61.1	-61.8	-68.9 [*]
P(but)(phen)OPhF	-57.2	-60.0	-61.5	-66.7
P(hfb)(prop)OPhF	-54.4	-59.0	-61.4	-63.8
P(hfb)(Net)OPhF	-54.5	-59.9	-61.0	-68.4 [*]
P(hfb)(Set)OPhF	-54.7		-60.8	-64.0

^{*}more than one equivalent of NaOPhF was used;

The neutral phosphorane has the least electron density on its unidentate ligand oxygen and in the phenyl group and hence the highest resonance interaction.

The phosphoride produced by the attack of FPhO⁻ ion on the phosphorane contains more negative charge than the original phosphorane. The charge is more delocalised over the ligands of the six-co-ordinate phosphorus anion and hence less π -electron density will occur than in the case of the FPhO⁻ ion. The resonance interaction will be between the phosphorane and FPhO⁻ ion, as will the chemical shift.

In the case of trans-phosphorides, (cf. Table 11), the chemical shift is at a lower frequency than the corresponding cis-phosphoride. This suggests that in the trans-phosphoride more charge has been delocalised onto the ligands

than in the cis-phosphoride. As a result less electron density can be expected on the central phosphorus atom (cf. CHAPTER 4.3.6).

Table 11

phosphoride	$\delta F/\text{ppm}$	
	trans	cis
$\text{P}(\text{chl})(\text{pin})(\text{OPhF})_2^-$	-63.0	-59.9, -61.3
$\text{P}(\text{hfb})(\text{Set})(\text{OPhF})_2^-$	-61.9	-60.8
$\text{P}(\text{chl})(\text{Net})(\text{OPhF})_2^-$	-62.2	-59.9, -60.6, -61.4

4.2 Coupling Constants

4.2.1 General

Two nuclei, having both a spin, show an interaction between them via their σ - and π -electrons. This interaction is an energy expressed as J , the coupling constant.

When the two nuclei are close the Contact Term (or Fermi Term) is dominant in the coupling constant. The term relates to the ground state wave functions and depends mainly on s-electrons.

Two other terms, the electron dipole and the electron-orbital term, become more important when the nuclei are farther apart. These two terms depend on the presence of p- and d-orbitals (98).

For the fluorine atom with its low lying p-orbitals, the dipole and orbital term play a more significant role than in the case of proton.

In this section all coupling constant values are taken from ^{31}P NMR measurements.

4.2.2 $^1\text{J}(^{31}\text{P}, ^{19}\text{F})$

4.2.2.1 Introduction

The $2s$ -orbital of fluorine is of very low energy and hardly contributes to the P-F bond. Therefore the coupling constant $^1\text{J}_{\text{PF}}$ differs greatly from the coupling constants of other atoms, whose s -orbitals contribute more towards the bond (99).

The lower the excitation energy, ΔE , and the larger the s -orbital population on the central phosphorus atom, the larger the $^1\text{J}_{\text{PF}}$ will be since the (absolute) value of the Fermi Term in the coupling constant will be enlarged (95, 100).

4.2.2.2 trans/cis-Phosphorides

Table 12

phosphoride	$^1\text{J}_{\text{PF}}/\text{Hz}$	
	trans	cis
$\text{P}(\text{chl})(\text{pin})\text{F}_2^-$	768.1 ± 0.5 (a)	735.4 737.9 ± 0.5
$\text{P}(\text{hfb})(\text{pin})\text{F}_2^-$	766 ± 1	718 732 ± 5
$\text{P}(\text{pin})(\text{phen})\text{F}_2^-$	757 ± 5	723.5 726.5 ± 0.5
$\text{P}(\text{eth})(\text{hfb})\text{F}_2^-$	756.3 ± 0.5	728 738 ± 5
$\text{P}(\text{pfp})(\text{phen})\text{F}_2^-$	799.8 ± 0.5	(b)
$\text{P}(\text{chl})(\text{Net})\text{F}_2^-$	789.0 ± 0.3	747 811 ± 5

(a) machine accuracy;

(b) cis-phosphoride was not observed;

The value of the coupling constant of trans-phosphoride is usually 20 to 40 Hz larger than for the corresponding cis-phosphoride.

trans-Phosphorides resonate at a higher frequency than cis-phosphorides (cf. CHAPTER 4.1.2.5), which indicates more paramagnetic screening and a lower excitation energy for the trans-isomer. The observed decrease in coupling value can be accounted for if the s-electron population on the central phosphorus atom in cis-phosphorides is larger than in trans-phosphorides.

Table 13

phosphoride	$^1J_{PF}/\text{Hz}$	
	trans	cis
P(hfb)(Set)F ₂ ⁻	882.5 ±0.5 ^(a)	864 882 ±1
P(hfb)(Net)F ₂ ⁻	820 ±1	780 804, 813 ±1 (b)
P(hfb)(Npr)F ₂ ⁻	771 ±5	740 794 ±5
P(but)(pfp)(OPhF)F ⁻	713 ±5	802 ±2
P(pfp)(phen)(NMe ₂)F ⁻	708 ±5	(c)
P(pent)(pin)F ₂ ⁻	801 ±5	(c)

(a) machine accuracy;

(b) more than one cis-isomer observed;

(c) not observed;

In general the values of the coupling constant vary between 708 and 882 Hz. This is in the range expected for six-co-ordinate phosphorus-fluoro species (12, 96, 100, 101).

When the bidentate ligand is attached to the phosphorus atom with a less electronegative element than

oxygen (e.g. S, N or C) there is an increase in the value of the $^1J_{PF}$ coupling constant. On the other hand when in a trans-phosphoride the trans fluorine atom is replaced by a less electronegative element (e.g. O or N) there is a decrease in the value of the coupling constant.

4.2.2.3 cis-Phosphorides

Table 14

phosphoride	$^1J_{PF}/\text{Hz}$		
P(chl)(prop)F ₂ ⁻	737	752	± 1 (a)
P(hfb)(prop)F ₂ ⁻	728	747	± 1
P(but)(pfp)F ₂ ⁻	771	786	± 5
P(hfb)(prop)(OPhF)F ⁻	762	(b)	± 1
P(eth)(hfb)(OPhF)F ⁻	762	767	± 5

(a) machine accuracy;
 (b) one cis-isomer observed;

Replacing a phospholane ring by a phosphorinane ring does not have a significant effect on the value of the coupling constant $^1J_{PF}$.

Again it can be concluded from Table 14 that when a less electronegative atom is introduced next to the central phosphorus atom, the coupling value increases.

4.2.3 $^6J(^{31}\text{P}, ^{19}\text{F})$

For this long range coupling constant the Fermi-Contact Term will be small. The dominant factors are now the dipolar and orbital term. Since the σ - and π -electrons of the phenyl ring in phosphoranes and phosphorides differ

very little, the expected values for the respective ${}^6J_{PF}$ coupling constants will be of the same order and no significant differences are to be expected (cf. Table 15).

Table 15

	${}^6J_{PF}/\text{Hz}$	
	P(5)	cis-P(6) (a)
P(chl)(pin)OPhF	3.9 \pm 0.1 (b)	2.9 \pm 0.3
P(eth)(hfb)OPhF	4.1 \pm 0.1	3.6 \pm 0.5
P(hfb)(phen)OPhF	4.4 \pm 0.1	4.1 \pm 0.2
P(hfb)(Set)OPhF	3.4 \pm 0.5	4.0 \pm 0.1

(a) phosphoride of general formula P(bid)(bid')-(OPhF)₂⁻;
 (b) machine accuracy;

No values of ${}^6J_{PF}$ could be observed at any one temperature for the following six-co-ordinate phosphorus anions: cis-P(but)(phen)(OPhF)₂⁻, cis-P(chl)(prop)(OPhF)₂⁻, cis-P(hfb)(prop)(OPhF)₂⁻, trans-P(chl)(pin)(OPhF)₂⁻, trans-P(hfb)(Set)(OPhF)₂⁻ and phosphorides containing the 1,3,2-oxazaphospholane ring.

For the cis-phosphorides it is possible that the dissociation of FPhO-ligand to produce spirophosphorane becomes dominant. This can also be the case for both trans-examples. Poor resolution of the NMR spectrum may not be excluded at low temperatures.

4.3 ${}^{31}\text{P}$ Chemical Shifts

4.3.1 General

Tervalent phosphorus nuclei resonate over a range in

chemical shift of about 500 ppm. In both the pentavalent and hexavalent state a range of about 100 ppm is found, with the six-co-ordinate species resonating at lower frequency. In principle the ^{31}P chemical shift is determined by the same terms as in the case of fluorine (87, 102).

4.3.2 Phosphoranes / Phosphorides

Table 16

phosphorane	$\delta\text{P/ppm}$	phosphoride	$\delta\text{P/ppm}$
P(but)(pfp)OPh	+19.6	$\underline{\text{t}}\text{-P(but)(pfp)F}_2^-$	-88.6
P(hfb)(Set)OPhF	+1.6	$\underline{\text{t}}\text{-P(hfb)(Set)OPhF}_2^-$	-91.8
P(pent)(pin)OPhF	-17.8	$\underline{\text{t}}\text{-P(pent)(pin)F}_2^-$	-102.5
P(phen)(pin)F	-30.6	$\underline{\text{t}}\text{-P(phen)(pin)F}_2^-$	-101.9
P(phen)(pfp)NMe ₂	-30.7	$\underline{\text{t}}\text{-P(phen)(pfp)NMe}_2\text{F}^-$	-93.6
P(phen)(pin)OPhF	-37.9	$\underline{\text{c}}\text{-P(phen)(pin)OPhF}_2^-$	-110.1
P(hfb)(prop)OPhF	-51.0	$\underline{\text{c}}\text{-P(hfb)(prop)F}_2^-$	-124.6

By introducing a sixth ligand attached to the phosphorus nucleus, the nucleus becomes increasingly shielded and its chemical shift moves 60 to 80 ppm to lower frequency of the five-co-ordinate phosphorus species (44, 82).

4.3.3 uni/bis/trischelate Phosphorides

Of the six-co-ordinate phosphorus anions the trischelate anions resonate at the highest frequency (cf. Table 17). Substitution of one bidentate ligand by two unidentate ligands increases the chemical shielding of the phosphorus

nucleus (44).

Table 17

type	phosphoride	$\delta P/\text{ppm}$
trischelate	$\text{P}(\text{chl})(\text{chl})(\text{pin})^-$	-83.3
	$\text{P}(\text{phen})(\text{phen})(\text{phen})^-$	-82.5
bischelate	$\underline{\text{c}}-\text{P}(\text{chl})(\text{pin})(\text{OPhF})_2^-$	-107.0
	$\underline{\text{c}}-\text{P}(\text{phen})(\text{pfp})(\text{OPhF})_2^-$	-107.1
	$\underline{\text{c}}-\text{P}(\text{phen})(\text{pin})\text{F}_2^-$	-105.9
unichelate	$\text{P}(\text{eth})\text{F}_4^-$	-119.4
	$\text{P}(\text{pin})\text{F}_4^-$	-125.4

The reason for this increased shielding may possibly be due to an increase in back-bonding by the donor atom of the unidentate ligand over that of the bidentate ligand (44, 82).

4.3.4 Increase in Chelate Size

Replacing a dioxaphospholane ring, four membered chelate, by a dioxaphosphorinane ring, five membered chelate, produces an increase in chemical shielding of about 20 ppm. (49), cf. Table 18.

Because of the greater flexibility of the phosphorinane ring it is possible that its oxygen donor atoms are in a better position for back-donation than in the case of the more rigid phospholane ring.

Table 18

<u>cis</u> -phosphoride	$\delta P/\text{ppm}$	<u>cis</u> -phosphoride	$\delta P/\text{ppm}$
P(hfb)(prop)F ₂ ⁻	-124.6	P(eth)(hfb)F ₂ ⁻	-101.1
P(chl)(prop)F ₂ ⁻	-121.3	P(chl)(pin)F ₂ ⁻	-102.3
P(hfb)(prop)(OPhF)F ⁻	-127.1	P(eth)(hfb)(OPhF)F ⁻	-102.5*
P(hfb)(prop)(OPhF) ₂ ⁻	-130.9*	P(eth)(hfb)(OPhF) ₂ ⁻	-105.5

*second isomer observed;

4.3.5 Electronegativity of Unidentate Ligand

Table 19

phosphoride	$\delta P/\text{ppm}$	
	(OPhF)	(F)
<u>cis</u> -P(chl)(prop)(uni) ₂ ⁻	-127.5*	-121.3
<u>cis</u> -P(hfb)(pin)(uni) ₂ ⁻	-110.5	-105.2
<u>trans</u> -P(chl)(pin)(uni) ₂ ⁻	-103.7	-99.6
<u>trans</u> -P(hfb)(Set)(uni) ₂ ⁻	-91.8	-88.1

*second isomer observed at -125.4 ppm;

Electronegative atoms such as fluorine usually produce a decrease in shielding, probably due to the electron withdrawal effect through the σ -electrons (91, 96). This is true irrespective of the configuration (cis or trans) or the nature of the bidentate ligands present.

4.3.6 trans/cis-Phosphorides

Using simple model calculations values of phosphorus

chemical shifts were predicted for different six-co-ordinate phosphorus species (9, 104). It was indicated that the phosphorus nucleus in cis-isomers resonates at a lower frequency than in the corresponding trans-isomers.

Table 20

phosphoride	$\delta P/\text{ppm}$	
	<u>trans</u>	<u>cis</u>
P(chl)(pin)(OPhF) ₂ ⁻	-103.7	-107.0
P(hfb)(pin)F ₂ ⁻	-102.3	-105.2
P(eth)(hfb)F ₂ ⁻	-98.8	-101.1
P(hfb)(Set)F ₂ ⁻	-88.1	-89.5
P(hfb)(Set)(OPhF) ₂ ⁻	-91.8	-96.0 (a)
P(phen)(pin)F ₂ ⁻	-101.9	-105.9
P(but)(pfp)(OPh)F ⁻	-90.2	-94.4
P(chl)(Net)(OPhF) ₂ ⁻	-102.7	-103.3 (b)

(a) second isomer -96.8 ppm;
(b) second isomer -104.3 ppm;

The experimental data, cf. Table 20, is in agreement with the predictions made in the literature. It is possible that in trans-anions more negative charge is delocalised over the ligands than in the case of cis-anions.

CHAPTER 5

Experimental

Proton NMR spectra were recorded on a Varian T60 instrument, using deuteriochloromethane as solvent, unless otherwise stated. Fluorine and phosphorus NMR spectra were recorded on a Jeol PS100 (94.1 MHz) and a JNM FX60 machine (24.2 MHz, proton decoupled, Fourier Transform) respectively, using THF as solvent unless otherwise stated.

The references used were internal tetramethylsilane, external benzotrifluoride and 85% H_3PO_4 , with the positive chemical shift-high frequency convention. The values of the fluorine chemical shifts are correct to within 2 ppm and the phosphorus chemical shifts to within 0.5 ppm.

All operations were carried out under dry, oxygen-free nitrogen gas with glass apparatus dried prior to use at 120°C . Celite filter aid was used where chloride salts had to be filtered.

All chemicals and solvents were dried and distilled before use. Diethyl ether and petroleum spirit were treated with phosphorus pentoxide followed by sodium wire. Pyridine and triethylamine were heated to reflux over and distilled from potassium hydroxide. Benzene and hexane were dried with sodium wire, while tetrahydrofuran was dried with lithium aluminium hydride or sodium/benzophenone. Dichloromethane and trichloromethane were treated with phosphorus pentoxide.

5.1 Preparation of P(3)

2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (84)

Phosphorus trichloride (0.10 mol) in diethyl ether (100 cm³) was slowly added to a stirred mixture of 2,3-dimethylbutan-2,3-diol (0.10 mol) and pyridine (0.10 mol) in diethyl ether (200 cm³) at 0°C. When addition was completed the reaction mixture was heated to reflux for one hour. Filtration and removal of the solvent, followed by reduced pressure distillation gave the product (70%; b.p._{0.35} 39-41°C).

$\delta P(\text{CDCl}_3)$ +174.7 ppm.

2-Chloro-3-methyl-1,3,2-oxazaphospholan (94)

Prepared as described above, using 2-N-methylaminoethanol (80 mmol) and triethylamine (80 mmol) with benzene as the solvent (30%; b.p._{0.1} 30-32°C).

2-Chloro-3-isopropyl-1,3,2-oxazaphospholan

Prepared as above, using 2-N-isopropylaminoethanol (50 mmol) and triethylamine (50 mmol) (34%; b.p._{0.05} 56-58°C).

2-Chloro-4-methyl-1,3,2-dioxaphospholan (106)

Propan-1,2-diol (0.20 mol) and phosphorus trichloride (0.20 mol), each made up to 50 cm³ with trichloromethane, were allowed to flow through a common addition tube into a flask with well stirred trichloromethane (50 cm³). Immediately after the addition the mixture was distilled at atmospheric pressure until the bath temperature reached 100°C. The remainder of the solvent was removed on a rotary evaporator and the product distilled under reduced pressure (58%;

b.p.₃₅ 56-58°C).

$\delta P(C_6H_6)$ +170.2 ppm.

2-Chloro-1,3,2-dioxaphospholan (106)

Ethan-1,2-diol (0.25 mol) was added to a stirred solution of phosphorus trichloride (0.25 mol) in trichloromethane (50 cm³) at such a rate that the solvent was heated to reflux. At the conclusion of the addition the solvent was removed and the product distilled under reduced pressure (40%; b.p.₃₀ 46-50°C).

2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan

Prepared as described above, using 2,2-dimethylpropan-1,3-diol (0.25 mol) (64%; b.p._{0.15} 36-38°C).

2-Chloro-1,3,2-oxathiaphospholan

Prepared as above, using 2-mercaptoethanol (0.25 mol) (27%; b.p._{0.5} 50-52°C).

δP +204.7 ppm.

2-Bromo-4,5-dimethylphosphol-4-en (107)

2,3-Dimethylbuta-1,3-diene (115) (60 mmol) was added dropwise to a stirred mixture of white phosphorus (40 mmol) and phosphorus tribromide (20 mmol). On addition the reaction mixture warmed to 30-40°C. When addition was completed and the temperature had dropped to room temperature the mixture was distilled under reduced pressure (57%; b.p._{0.1} 54-58°C).

δP +106.5 ppm (quint, ²J_{PH} 20 Hz).

2-Fluoro-1,3,2-benzodioxaphosphole (108)

Commercial 2-chloro-1,3,2-benzodioxaphosphole (30 mmol) was added slowly to antimony trifluoride (30 mmol) and the reaction mixture was maintained at 50-100°C (oil bath) for two hours. The reaction product was then distilled from the reaction flask under reduced pressure (89%; b.p.₆ 36.5°C).

$\delta P(\text{CDCl}_3) +123.5$ ppm (d, $^1J_{\text{PF}}$ 1304 \pm 5 Hz);

$\delta F(\text{CDCl}_3) +26.8$ ppm (d, $^1J_{\text{PF}}$ 1302 \pm 15 Hz).

2-(N,N-dimethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (109)

A mixture of 2,3-dimethylbutan-2,3-diol (10 mmol) and tris(N,N-dimethylamino)phosphine (10 mmol) in benzene (30 cm³) was heated to reflux for one hour. The solvent was removed and the product distilled under reduced pressure (62%; b.p._{0.06} 54-55°C).

$\delta P +141.6$ ppm.

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (110)

Absolute ethanol (50 mmol) in diethylether (20 cm³) was added dropwise to a stirred mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (50 mmol) and pyridine (50 mmol) in diethyl ether (100 cm³) at 0°C. When addition was completed the reaction mixture was heated to reflux for one hour. Filtration and removal of the solvent, followed by reduced pressure distillation gave the product (43%; b.p._{0.9} 48°C).

2-(p-Fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan

2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (40 mmol) in diethyl ether (25 cm³) was added slowly to a stirred mixture of *p*-fluorophenol (40 mmol) and pyridine (40 mmol) in diethyl ether (100 cm³) at 0°C. After the addition the mixture was heated to reflux for one hour. Filtration and removal of the solvent, followed by distillation under reduced pressure gave the product (80%; b.p._{0.2} 82-84°C).

$\delta P(CDCl_3)$ +138.4 ppm;

$\delta F(CDCl_3)$ -57.7 ppm.

2-(*p*-Fluorophenoxy)-3-methyl-1,3,2-oxazaphospholan

Prepared as above, using 2-chloro-3-methyl-1,3,2-oxazaphospholan with triethylamine and *p*-fluorophenol on a 20 mmol scale (35%; b.p._{0.15} 86-88°C).

$\delta P(CDCl_3)$ +135.1 ppm; $\delta F(CDCl_3)$ -56.6 ppm.

2-(*p*-Fluorophenoxy)-3-isopropyl-1,3,2-oxazaphospholan

Prepared on 0.10 mol scale from 2-chloro-3-isopropyl-1,3,2-oxazaphospholan, triethylamine and *p*-fluorophenol (73%; b.p._{0.05} 88-90°C).

$\delta P(CDCl_3)$ +134.7 ppm; δF -58.4 ppm.

2-(*p*-Fluorophenoxy)-4-methyl-1,3,2 dioxaphospholan

Prepared from 2-chloro-4-methyl-1,3,2-dioxaphospholan, triethylamine and *p*-fluorophenol on 100 mmol scale (70%; b.p._{0.2} 71-72°C).

$\delta P(CDCl_3)$ +131.9 (70%), +134.5 ppm (30%); δF -57.8 ppm.

2-(*p*-Fluorophenoxy)-1,3,2-dioxaphospholan

Prepared on 0.10 mol scale with 2-chloro-1,3,2-dioxa-

phospholan, pyridine and *p*-fluorophenol (56%; b.p._{0.4} 68°C).

δP +128.5 ppm; $\delta F(CDCl_3)$ -55.7 ppm.

2-(*p*-Fluorophenoxy)-1,3,2-oxathiaphospholan

Prepared from 2-chloro-1,3,2-oxathiaphospholan, triethylamine and *p*-fluorophenol on 60 mmol scale (50%; b.p._{0.5} 102-106°C).

$\delta P(CDCl_3)$ +171.2 ppm; $\delta F(CDCl_3)$ -54.9 ppm.

2-(*p*-Fluorophenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinan

Prepared on 40 mmol scale from 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan, triethylamine and *p*-fluorophenol (52%; b.p._{0.1} 102-103°C).

δP +115.6 ppm; $\delta F(CDCl_3)$ -56.6 ppm.

2-(*p*-Fluorophenoxy)-1,3,2-benzodioxaphosphole

Prepared on 10 mmol scale with commercial 2-chloro-1,3,2-benzodi-oxaphosphole, pyridine and *p*-fluorophenol (80%; b.p._{0.2} 94-96°C).

$\delta P(CDCl_3)$ +125.9 ppm; $\delta F(CDCl_3)$ -54.4 ppm.

5.2 Preparation of P(5)

35 5',6',7',8'-Tetrachloro-2-(*p*-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-benzodioxaphosphole (66)

Commercial tetrachloro-1,2-benzoquinone (10 mmol) in diethyl ether (20 cm³) was added slowly to 2-(*p*-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (10 mmol) in diethyl ether (20 cm³). The reaction mixture was then left overnight at room temperature. Filtration of the product

followed by recrystallisation from petroleum spirit gave the phosphorane (60%; m.p. 132-133°C). $C_{24}H_{16}Cl_4FO_5P$ requires C 42.9%, H 3.20%, Cl 28.1% and P 6.14%; found C 42.8%, H 3.28%, Cl 28.3% and P 6.09%.

δP -35.7 ppm (d, $^6J_{PF}$ 3.9 \pm 0.1 Hz); δF (CDCl₃) -54.3 ppm;
 δH 1.22 (12H, s), 6.77 (2H) and 6.87 ppm (2H).

Hexafluorobiacyl (111)

Commercial 2,3-dichlorohexafluorobuta-2-ene (30 g) was added over a period of two hours to a well stirred mixture of chromium trioxide (28 g), fuming sulphuric acid (86 cm³) and concentrated sulphuric acid (32 cm³), while the bath temperature was maintained at 60°C. After the addition was completed the mixture was stirred for one hour at 65°C and one hour at 65-70°C. The product was collected in an acetone/dry ice trap and impurities were distilled off at 0°C for thirty minutes. The crude product was stored at -50°C. Prior to use the product was distilled through a Vigreux column with bath temperature at 30-40°C and collected in an acetone/dry ice trap. Impurities were removed over a period of two minutes at reduced pressure (0.1 mmHg) at -78°C (25%).

38 4',5'-Bis(trifluoromethyl)-2-(p-fluorophenoxy)-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-dioxaphospholen (82)

A solution of 2-(p-fluorophenoxy)-1,3,2-dioxaphospholan (15 mmol) in THF (5 cm³) was slowly added to hexafluorobiacyl (20 mmol) in THF (10 cm³) at -78°C. After addition was completed the mixture was allowed to warm to 0°C and

stirred for thirty minutes at 0°C. Evaporation of the solvent gave the phosphorane in quantitative yield (m.p. 24-25°C).

$C_{12}H_8F_7O_5P$ requires C 36.4%, H 2.0% and P 7.8%; found C 35.6%, H 2.3% and P 7.1%.

δP -29.0 ppm (dsept, $^4J_{PF}$ 1.0 and $^6J_{PF}$ 4.1 ± 0.1 Hz);

δF -1.9 (6F,s) and -55.3 ppm (1F);

δH 3.8-4.2 (4H,m), 6.69 (2H) and 6.79 ppm (2H).

41 2-Fluoro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-benzodioxaphosphole (112)

A solution of 2,3-dimethylbutan-2,3-diol (4 mmol) in diethyl ether (10 cm³) was added slowly to a solution of 2-fluoro-1,3,2-benzodioxaphosphole (4 mmol) in diethyl ether (25 cm³) at -78°C. N-Chlorodi-isopropylamine (4 mmol) in diethyl ether (10 cm³) was then slowly added and the mixture kept at -78°C for thirty minutes. After leaving overnight at room temperature, filtration followed by evaporation of the solvent gave the phosphorane (80%). $C_{12}H_{16}FO_4P$ requires C 52.6%, H 5.88% and P 11.3%; found C 52.4%, H 6.04% and P 11.4%.

δP -30.6 ppm (d, $^1J_{PF}$ 981 ± 5 Hz);

δF -0.39 ppm (d, $^1J_{PF}$ 982 ± 15 Hz).

51 2-(N,N-Dimethylamino)-4,4,5,5-tetramethyl-4,5-bis-(trifluoromethyl)-1,3,2-dioxaphospholen-2-spiro-2'-1',3',2'-dioxaphospholan

A solution of 2-(N,N-dimethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (1 mmol) in diethyl ether (5 cm³) was slowly added to hexafluorobiacyl (1.5 mmol) at -78°C. The

reaction mixture was allowed to warm slowly to room temperature. The mixture was then stirred for fifteen minutes after which the solvent was removed. The product was then left for thirty minutes at 40°C under reduced pressure (0.1 mmHg). From the residue the phosphorane separated out slowly.

$C_{12}H_{18}F_6NO_4P$ requires C 37.3%, H 4.7% and N 3.6%; found C 37.2%, H 4.7% and N 3.2%.

δP -30.7 ppm; δF (CDCl₃) -0.6 ppm;

δH 1.28 (12H,s), 2.80 ppm (6H,d, $^3J_{PH}$ 10 Hz).

60 2-(p-Fluorophenoxy)-4',5'-bis(trifluoromethyl)-1,3,2-oxathiaphospholan-2-spiro-2'-1',3',2'-dioxaphospholen

Prepared as phosphorane 51, using 2-(p-fluorophenoxy)-1,3,2-oxathiaphospholan and hexafluorobiacyl. Quantitative yield. $C_{12}H_3F_7O_4PS$ requires C 35.0%, H 2.0% and P 7.5%; found C 34.0%, H 1.9% and P 6.9%.

δP +1.6 ppm (d, $^6J_{PF}$ 3.4 \pm 0.5 Hz);

δF -1.43 (3F,q, $^5J_{FF}$ 9 \pm 1 Hz), -3.16 (3F,q, $^5J_{FF}$ 9 \pm 1 Hz)

and -54.9 ppm (1F);

δH 2.73-4.77 (4H,m), 6.82 (2H) and 6.92 ppm (2H).

66 5',6',7',3'-Tetrachloro-2-(p-fluorophenoxy)-3-methyl-1,3,2-oxazaphospholan-2-spiro-2'-1',3',2'-benzodioxaphosphole

Prepared as phosphorane 35, using 2-(p-fluorophenoxy)-3-methyl-1,3,2-oxazaphospholan and tetrachloro-1,2-benzoquinone on 15 mmol scale. Evaporation of the solvent and recrystallisation from petroleum spirit gave the phosphorane, 70%, m.p. 98-101°C.

δP -38.0 ppm (d, $^6J_{PF}$ 3.9 \pm 0.3 Hz); δF -56.2 ppm;

δH 3.03 (3H,d, $^3J_{PH}$ 10 Hz), 2.53-4.50 (4H,m), 6.82 (2H) and 6.92 (2H).

72 2-(p-Fluorophenoxy)-5',5'-dimethyl-4,5-bis(trifluoromethyl)-1,3,2-dioxaphospholen-2-spiro-2'-1',3',2'-dioxaphosphorinan

Prepared as phosphorane 51, using 2-(p-fluorophenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinan (5 mmol) and hexafluorobiacetyl (7 mmol). $C_{15}H_{14}F_7O_5P$ requires C 41.1%, H 3.2% and P 7.1%; found C 39.4% H 3.2% and P 6.9%.

δP -51.0 ppm (dsept, $^4J_{PF}$ 1.0 and $^6J_{PF}$ 4.3 \pm 0.2 Hz);

δF -1.27 (6F,s) and -55.6 ppm (1F);

δH 0.98 (3H,s), 1.13 (3H,s), 3.6-4.4 (4H,m), 6.88 (2H) and 6.99 ppm (2H).

76 5,6,7,8-Tetrachloro-2-(p-fluorophenoxy)-5',5'-dimethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphosphorinan

Prepared as phosphorane 66, using 2-(p-fluorophenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinan and tetrachloro-1,2-benzoquinone on 5 mmol scale. $C_{17}H_{14}FO_5P$ requires C 41.7%, H 2.9%, and Cl 28.9%; found C 39.4%, H 3.0% and Cl 29.3%.

δP -50.3 ppm (d, $^6J_{PF}$ 4.2 \pm 0.3 Hz); δF -55.2 ppm;

δH 1.04 (3H,s), 1.09 (3H,s), 3.84 (2H,m), 4.17 (2H, s), 6.86 (2H) and 6.96 (2H).

82 4'-Acetyl-2-ethoxy-4,4,5,5,5'-pentamethyl-3'-phenyl-1,3,2-dioxaphospholan-2-spiro-2'-1',2'-oxaphosphol-4'-en (trans) (110)

A mixture of 3-benzylidenepenta-2,4-dione (50 mmol) and 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (50 mmol) in benzene-hexane (1:4; 10 cm³) was allowed to react overnight at 40°C. Evaporation of solvent followed by recrystallisation

(x3) from petroleum spirit produced the trans-isomer (i.e. the phenyl group is trans with respect to the ethoxy ligand) (60%; m.p. 107°C). $C_{20}H_{29}O_5P$ requires C 63.1%, H 7.7% and P 8.1%; found C 62.9%, H 7.9% and P 8.2%.

$\delta P(CH_2Cl_2)$ -18.5 ppm.

81 4'-Acetyl-2-(p-fluorophenoxy)-4,4,5,5,5'-pentamethyl-3'-phenyl-1,3,2-dioxaphospholan-2-spiro-2'-1',2'-oxaphosphol-4'-en (trans)

Prepared as phosphorane 81, using 2-(p-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan and 3-benzylidene-penta-2,4-dione on 10 mmol scale. Quantitative yield, m.p. 129.5-130.5°C. $C_{24}H_{28}FO_4P$ requires C 64.6%, H 6.32%; found C 64.1% and H 6.35%.

δP -17.8 ppm (d, ${}^6J_{PF}$ 2.9 \pm 0.3 Hz); δF -56.1 ppm.

84 2-(p-Fluorophenoxy)-4',5'-dimethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-phosphol-4'-en

A solution of p-fluorophenol (8 mmol) in diethyl ether (20 cm³) was added slowly to a mixture of 2-chloro-4',5'-dimethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-phosphol-4'-en (8 mmol) and pyridine (8 mmol) in diethyl ether (50 cm³) at 0°C. After the addition was completed the reaction mixture was heated to reflux for two hours. Filtration and removal of the solvent gave the product, which was kept for thirty minutes at room temperature under reduced pressure (0.1 mmHg). The solid was then washed with petroleum spirit (x2) and dried for one hour at 40°C, 0,05 mmHg.

δP +13.3 ppm (dq, ${}^6J_{PF}$ 3.2 \pm 0.5 and ${}^2J_{PH}$ 13 \pm 1 Hz);

δF -57.5 ppm;

δH 1.70 (6H,s), 2.60 (4H,d, $^2J_{PH}$ 14Hz), 6.64-7.15 (4H,m),
6.72 (2H) and 6.83 ppm (2H).

94 2-(p-Fluorophenoxy)-4,4,4',4',5,5,5',5'-octamethyl-
2,2'-spiro-1,3,2-dioxaphospholan

Prepared as phosphorane 41, using 2,3-dimethylbutan-2,3-diol, 2-(p-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan on 5 mmol scale. Recrystallisation from petroleum ether (m.p. 102-104°C). $C_{18}H_{28}F_2O_5P$ requires C 57.7%, H 7.5% and P 8.3%; found C 57.6%, H 7.4% and P 8.3%.

δP -44.8 (d, $^6J_{PF}$ 2.7 \pm 0.3 Hz); δF -58.5 ppm;

δH 1.12 (12H,s), 1.23 (12H,s), 6.93 (2H) and 7.00 ppm (2H).

96 2-(p-Fluorophenoxy)-4,4,5,5-tetramethyl-4',4',5',5'-
tetrakis(trifluoromethyl)-2,2'-spiro-1,3,2-dioxaphospholan (66)

Commercial hexafluoroacetone (26 mmol, 4.3 cm³) was condensed into a solution of 2-(p-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (13 mmol) in diethyl ether (25 cm³) at -78°C. The reaction mixture was stirred for thirty minutes at -78°C and then allowed to warm slowly to room temperature, where it was kept for an additional one hour. Removal of the solvent and twice washing with absolute ethanol gave the phosphorane in quantitative yield (m.p. 115-116°C). $C_{18}H_{16}F_{13}O_5P$ requires C 36.6%, H 2.73% and P 5.25%; found C 36.7%, H 2.74% and P 5.25%.

δP -39.5 ppm (d, $^6J_{PF}$ 3.5 \pm 0.5 Hz);

δF -4.86 (12F) and -55.4 ppm (1F);

δH 1.09 (6H,s), 1.27 (6H,s), 6.91 (2H) and 7.01 (2H).

101 2-(N,N-Dimethylamino)-4,4,5,5,5'-pentamethyl-1,3,2-dioxaphospholan-2-spiro-2'-1',2'-oxaphosphol-4'en (114)

A mixture of 2-(N,N-dimethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (5 mmol) and commercial but-3-en-2-one (7 mmol) was maintained at room temperature for three hours. The excess reagent was then removed under reduced pressure at 50°C. Quantitative yield. $C_{12}H_{24}NO_3P$ requires C 55.2%, H 9.26% and P 5.36%; found C 56.4%, H 9.34% and P 5.27%.

δP -14.5 ppm (m, J_{PH} 10, 20 and 40 Hz ± 1 Hz);

δH 1.16-1.43 (12H,m), 1.49 (3H,s), 1.95 (2H,d,J 21 Hz), 2.71 (6H,d,J 9 Hz), and 4.46 ppm (1H,d,J 42 Hz).

103 2-Bromo-5,6,7,8-tetrachloro-4',5'-dimethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-phosphol-4'en

A solution of tetrachloro-1,2-benzoquinone (10 mmol) in diethyl ether (20 cm³) was added to 2-bromo-4,5-dimethylphosphol-4-en (10 mmol) in diethyl ether (10 cm³) and the reaction mixture was then left overnight at room temperature. The product was filtered off, washed thrice with diethyl ether and then maintained for one hour at room temperature under reduced pressure (0.05 mmHg). Quantitative yield.

$C_{12}H_{10}BrCl_4O_2P$ requires C 32.8%, H 2.3%, Br 18.2% and Cl 32.3%; found C 32.8%, H 2.5%, Br 18.0% and Cl 32.6%.

104 2-Chloro-4',5'-dimethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-phosphol-4'-en (113)

Commercial 2-chloro-1,3,2-benzodioxaphosphole (20 mmol) was mixed with neat 2,3-dimethylbuta-1,3-diene (115) (20 mmol) and the reaction mixture was then left for four days at room temperature in the dark. The resulting solid was washed

(x3) with cold diethyl ether and kept for a period of one hour at room temperature under reduced pressure (1.5 mmHg). Quantitative yield (m.p. 94-96°C). $C_{12}H_{14}ClO_4P$ requires C 56.1%, H 5.5% and P 12.1%; found C 56.4%, H 5.7% and P 12.2%.

δP +21.4 ppm (quint, $^2J_{PH}$ 15 \pm 1 Hz);

δH 1.85 (6H,s), 3.25 (4H,d, $^2J_{PH}$ 14 Hz) and 6.87 ppm (4H).

2-(p-Fluorophenoxy)-4,4,5,5-tetramethyl-4',5'-bis(trifluoromethyl)-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-dioxaphospholen

Prepared as phosphorane 51, using 2-(p-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (10 mmol) and hexafluorobiacetyl (15 mmol).

$\delta P(CDCl_3)$ -36.9 ppm (d, $^6J_{PF}$ 3.9 \pm 0.5 Hz);

δF -2.40 (6F,s) and -54.9 ppm (1F);

δH 1.37 (12H,s), 6.85 (2H) and 6.93 ppm (2H).

5',6',7',8'-Tetrachloro-2-(p-fluorophenoxy)-4-methyl-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-benzodioxaphosphole

Prepared as phosphorane 35, using 2-(p-fluorophenoxy)-4-methyl-1,3,2-dioxaphospholan and tetrachloro-1,2-benzoquinone on 10 mmol scale.

δP -28.4 (d, 50%) and -29.0 ppm (50%, d, $^6J_{PF}$ 3.9 \pm 0.5 Hz);

δF -55.6 ppm;

δH 1.38 (3H,d,J 5 Hz), 3.2-3.6 (1H,m), 3.8-4.6 (2H,m),

6.89 (2H) and 7.00 ppm (2H).

126 2-(p-Fluorophenoxy)-4',5'-bis(trifluoromethyl)-3-isopropyl-1,3,2-oxazaphospholan-2-spiro-2'-1',3',2'-dioxaphospholen

Prepared as phosphorane 51 on 7 mmol scale with 2-(p-

fluorophenoxy)-3-isopropyl-1,3,2-oxazaphospholan and hexafluorobiacetyl. $C_{15}H_{15}F_7NO_4P$ requires C 41.2%, H 3.5% and N 3.2%; found C 39.0%, H 3.9% and N 3.2%.

δP -40.1 ppm;

δF -0.96 (3F,q, $^5J_{FF}$ 9 \pm 1 Hz), -2.75 (3F,q, $^5J_{FF}$ 9 \pm 1 Hz) and -55.7 ppm (1F);

δH 1.14 (3H,d, $^3J_{HH}$ 7 Hz), 1.28 (3H,d, $^3J_{HH}$ 7 Hz), 2.86-4.53 (5H,m), 6.78 (2H) and 6.83 ppm (2H).

127 2-(p-Fluorophenoxy)-3-methyl-4',5'-bis(trifluoromethyl)-1,3,2-oxazaphospholan-2-spiro-2'-1',3',2'-dioxaphospholen

Prepared as phosphorane 51, using 2-(p-fluorophenoxy)-3-methyl-1,3,2-oxazaphospholan (6 mmol) and hexafluorobiacetyl (9 mmol). $C_{13}H_{11}F_7NO_4P$ requires C 39.1%, H 2.7% and N 3.4%; found C 36.0%, H 2.5% and N 3.1%.

δP -40.1 ppm (d, $^6J_{PF}$ 3.4 \pm 0.5 Hz);

δF -1.28 (3F,q, $^5J_{FF}$ 10 \pm 1 Hz), -2.87 (3F,q, $^5J_{FF}$ 10 \pm 1 Hz) and -55.6 (1F);

δH 2.63-4.13 (4H,m), 2.92 (3H,d, $^3J_{PH}$ 10 Hz), 6.78 (2H) and 6.83 ppm (2H).

5.3 Generation of P(6)

Prior to use all glassware was heated at 200°C for 24 hours and allowed to cool in a dry nitrogen atmosphere. Dried THF was stored over 4A molecular sieves and kept in the dark in a dry box. The transfer of all samples was carried out in a dry box. The weights of equivalent amounts of phosphorane and NaOPh^F (TBAF) are accurate within 5%. Final concentrations of samples with respect to phosphorane ranged from 0.10 to

0.50 M for fluorine NMR experiments and from 0.05 to 0.25 M for phosphorus NMR experiments.

¹⁹F NMR Experiments

An external D₂O lock was used and the data of the external reference benzotrifluoride was taken at room temperature and transferred to the measurements at low temperatures, resulting in an accuracy of the chemical shift of 0.5 ppm and of the coupling constants of 2-5%.

The required amounts of phosphorane and NaOPhF (TBAF) were dissolved separately in 0.20 cm³ of solvent. The NMR tube was filled with the phosphorane solution, which after ten minutes was frozen with the help of liquid nitrogen. The cooled solution of NaOPhF (TBAF) was then allowed to settle on top of the frozen phosphorane sample, after which the whole of the reaction mixture was kept in liquid nitrogen. The NMR tube was removed from liquid nitrogen and immediately allowed to warm inside the probe of the NMR instrument to the temperature of the probe (usually between -70 and -90°C).

Mixing of the phosphorane and NaOPhF (TBAF) layers occurred by lowering a rod into the opened NMR tube, without removal of the sample from the probe. The term "careful warming" implies removal of the sample from the probe for ten seconds, this including wiping and drying with wash acetone. "Warming to room temperature" implies that the sample was kept for a short period (ten to sixty seconds) at room temperature and then returned to the cooled probe.

^{31}P NMR Experiments

The signal of the external standard 35% H_3PO_4 was locked onto d_6 -acetone and its data stored in the memory of the FT-machine. The experimental sample was then locked onto external d_6 -acetone, which was inserted into the NMR tube. All references were made to the standard stored in the memory. The accuracy of the chemical shifts is within 0.5 ppm.

When improved resolution was required the d_6 -acetone was put in the outer NMR tube and the experimental sample was placed in the inner NMR tube.

Preparation of the NMR sample was carried out as described for the ^{19}F NMR experiments, except that the phosphorane and NaOPhF (TBAF) were first separately dissolved in 0.60 cm^3 of solvent. Mixing of the sample occurred by moving the inner NMR tube, without removal of the sample from the cooled probe. Warming took place as described for ^{19}F NMR experiments.

Tetrabutylammonium fluoride (116, 117)

Tetrabutylammonium hydroxide (10% aqueous solution) was titrated with hydrofluoric acid (5% aqueous solution) until slightly acidic. The mixture was kept for two minutes under reduced pressure, lyophilised and dried over phosphorus pentoxide under reduced pressure. The sample was stored in a plastic container, over phosphorus pentoxide in vacuo.

δF -105.2 ppm;

δH 0.9-1.2 (12H,m), 1.2-2.1 (16H,m) and 3.2 ppm (8H,t,
J 8 Hz).

Sodium p-fluorophenoxide

A solution of p-fluorophenol (30 mmol) in diethyl ether (10 cm³) was slowly added to a stirred solution of sodium hydride (25 mmol) in diethyl ether (10 cm³) until no more hydrogen gas was given off. After removal of the solvent the product was washed (x3) with cold diethyl ether, this followed by drying at 60°C for six hours under reduced pressure (0.1 mmHg). Quantitative yield.

δF -72.3 ppm;

δH 6.53 (2H) and 6.67 ppm (2H).

Below -73°C the sodium p-fluorophenoxide sample showed two signals, δF -70.1 and -73.9 ppm, in ratio 1:7 respectively. The appearance of two ¹⁹F NMR signals could be caused by species associated in different fashions (113).

ESR Measurements

When phosphorane 84, P(but)(phen)OPhF, was treated with three equivalents of NaOPhF below -80°C an ESR spectrum was obtained, showing at least eight lines, irregular in intensity, with an average spacing, \underline{a} 130 Gauss, at -164°C. Upon warming to room temperature the radicals disappeared.

When a trace of 1,2-dihydroxybenzene was treated with NaOPhF at -80°C a multi-line spectrum was obtained with a triplet structure, \underline{a} 4.1 Gauss, showing hyperfine splittings, \underline{a} 0.55 Gauss. Upon warming to room temperature the radicals disappeared.

An explanation could be that FPhO⁻ acts as an electron donor, either to another FPhO⁻ species or to the dioxybenzene-group (119). The absence of a large \underline{a}_F may indicate a π -radical

(120, 121). Two radicals (or more) might be present, especially in the case of phosphorane 84 with FPhO^- . It is possible that more reactions described in this work involve radicals.

Tetrabutylammonium p-fluorophenoxide (122)

Commercial tetrabutylammonium hydroxide (3.3 g, 40% aqueous solution) was shaken vigorously with a solution of p-fluorophenol (4 mmol) in trichloromethane (5cm^3). Separation of the layers and removal of the solvent followed by a period of two hours under reduced pressure (0.5 mmHg) at room temperature gave a yellow product.

δH 0.7-1.1 (12H,m), 1.1-1.9 (16H,m), 3.0 (8H,t,J 6 Hz), 6.47 (2H) and 6.60 ppm (2H).

The product was impure.

Caesium fluoride

Commercial caesium fluoride was dried at 240°C under reduced pressure (0.05 mmHg) for a period of six hours.

5.4 Isolation of P(6)

37 Attempted Preparation of $\text{P}(\text{chl})(\text{pin})(\text{OPhF})_2^-$ (42)

A mixture of 5',6',7',8'-tetrachloro-2-(p-fluorophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-spiro-2'-1',3',2'-benzodioxaphosphole (40 mmol), p-fluorophenol (40 mmol) and triethylamine (40 mmol) in diethyl ether (25cm^3) was set aside for two days at room temperature. The resulting solid was filtered off and washed with diethyl ether and dried under reduced pressure.

Elemental analysis and ^{31}P NMR spectroscopy indicated

that the product was the triethylammonium salt of the trischelate $P(chl)_2(pin)^-$ and not the required product. The mother liquid showed no trace of the required product either. m.p. 194-195°C, $C_{24}H_{28}Cl_8NO_6P$ requires C 38.9%, H 3.81% and N 1.89%; found C 39.1%, H 3.89% and N 1.87%.

$\delta P(DMF)$ -81.3 ppm.

Attempted preparations of trischelate phosphorus anions containing an oxazaphospholane ring.

Attempted Preparation of $P(phen)_2(Net)^-$

A solution of 2-N-methylaminoethanol (10 mmol) and triethylamine (10 mmol) in trichloromethane (10 cm³) was added to a stirred solution of 2-chloro-2,2'-spiro-1,3,2-benzodioxaphosphole (10 mmol, prepared according to (123)) at 0°C. After stirring for thirty minutes at 0°C the mixture was left overnight at room temperature. The resulting precipitate was filtered, washed twice with diethyl ether and treated (x2) with hot water, followed by washing with diethyl ether. The product was dried for one hour at 140°C under reduced pressure (0.2 mmHg).

The elemental analysis showed that the isolated product did not contain the oxazaphospholane ring and indicated that it was the triethylammonium salt of trischelate $P(phen)_3^-$ (decomposition above 236°C). $C_{24}H_{28}NO_6P$ requires C 63.0%, H 6.17% and N 3.06%; found C 62.2%, H 6.39% and N 2.90%.

$\delta P(DMSO)$ -82.5 ppm.

When the reaction was repeated with the disodium salt of 2-N-methylaminoethanol, the product had an identical

^{31}P NMR chemical shift, δP -32.9 ppm, to that quoted above.

Reaction of disodium salt of 1,2-dihydroxybenzene with one equivalent of $\text{P}(\text{chl})(\text{Net})\text{OPhF}$

When the reaction was carried out at -88°C the ^{31}P NMR spectrum showed initially two absorptions due to six-coordinate phosphorus anions, δP -85.1 and -91.8 ppm, in the ratio 3:1 respectively. Upon further mixing of the reagents the phosphorane was finally replaced by two species, δP -85.1 and + 17.3 ppm.

Discussion

It is possible that a trischelate anion containing an oxazaphospholane ring is produced initially, δP -91.8 ppm, but upon further reaction is converted into a trischelate anion containing catechol type ligands only (82, 124).

Attempted Preparation of $\text{P}(\text{eth})_2(\text{Net})^-$

A solution of 2-(p-fluorophenoxy)-2,2'-spiro-1,3,2-dioxaphospholan (2 mmol), δP -29.8 ppm (112), in diethyl ether (10 cm³) was added to a mixture of the disodium salt of 2-N-methylaminoethanol in diethyl ether (20 cm³) at -78°C . After stirring for thirty minutes at -78°C the solution was allowed to warm slowly to room temperature. The solid was filtered, washed with diethyl ether and dried at room temperature under reduced pressure (0.05 mmHg) for one hour. The resulting solid was highly sensitive to moisture.

Elemental analysis indicated that it was not the required product, found C 40.14%, H 5.25% and N 2.45% resulting in an empirical formula $(\text{C}_{19.1}\text{H}_{29.8}\text{N}_{1.00})_n$.

$\delta\text{P}(\text{DMSO})$ -85.7 ppm.

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Formation and Isomerisation Processes of Six-co-ordinate
Phosphorus Anions

by

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Summary

A series of spirophosphoranes was prepared in order to study different aspects of nucleophilic substitution at five-co-ordinate phosphorus. The phosphoranes were treated with nucleophiles under temperature controlled conditions and the reactions were monitored by fluorine and phosphorus n.m.r. spectroscopy.

The half-lives of the resulting phosphorides could be extended by increasing the electron withdrawing properties of the ligands and by introducing ligands with low lying empty orbitals.

Wherever possible nucleophilic attack was assisted by the greatest number of antiperiplanar lone pair interactions from the donor atoms (stereoelectronic effects). This led to the kinetically controlled formation of the trans-isomer of some six-co-ordinate bis(bidentate) phosphorus anions, which under thermodynamic conditions produced the more stable cis-isomer(s).

In some cases the trans-cis isomerisation proceeded via a dissociative mechanism, this involving a unidentate ligand. Some cis-phosphorides underwent intramolecular isomerisation processes, possibly via trigonal prismatic intermediates.

Six-co-ordinate phosphorus anions containing a phosphorinane ring or non-equivalent bidentate/unidentate ligand donor atoms were short-lived. Increasing steric hindrance by introduction of substituents onto a donor atom disfavoured the formation of phosphorides.

Only one equilibrium between a phosphorane and a phosphoride became rapid on the n.m.r. timescale on increasing the temperature; all other equilibria were slow on the n.m.r. timescale.

Introduction of an oxazaphospholane ring into a phosphorane decreased the half-life of the generated phosphoride and introduced in some cases a rigidity at the nitrogen centre.

A review of fluorine and phosphorus n.m.r. data of chemical shifts and coupling constants of six-co-ordinate phosphorus anions is given.