Geminally Bis(supermesityl) Substituted Phosphorus Compounds and A Study of 5,6-Substituted-Acenaphthenes

By

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A thesis submitted in partial fulfilment for the award of

Doctor of Philosophy

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Declaration

I, Conor Gareth Edward Fleming, hereby certify that this thesis, which is approximately 39,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

I was admitted as a research student in September 2008 and as a candidate for the degree of Doctor of Philosophy in August 2009; the higher study for which this is a record was carried out in the University of St Andrews between 2008 and 2013.

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Abstract

This thesis describes the effect of placing a phosphorus atom in a sterically strained environment with particular emphasis on the geminal disubstitution of two 2,4,6-tri-*tert*-butylphenyl (Mes*) groups on a single phosphorus centre and intramolecular sub-van der Waals interactions between *peri*-substituted atoms on naphthalene and acenaphthene.

Chapter 2 outlines the reactive chemistry of a sterically encumbered phosphinic chloride $(\mathrm{Mes^*})_2\mathrm{P(=O)Cl}$, which was shown to have extremely low reactivity at the phosphorus centre. It has however, been demonstrated that synthetically significant transformations are possible. The phosphine oxide $(\mathrm{Mes^*})_2\mathrm{P(=O)H}$ and a secondary phosphine $\mathrm{Mes^*(2,4\text{-}}t\mathrm{Bu_2C_6H_3)PH}$ were obtained from the reduction of $(\mathrm{Mes^*})_2\mathrm{P(=O)Cl}$ with hydridic reagents under forcing conditions. The corresponding phosphinite was acquired from the deprotonation of $(\mathrm{Mes^*})_2\mathrm{P(=O)H}$, which furnished very crowded tertiary phosphine oxides $(\mathrm{Mes^*})_2\mathrm{P(=O)R}$ (R = Me and Et) on reactions with electrophiles. We have been unable to chlorinate or deprotonate $\mathrm{Mes^*(2,4\text{-}}t\mathrm{Bu_2C_6H_3)PH}$, however the reaction with elemental sulfur afforded the affiliated phosphine sulfide $\mathrm{Mes^*(2,4\text{-}{}^tBu_2C_6H_3)P(=S)H}$, albeit under forcing conditions. Our computations (B3LYP and M06-2X level) show that strain energies of geminally substituted compounds are extremely high (180 to 250 kJ $\mathrm{mol^{-1}}$), the majority of the strain is stored as boat distortions to the phenyl rings in Mes* substituents.

Chapter 3 describes the strain inherent with non-bonding atomic distances shorter than the sum of their van der Waals radii, specifically heteroatom substitution of the *peri*-positions of naphthalene and acenaphthene. It also documents the importance of amine protecting groups in chlorophosphine chemistry. The preparation of $\mathrm{Ace[P(Ph)N(^iPr)_2]Br}$ (Ace = acenaphthene-5,6-diyl) and $\mathrm{Ace[P(Ph)N(^iPr)_2]_2}$, plus the elucidation of the molecular structures of $\mathrm{Mes^*P[N(CH_3)_2]_2}$, $\mathrm{Ace[P(Mes)N(^iPr)_2]Br}$ (Mes = 2,4,6-tri-methylphenyl) and $\mathrm{Ace[P(^tBu)N(Et)_2]Br}$ sufficiently demonstrate the ring distorting characteristics of structurally encumbered molecules. The reaction of $\mathrm{Ace[P(Ph)N(^iPr)_2]Br}$ and $\mathrm{Ace[P(Ph)N(^iPr)_2]_2}$ with a methylating agent was also investigated.

Acknowledgements

First and foremost, I would like to thank my supervisor Dr. Petr Kilian who has provided expert guidance and support throughout my time at St Andrews. I also thank him for his assistance in producing this thesis. Any errors and/or omissions contained within are attributable solely to me. Furthermore, I would like to thank Profs. Alex Slawin and Derek Woollins for their help and support through the years. I am indebted to our former group member Dr. Piotr Wawrzyniak for his practical help, especially at the start of my research and to Dr. Fergus Knight for his help towards the end of it. I would also like to thank Caroline Horsburgh (MS), Stephen Boyer (EA) and Melanja Smith & Dr. Tomas Lebl (NMR spectroscopy) for their technical expertise.

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Abbreviations

Ace	acenaphthene-5,6-diyl
Å	ångström (10^{-10} m)
~	approximately
Ar	aromatic group
B3LYP	Becke, three-parameter, Lee-Yang-Parr
br	broad (NMR spectroscopy, IR & raman)
^{n}Bu or *n*Bu	Butyl, *n*-C_4H_9
^{t}Bu or *t*Bu	tertiary butyl, *tert*-butyl or 2-methylpropan-2-yl
Calc.	calculated
δ	chemical shift (NMR spectroscopy)
C_q	quaternary carbon
°	degrees
°C	degree Celsius
COSY	correlation spectroscopy
d	doublet (NMR spectroscopy)
dd	doublet of doublets (NMR)
ddd	doublet of double doublets (NMR spectroscopy)
dt	doublet of triplets (NMR spectroscopy)
DB	Dewar benzene, bicyclo[2.2.0]hexa-2,5-diene
DCM	methylene chloride
DIBAL	diisobutylaluminium hydride
DMF	dimethylformamide
dquart	doublet of quartets (NMR spectroscopy)
dquint	doublet of quintets (NMR spectroscopy)
DQF	double quantum filtered
Et	ethyl, C_2H_5
EPR	electron paramagnetic resonance
ES	electrospray
4c-4e	Four centre-four electron
g	grams
HF	Hartree–Fock

HMBC	heteronuclear multiple bond correlation spectroscopy
HSQC	heteronuclear single quantum correlation spectroscopy
$\cdots$	interaction between two centres not formally bonded
i	ipso
IR	infra-red spectroscopy
J	coupling constant (NMR spectroscopy)
K	kelvin
m	medium (IR & raman)
m	meta
M	molar
M	molecule (MS)
m	multiplet (NMR spectroscopy)
m/z	mass to charge ratio
Me	methyl, CH_3
Mes	2,4,6-tri-methylphenyl, mesityl
Mes*	2,4,6-tri-*tert*-butylphenyl, supermesityl
Mes*-Br	2-bromo-1,3,5-tri-*tert*-butylbenzene
Mes*-Li	2-lithio-1,3,5-tri-*tert*-butylbenzene
MHz	megahertz
ml	millilitres
mmol	millimoles
mol	moles
mp	melting point
MS	mass spectrometry
Nap	naphthalene-1,8-diyl
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance
o	ortho
P(III)	trivalent phosphorus
P(V)	pentavalent phosphorus
P^{III-}	phosphorus in oxidation state -3
P^{I}	phosphorus in oxidation state +1
P^{III}	phosphorus in oxidation state +3
P^{V}	phosphorus in oxidation state +5

p	para
Ph	phenyl, C_6H_5
Pn	pnictogen
ppm	parts per million
^{i}Pr or *i*Pr	isopropyl or propan-2-yl
quart	quartet
R	any alkyl or aryl group
s	singlet (NMR spectroscopy)
s	strong (IR & raman)
t	triplet (NMR spectroscopy)
tt	triplet of triplets (NMR spectroscopy)
THF	tetrahydrofuran
TMEDA	N,N,N′,N′-tetramethylethane-1,2-diamine
TMS	tetramethylsilane
triflate	trifluoromethanesulfonate, -OTf
Trip	2,4,6-tri-*iso*propylphenyl
·	unpaired electron
UV	ultra-violet
υ_{max}/cm^{-1}	wavenumbers
vs	very strong (IR & raman)
w/w	ratio of weight

Preamble

"The chemists are a strange class of mortals, impelled by an almost insane impulse to seek their pleasures amid smoke and vapour, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly that may I die if I were to change places with the Persian king."

— Johann Joachim Becher, *Physica subterranea* (1667)

Chapter 1 – Introduction to Phosphorus Chemistry and Bulky Substituents

1. Phosphorus and its chemistry

a. Phosphorus: occurrence and uses

The name phosphorus derives from the Greek Φωσφόρος (light carrier) which is due to the chemiluminescence of white phosphorus (or more correctly the partially oxidised products of it) when exposed to oxygen. Elemental phosphorus is not found in nature due to the high reactivity of its various elemental forms; white, red and black. Most natural sources have phosphorus atoms in the highest +5 oxidation state, this includes phosphate mineral deposits and calcium phosphate [$Ca_3(PO_4)_2$] in bone matter. Phosphates are used in large quantities in industry for the production of fertilizers, food additives and herbicides; the structural backbone of DNA and RNA is provided by phosphates making phosphorus an essential element for life. It is also present in phospholipids which form cell membranes and adenosine-5'-triphosphate (ATP) which transports chemical energy within cells.

There is a large array of laboratory applications for phosphorus compounds in many of the diverse disciplines of both organic and inorganic chemistry. An example is the production of carbon-carbon double bonds to make alkenes through the Wittig reaction, whose driving force is the creation of a strong phosphorus-oxygen double bond. The strength of the P=O double bond was a major factor in the research work presented here. The use of phosphines as ligands on metal centres is another large area of study with these trivalent phosphorus centres coordinating through their available lone pairs. There is a large body of literature on the synthesis of phosphines, phosphites, phosphates and well as some less common lower oxidation state compounds; we aim as part of this research effort to add some new and interesting structures to this chemical canon.

b. Phosphorus nomenclature

Phosphorus atoms display a range of oxidation states from five to minus three and these are reflected in the naming of such structures.

Phosphoric acid (H_3PO_4), phosphates ($O=P(OR)_3$), phosphonates ($O=PR(OR)_2$) and phosphinates $O=PR_2(OR)$ are all pentavalent phosphorus species. The suffixes oxide (e.g. trialkylphosphine oxide) or oxyhalide (e.g. phosphorus oxychloride) also indicate phosphorus in its highest oxidation state. Pentavalent phosphorus compounds with no oxygen exist and some examples are phosphoranes PR_5 and phosphorus pentahalides PX_5, see Figure 1.

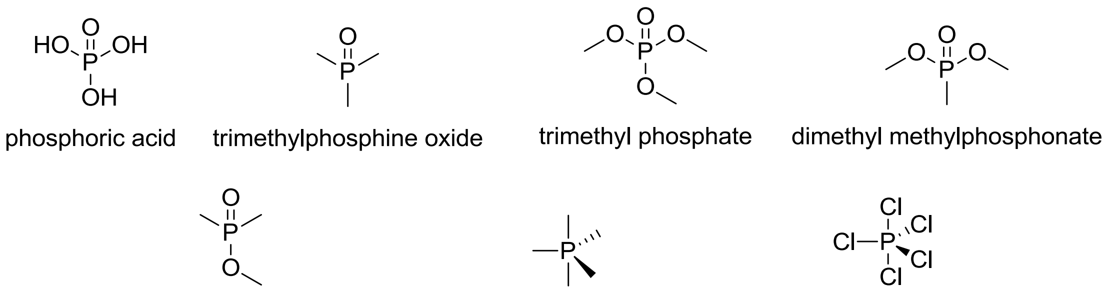


Figure 1 Examples of P^V compounds

Phosphonium cations are positively charged P^V compounds often formed via the alkylation of phosphines, which is a formal oxidation. They are also an important precursor to phosphoranes which are electroneutral mesomeric forms of phosphorus ylides, used in Wittig reactions. These are accessed through a deprotonation of a phosphonium salt, see Figure 2.

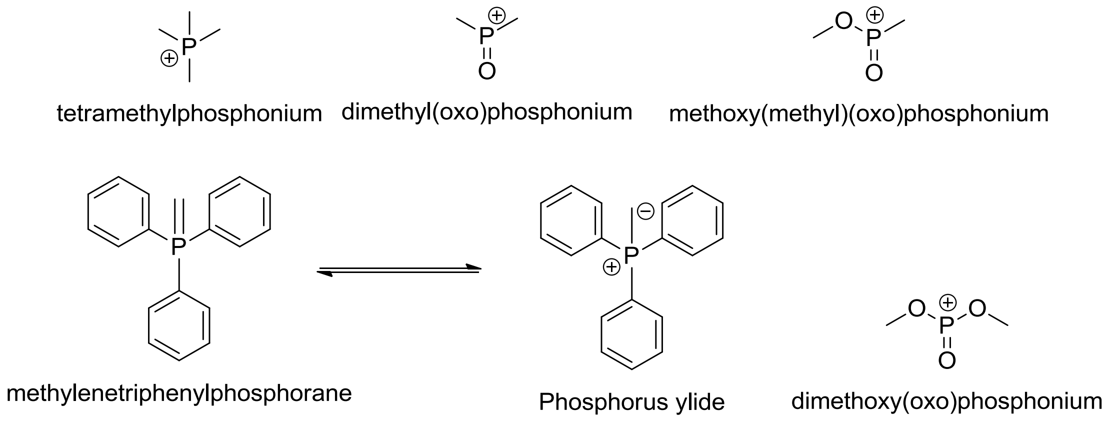


Figure 2 Examples of phosphonium and phosphorane structures

Examples of P^{III} organophosphorus compounds include phosphorous acid (H_3PO_3), phosphites ($P(OR)_3$), phosphonites ($P(OR)_2R$) and (oxy)phosphines ($P(OR)R_2$). Compounds devoid of oxygen in the +3 oxidation state are for example, phosphines PR_3 and phosphorus halides PX_3, see Figure 3.

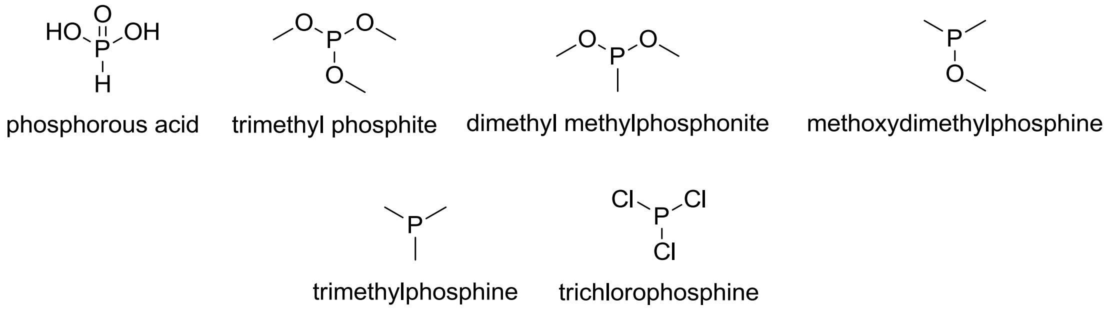
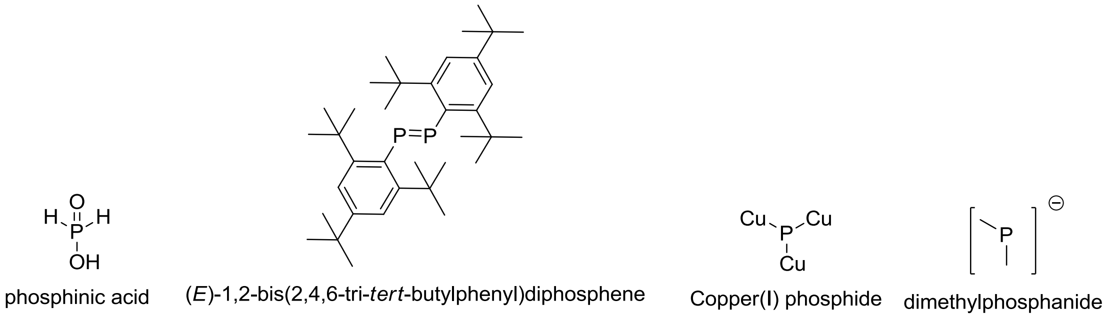


Figure 3 Examples of P^{III} compounds

Lower valence species are rarer but not unknown. Hypophosphorous acid (sometimes called phosphinic acid) is a monobasic P^I oxoacid. Other electroneutral P^I mono-organophosphorus compounds are rare, however stable diphosphenes have been presented in the literature.[1] Monovalent organophosphorus anions are called phosphanides (e.g. lithium dimethylphosphanide, $LiPMe_2$). Phosphides are compound of phosphorus with less electronegative elements, such as Na_3P and other metals, these contain phosphorus in oxidation state -3, see Figure 4.


phosphinic acid

(*E*)-1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene

Copper(I) phosphide

dimethylphosphanide

Figure 4 Examples of compounds with P^I and lower phosphorus oxidation states

Phosphines and phosphine oxides were the main focus during this research work. PH_3 is known simply as phosphine. The formal replacement of one or more hydrogen atom(s) by alkyl or aryl group(s) results in compounds known as primary PH_2R, secondary PHR_2 or tertiary PR_3 phosphines. The presence of phosphorus-hydrogen bonds makes a vast difference to the reactivity of these compounds, their air stability and the splitting pattern observed in ^{31}P NMR spectroscopy. See Figure 5 and NMR spectroscopic discussion.

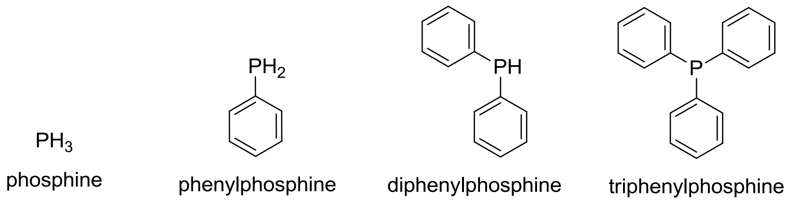


Figure 5 Nomenclature of phosphines

c. Phosphorus chemistry & reactions

Phosphorus atoms have an electronegativity of 2.19 on the Pauling scale. Phosphorus forms covalent bonds with a wide range of main group elements and hydrogen. Furthermore, the lone pairs present on phosphines are heavily relied upon to form dative bonds in organophosphorus metal-ligand chemistry. Some of these phosphorus compounds display sensitivity to oxygen and moisture so reactions must be conducted under an inert atmosphere such as N_2 or Ar. Phosphorus can adopt a wide range of geometries depending on the number and type of substituents attached to it. The simplest phosphorus centred compound PH_3 has a trigonal pyramidal geometry; as does PCl_3. Other geometries seen include distorted tetrahedral ($POCl_3$), trigonal bipyramidal (PCl_5) and octahedral {$[PCl_6]^-$}, see Figure 6.

Figure 6 Geometries which phosphorus can display

Tetrahedral phosphorus compounds can display chirality when four different substituents are bonded to it, just like asymmetric carbon centres, see Figure 7.

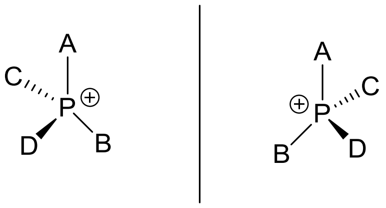


Figure 7 Chirality of tetrahedral phosphorus

Trigonal pyramidal structures also display optical isomerism as, for example the energy barrier to inversion (akin to an umbrella turning inside out) for PH_3 is too high (155.7[2] to 159.9[3] kJ/mol) for a noticeable rate of the inversion below about 100 °C. This is in contrast to NH_3 which undergoes rapid interconversion at room temperature with an energy barrier of 24.2 kJ/mol.[4,5]

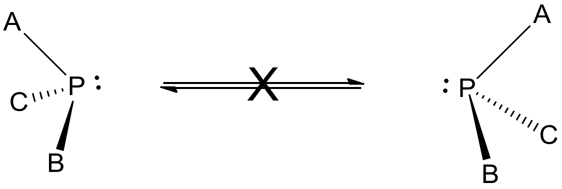


Figure 8 The reluctance of trivalent phosphorus to invert.

d. Phosphorus-oxygen double bonds

Phosphorus is noted for its oxophilicity. There is however controversy over the exact nature of P=O bonds.[6] It could be viewed as a formal polarised double bond with the more electronegative oxygen drawing electron density away from the phosphorus or as a P^{III} centre which donates its lone pair into an unoccupied orbital on the oxygen more akin to phosphines donation onto metals. The formation of a phosphorus-oxygen bond is the driving force behind the Wittig reactions. It is also the reason for the tautomerisation of certain trivalent P^{III} compounds to more energetically favourable pentavalent forms. The affinity phosphorus has for oxygen and the strength of the resultant P=O bond (544 kJ/mol) means that many trivalent compounds P^{III} are readily oxidised. By the same token it means that quite powerful reducing agents are needed to break this linkage and to synthesise P^{III} species. A strong hydridic reducing reagent such as $LiAlH_4$ is commonly required to achieve such reductions. A P=S double bond is much weaker (335 kJ/mol) in comparison. This is due to the larger size and lower electronegativity of the sulfur atom (2.58 vs. 3.44 for oxygen). The phosphorus-sulfur double bond is therefore much less polarised.

e. ^{31}P NMR spectroscopy and variable temperature measurements

Phosphorus is monoisotopic, the only natural isotope ^{31}P has a nuclear spin ½ with a high magnetogyric ratio. ^{31}P NMR spectroscopy is an indispensable tool for synthetic chemists as much structural information can be extracted from relatively simple ^{31}P NMR spectra. The use of deuterated solvents is not necessary for anything other than locking purposes. Aliquots of ongoing reactions can therefore be taken and interpreted to assess how the reaction is progressing; for monophosphorus compounds there will be only one starting material peak and one desired product peak. Thus in many respects it is analogous to TLC in organic chemistry. ^{31}P couples to other NMR spectroscopically active nuclei such as ^{1}H and ^{19}F and the splittings observed are a valuable tool in the elucidation of structure. For example, primary (triplet), secondary (doublet) and tertiary (singlet) phosphines are easy to differentiate between due to their splitting patterns. ^{31}P peaks can split and in turn be split by elements whose NMR spectroscopically active isotope is less than 100 % abundant, such as ^{195}Pt (33 %), ^{13}C (~1 %) and ^{77}Se (~7.6 %). This gives rise to satellite peaks in ^{31}P NMR spectroscopy, which can be used to reveal additional structural and well as connectivity information. Integration of the peaks is an accurate measure of the proportion of different phosphorus environments present as long as no decoupling techniques are used and full relaxation of FID is ensured.

Variable temperature NMR spectroscopy is a valuable technique in the spectroscopic toolbox. When the temperature of a particular molecular system is decreased, the thermal energy of the system is also lowered. This may result in the rotational barrier around a particular bond being insurmountable on an NMR spectroscopy timescale. This gives rise to anisochronicity of certain atoms which would normally be magnetically equivalent due to rotation. The coalescence temperature (T_C) is the point at which these distinct peaks begin to converged to become one peak. The energy of the rotational barrier (ΔG) is calculated via the Gutowsky-Holm and Eyring equations,[7] see Figure 9. The observation of ΔG allows the chemical environments around certain atoms to be probed.[8] Conversely, samples can be heated to allow them to overcome the rotational barrier around a particular bond which will sharpen broad peak, allowing them to be recorded and studied more readily.

$$K_C = \frac{\pi}{\sqrt{2}}\Delta\upsilon \qquad\qquad K_C = \frac{k_B T_C}{h} e^{-(\frac{\Delta G}{RT_C})}$$

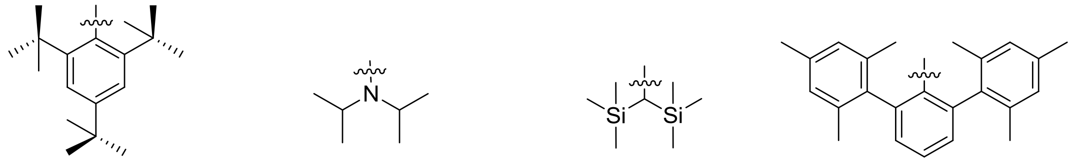
Where:
K_C = Rate constant
$\Delta\upsilon$ = The difference between the two peaks as the chemical-shift
k_B = Boltzmann constant
T_C = Coalescence temperature
H = Planck's constant
ΔG = Rotation-energy barrier
R = Gas constant

Figure 9 Gutowsky-Holm (left) and Eyring (right) equations

2. The use of sterically hindering substituents

a. Reactive species and steric protection

Compounds can be reactive for many different reasons such as their susceptibility to oxidation or the availability of a labile bond with a suitable leaving group. A number of methods have been developed to allow reactive species to be obtained and isolated more easily. The application of steric hindrance involves using relatively inert bulky groups to make accessing potential reaction centres difficult because they act as a shield around the reactive species. Groups such as 2,4,6-tri-*tert*-butylphenyl (colloquially known as supermesityl or Mes*),[9,10] bis(trimethylsilyl)methyl, diisopropylamino and motifs with multiple aromatic rings [11] are excellent at providing this protection, for examples see Figure 10.



1,3,5-tri-*tert*-butylphenyl, Mes*

diisopropylamino

bis(trimethylsilyl)methyl

2,6-dimesitylterphenyl

Figure 10 Examples of common protecting groups

These sterically protected manifolds when put in place make the main group centre more resistant to certain reaction types such as dimerisation; the presence of this steric bulk makes formation of a dimer less energetically favourable.[12] Due to the fact that these protected species are stable under normal laboratory conditions the full toolbox of spectroscopic and crystallographic methods are available.

The use of steric protection compares favourably to the other acknowledged procedures for studying reactive species. In matrix isolation a reactive molecule is frozen in a spectroscopically transparent inert material and can not move or dimerize by reacting with another molecule of the reactive species. Spectroscopic techniques are limited to infrared and UV-visible spectroscopy.

In chemical trapping, a second reactive compound is present in the reaction vessel with the precursor to what you want to study. The initial reaction to generate the reactive species is followed by an immediate second reaction which snares the reactive compound.[13] For example in Figure 11, the 1,3-diene reacts with the dienophile $GeMe_2$ and thus traps it. All spectroscopic and crystallographic methods are available as the final product is stable. However the product which is recovered is not exactly what is under investigation and so spectroscopic information must therefore be inferred.

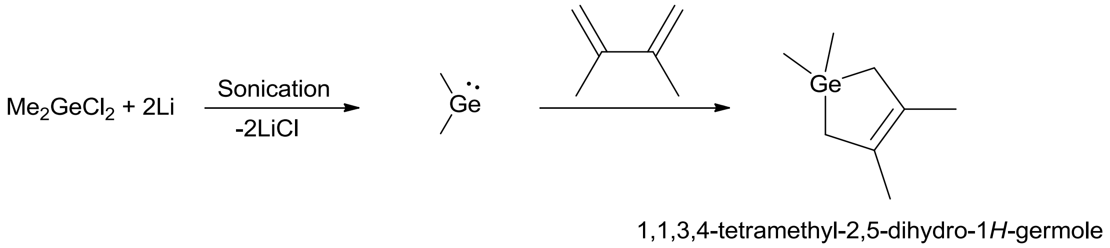


Figure 11 An example of chemical trapping

The use of high vacuum allows reactive species to exist without interacting with other molecules. It bestows only limited access to spectroscopic examination such as IR and microwave spectroscopy. This method is frequently used in astrophysics[14](to give one example) to study the chemical composition of far off bodies. Space, with a density of approximately 1 atom per cubic centimetre,[15] low temperature and little O_2 can be conceptualised as the ultimate Schlenk line. Many seemingly impossible compounds have been observed there. The disadvantage inherent with high vacuum is the difficulty of working with such compounds in a standard synthesis laboratory context. The use of specialised equipment increases complexity and precludes the scaling up of such reaction to a preparative or potentially commercial dimension.

b. Sterically protected phosphorus compounds in the literature

As has been alluded to before,[1] diphosphenes have been prepared previously and these unusual P^I compounds are stabilised to a reasonable degree by the use of bulky groups.[16,17] These compounds are made from the corresponding dichlorophosphine which are reductively coupled to form the phosphorus-phosphorus double bonded structures. Diphosphenes display some of the lowest field (i.e. highest ppm values) in ^{31}P NMR spectroscopy (δ_P 494 for Mes*P=PMes*,[16] δ_P 598.6 for $(Me_3Si)_3CP=PC(SiMe_3)_3$,[17] see Figure 12. The rarity of the phosphorus-phosphorus double bond is the result of them being energetically unfavourably and thus their study has not been a major branch of main group element research.

(*E*)-1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene

(*E*)-1,2-bis(tris(trimethylsilyl)methyl)diphosphene

Figure 12 Some examples of diphosphenes

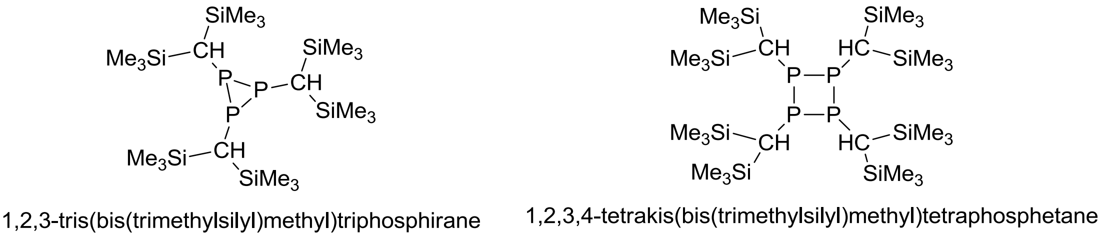
These diphosphenes mostly adopt a trans configuration in the solid state to avoid steric clashes. The phosphorus-phosphorus bond lengths are 2.024(2) Å for

Mes*P=PMes* and 2.004(6)-2.014(6) Å for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ respectively, which correlates well with the sum of double bond covalent radii (2.00 Å).[18,19] This is a clear indication that a double bond is formed. These compounds are stable enough to be handled in air. Other variations of symmetrical diphosphenes have been produced with other substituents on the phosphorus, such as $(Me_3Si)_2NP{=}PN(SiMe_3)_2$[20] and $(^tBuMe_2Si)_2NP{=}PN(Si^tBuMe_2)_2$.[21] These have proved to be less stable in air and tend to dimerise. Unsymmetrical structures have also been synthesised,[22,23] see Figure 13.

(*E*)-1-mesityl-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene (*E*)-1-(2,4,6-tri-*tert*-butylphenyl)-2-(tris(trimethylsilyl)methyl)diphosphene

Figure 13 Some examples of unsymmetrical diphosphenes made from Mes^*PH_2

The synthesis of unsymmetrical compounds is achieved by treating a stoichiometric mixture of Mes^*PH_2 and $RPCl_2$ with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). Mes*P=PMes and $Mes^*P{=}PC(SiMe_3)_3$ can be handled in air.[18] A slight decrease in substrate bulk can have a big impact on the product recovered from reductively coupling of dichlorophosphine. The reaction of $(Me_3Si)_2CHPCl_2$ with Mg yields a mixture of oligophosphines $((Me_3Si)_2CHP)_3$ and $((Me_3Si)_2CHP)_4$[18], as shown in Figure 14.



1,2,3-tris(bis(trimethylsilyl)methyl)triphosphirane

1,2,3,4-tetrakis(bis(trimethylsilyl)methyl)tetraphosphetane

Figure 14 Oligomerised products of reductive coupling of $(Me_3Si)_2CHPCl_2$

The protection of reactive monophosphorus compounds is achieved in a similar way. Groups such as Mes* and terphenyls offer a lot of steric protection by encasing the reactive phosphorus centre, which makes the formation of oligomeric species energetically highly unfavourable. This shielding nature has been exploited to synthesise extremely sterically hindered phosphines. Numerous examples of the facile reaction of terphenyl lithiums with PCl_3[24] or alkyl- and aryldichlorophosphine[25] have been reported in the chemical literature, see Figure 15. These can then be the starting point for further synthesis such as reductive coupling to produce a range of diphosphenes or as ligands for metals.[26,27] Structure which utilise even bulkier terphenyls, such as $2,6\text{-}(2,4,6\text{-}{}^{i}Pr_3C_6H_2)_2C_6H_3$, than those shown in Figure 14 have been reported,[28] which indicates that it is a valuable motif for the achievement of steric protection.

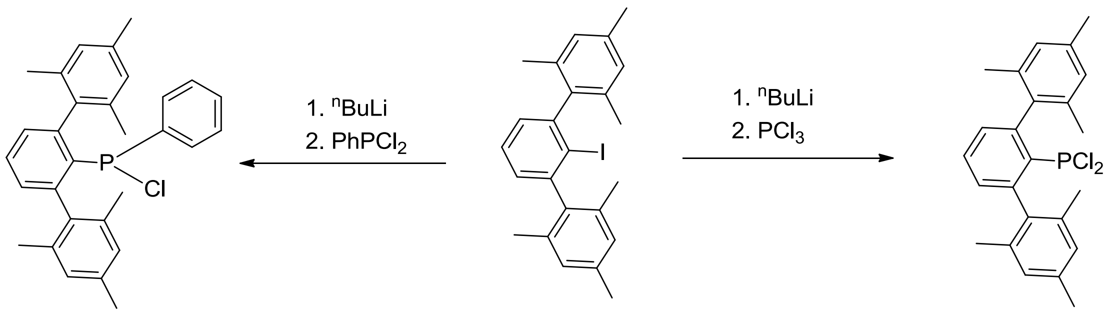


Figure 15 Reactions of terphenyls with chlorophosphines

c. Supermesityl and 2,4,6-triisopropylphenyl

2,4,6-tri-*tert*-butylphenyl (Mes*) is one of the most popular choices of sterically protective group in the chemical canon with the Cambridge Structural Database holding around 1500 structure which contain one or more supermesityl group; almost half of these involve a phosphorus atom bonded directly to a supermesityl group. 2-Bromo-1,3,5-tri-*tert*-butylbenzene (Mes*-Br) is made in a straightforward manner in large scale from benzene via a Friedel–Crafts alkylation[29] followed by a bromination.[30,31] This is the standard precursor used to introduce the Mes* motif onto a wide range of atomic centres. Also, the *ortho*-positioned ^{t}Bu groups provide a high degree of steric hindrance by flanking the reactive centre; these encapsulating properties allow the production of many fascinating structures and bonding configurations. The geometric constraint which Mes* substituents impose are particularly favourable for preventing the oligomerisation of low-valent species, however the presence of a Mes* groups affects the reactivity patterns of the more mundane phosphorus species in which it is attached to. The reaction of two equivalents of 2-lithio-1,3,5-tri-*tert*-butylphenyl with PCl_3 yields only the single addition product dichloro(2,4,6-tri-*tert*-butylphenyl)phosphine **1**.[32] Geminal disubstitution of two Mes* groups onto a central phosphorus atom is prevented by the steric interaction between ^{t}Bu groups positioned *ortho* to the reaction site and thus chlorobis(2,4,6-tri-*tert*-butylphenyl)phosphine **2** is not recovered, see Figure 16. The implication of this will be dealt with in Chapter 2.

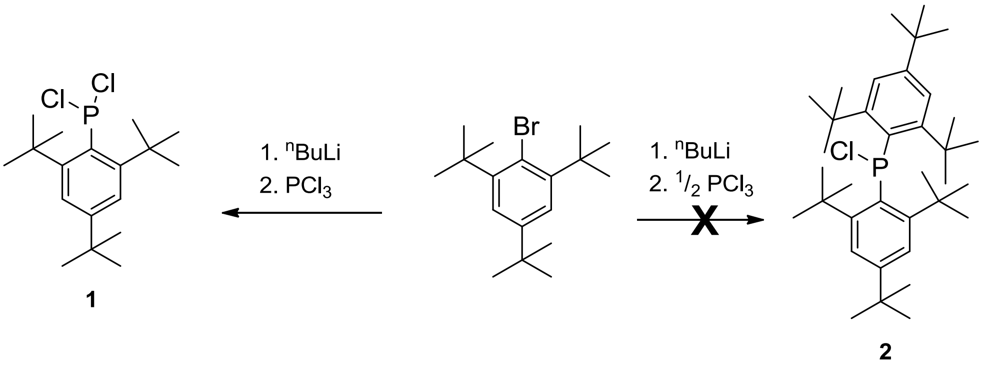


Figure 16 The reaction of Mes*-Li with PCl_3

Although the supermesityl group is large, halophosphines bearing it are highly reactive and will interact if the sterics allow. The dichloroarylphosphine Mes*PCl_2 can undergo further reaction such as the reductive coupling to a diphosphene[16] or can be treated with another nucleophile.[33]

Supermesityl groups also provide electronic stabilisation by delocalisation of electron density over the aromatic ring. Delocalisation over the conjugated system of disupermesityldiphosphene (Mes*P=PMes*) gives rise to its red-orange colour.[1,18]

Sterically bulky protecting groups in general (and Mes* in particular) have been widely used in low co-ordination main group chemistry and the stabilisation of open shell species. Their role is this regard has been reviewed recently.[34,35,36] As has been mentioned before, a relatively small change in the bulk of the protective group can have a profound effect on the chemistry observed. An exemplification of this is the contrasting reactivity of metalated Mes* and 2,4,6-tri-*iso*propylphenyl (Trip) groups with pnictogen trihalides (PnX_3). As seen before,[32] the reaction of Li-Mes* with PCl_3 affords the single addition product **1** exclusively; on the other hand the respective tris(2,4,6-triisopropylphenyl) phosphine, arsine, stibine and bismuthine have been isolated in moderate to poor yields from reactions of three equivalents of Cu-Trip and $PnCl_3$,[37] see Figure 17.

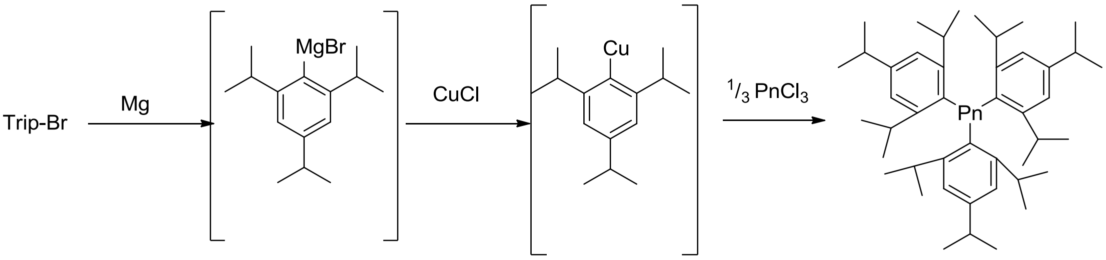


Figure 17 Synthesis of $Trip_3Pn$

Furthermore, Trip substituents have been used to compose a range of extremely hindered tertiary phosphines with either one or two terphenyl groups also attached. These species are synthesised at low yields by the reaction of arylcopper(I) reagents with bulky diarylphosphine chlorides,[38] see Figure 18.

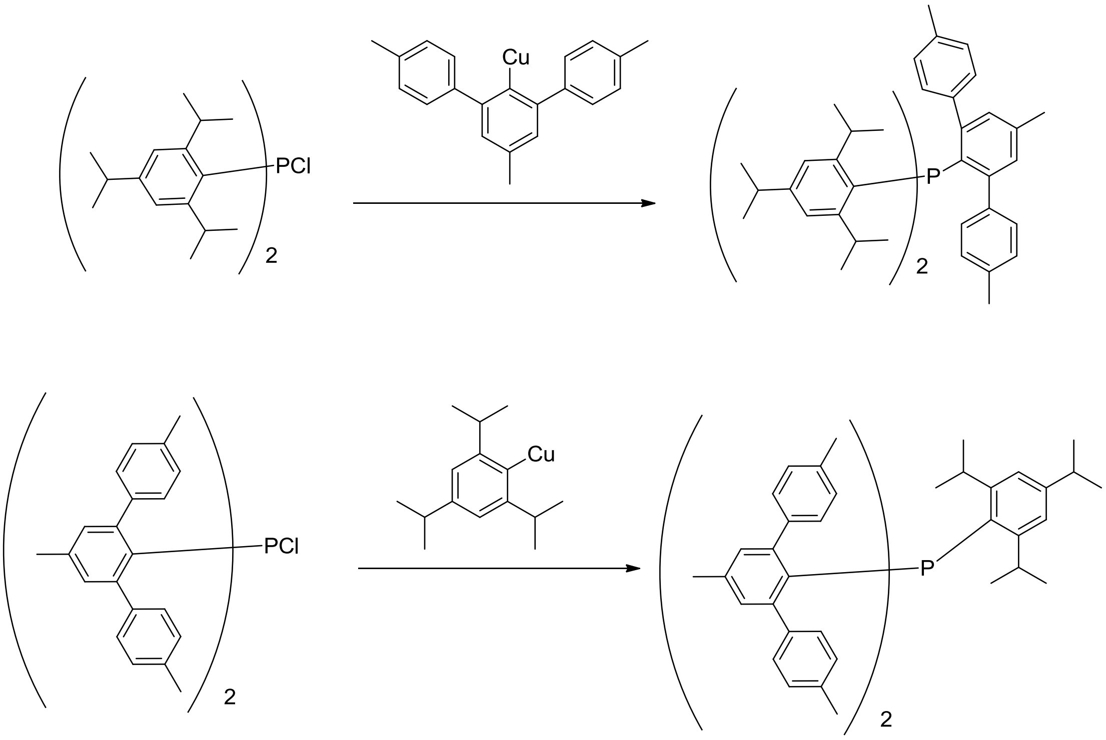


Figure 18 Mixed Trip and Terphenyl tertiary phosphines

There has been some research work into the use of other bulky protecting groups such as 2,6-bis(dimethylsilyl)phenyl, which share the flanking protective motif of Mes*.[39,40] There are of course a myriad of sterically bulky group in synthetic use today, from aromatic systems to amino and silyl groups,[41] it is the prerogative of the researcher what is the most suitable system to be utilised.

3. Main group Radicals

a. Introduction to main group radicals

Main group radicals are generally considered to be transient species whose lifetimes are brief. They may appear as reactive intermediates that quickly proceed to a more stable product. The triphenylmethyl [$(C_6H_5)_3C\cdot$] radical was synthesised by Gomberg[42] in 1900 and the structure was successfully elucidated in 1968.[43] This was the first persistent carbon centred radical produced and opened up new possibilities for synthesising stable and persistent main group centred radicals.

b. Radical nomenclature and generation

Griller and Ingold proposed a systematic way of categorising carbon centred radicals:[44]

Stable radicals are those that can be stored and worked with under ordinary laboratory condition; no special storage precautions beyond the exclusion of moisture and oxygen should be required.

Persistent radicals require special precaution to prevent decomposition such as low concentration in a solution and/or at low temperature or low pressure.

This categorisation could be equally applied to other main group radicals.

Main group radicals have been adequately reviewed recently[35,45] so we will not dwell on the matter. Radicals can be generated via a one electron reduction/oxidation to yield a radical anion/cation.[46] They can also be produced via thermolysis, photolysis[47] or radiolysis of suitable precursors.

c. Phosphorus radicals nomenclature

Like every other main group element the synthesis of novel persistent phosphorus radicals has been the subject of academic curiosity for some time. There have been many leaps forward in the field of persistent and stable P-centred radical chemistry since the first compounds were reported in 1966.[48] These have been characterised and catalogued, but this is an area of study which is still in its infancy. The further chemistry of these radicals has not been developed.[49] Figure 19 summarises the naming conventions of phosphorus radicals.

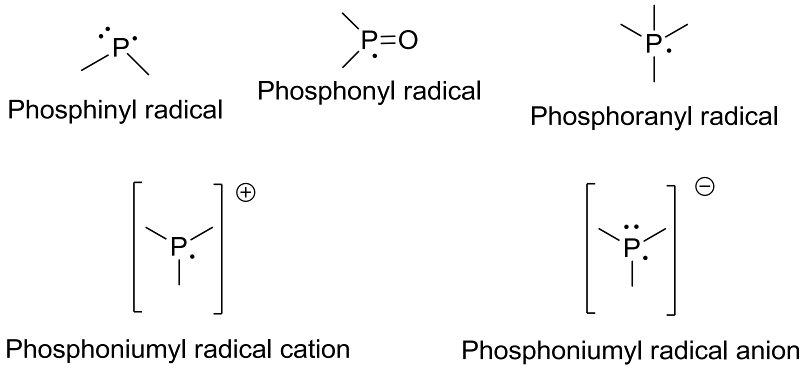


Figure 19 Phosphorus radical nomenclature[36]

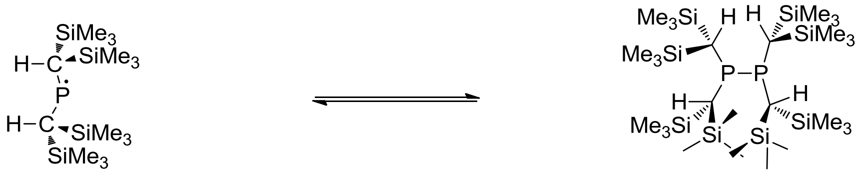
d. Phosphorus radical examples

The so-called “jack-in-the-box” compounds[50,51] have been developed in the group of Lappert. These phosphinyl radicals show good persistence in solution and gas phase, see Figure 20.

bis(bis(trimethylsilyl)methyl)phosphinyl   *N*,*N*-diisopropyl-*N*,*N*-bis(trimethylsilyl)phosphinyldiamine

Figure 20 Examples of jack-in-the box compounds

The key to their stability is the large bulky substituents attached to the phosphorus centre. The forming of their respective dimers in the solid state necessitates a conformational change from syn/syn to syn/anti to allow more effective packing. As a result of this change the solid diphosphine dimer acquires a large potential energy reservoir due to the bulky ligands being restricted, see Figure 21.



bis(bis(trimethylsilyl)methyl)phosphinyl   1,1,2,2-tetrakis(bis(trimethylsilyl)methyl)diphosphine

Figure 21 Packing in $[(Me_3Si)_2CH]_2P\text{-}P[CH(Me_3Si)_2]_2$

In the dimer there is significant crowding both between groups attached to the same phosphorus and between those bonded to the other phosphorus. When melting of the solid dimer occurs, the P-P bond breaks and the monomers spring apart, hence jack-in-the-box.

The sterically hindered diphosphene Mes*P=PMes* can undergo transformation to a diphosphanyl radical in the presence of a radical initiator.[9,10] see Figure 22. The diphosphanyl radical where R = Me is stable enough to be isolated as a solid,[52] when stored below -30^{o}C with about 10% of it being in dimer form. In solution (3 x 10^{-2} molL^{-1} in n-hexane) it has a half life of 90 minutes at 25 °C.[52]

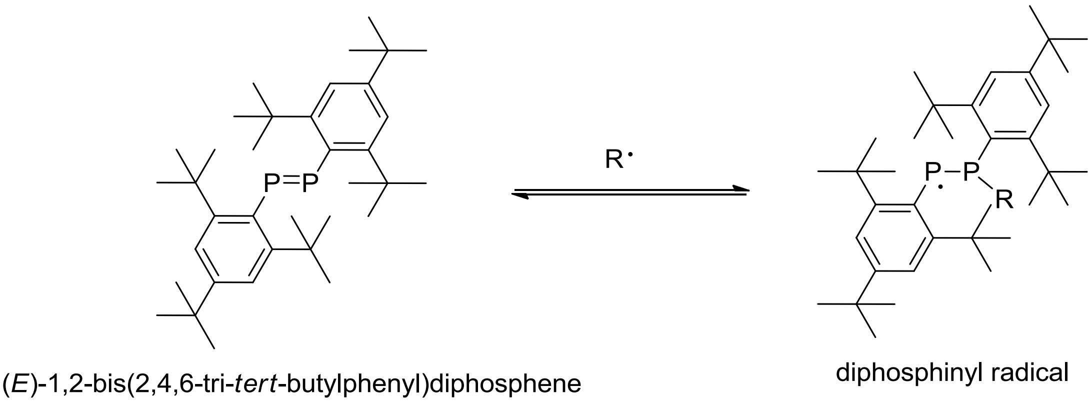


Figure 22 Radical derived from Mes*P=PMes*

The R· groups is typically generated photochemically in situ from a precursor. We were also interested to note the isolation and characterisation of the bis(terphenyl) system 1,2-bis(2,6-dimesitylterphenyl)diphosphene,[53] which has not as of yet been the basis for main group radical chemistry.

A 1,3-diphosphaallyl radical has an unpaired electron which is delocalized between two non-adjacent phosphorus centres.[54] The radical shows good persistence in solution aided by the bulky diisopropyl amino group, see Figure 23.

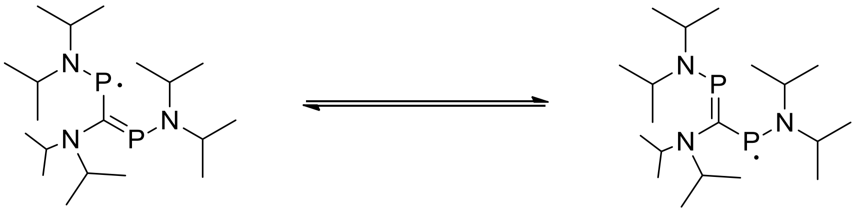


Figure 23 Delocalisation of the unpaired electron across two phosphorus sites in 1,3-diphosphaallyl radical

e. Spin labelling and EPR

Spin labelling is a technique which involves attaching a paramagnetic motif to a diamagnetic molecule and then tracking it. Once labelled, molecules are detected using electron paramagnetic resonance (EPR) spectroscopy which has a structure sensitive pattern of g-factor and hyperfine coupling (which are the equivalents of chemical shift and spin-spin coupling respectively in NMR spectroscopy). Radicals by definition are paramagnetic and could be a potential source of such labelling molecule but to be a desirable candidate these radicals must have favourable properties such as being easily functionalised, potentially being compatible with biological system and having favourable spectral characteristics. EPR has been used to probe $Mes^*_2P\cdot$-PMeMes*[10,52] which yielded much information about reorganisation via bond rotation within the molecular structure. The restriction of EPR to paramagnetic species has a massive advantage over other spectroscopic techniques in regard to sensitivity. We had hoped to produce some suitable phosphinyl radicals for potential use as spin labels.

Phosphorus radicals are notable because of their scarcity. An understanding of the means of stabilization of main group radicals was a huge asset in this synthesis undertaken, even though no new radicals were isolated.

Chapter 2 - Geminally Bis(supermesityl) Substituted Phosphorus Compounds

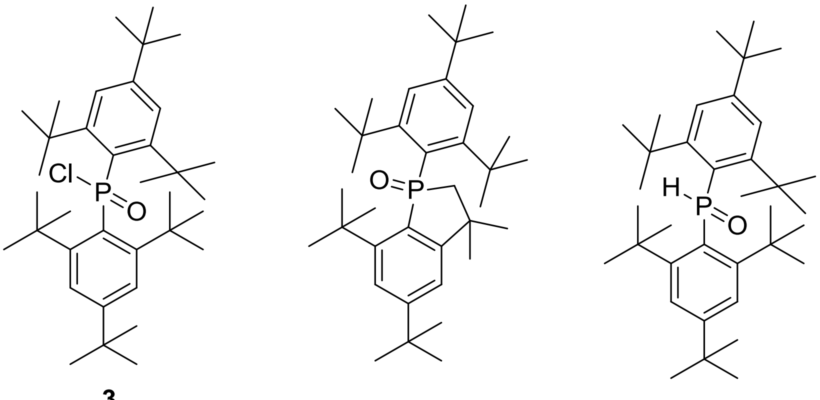
1. Supermesityl and steric hindrance

a. Mes* in Main Group Chemistry

As has been discussed in the previous chapter, the extremely bulky group 2,4,6-tri-*tert*-butylphenyl (supermesityl, Mes*) has been employed to stabilise a wide range of low co-ordinate main group species.[55,56] The preparation of the first stable diphosphene Mes*P=PMes* 30 years ago[1] demonstrated the ability of Mes* to provide steric protection to phosphorus centred reactive species. It should however be mentioned that the synthesis of phosphorus centres with extremely sterically encumbering groups attached to them is still somewhat of a minority area of research. The current lack of commercial application for these compounds has restricted their study to that of purely academic interest. There are many potential applications in low co-ordination main group and organometallic chemistry for using Mes* as a means of stabilisation. The research detailed here shows only a small proportion of the possibilities involving phosphorus centres.

b. The production and previous studies of $Mes^*_2P(=O)Cl$ in the literature

The following summary review of the literature demonstrates that the geminal disubstitution of two Mes* motifs onto a single phosphorus centre is a daunting (although by no means impossible) enterprise due to the steric clashes between the *ortho*-positioned ^{t}Bu groups which shield the phosphorus centre. The first example of such a structure was reported in 1979 by Yoshifuji, the phosphinic chloride $Mes^*_2P(=O)Cl$ **3** was synthesised via the reaction of Mes*Li and $POCl_3$, see Scheme 1.[57,58] **3** is an air stable solid and the presence of two supermesityl groups appended to a single phosphorus centre makes it an ideal starting material for further investigation. The reactivity of **3** was studied in some detail; when it is reacted with sodium azide (NaN_3), the anticipated product $Mes^*_2P(=O)(N_3)$ is not formed. Instead, an intramolecular dehydrohalogenation ensues with the formation of phosphindole **4** as the major product,[59] see Figure 24.



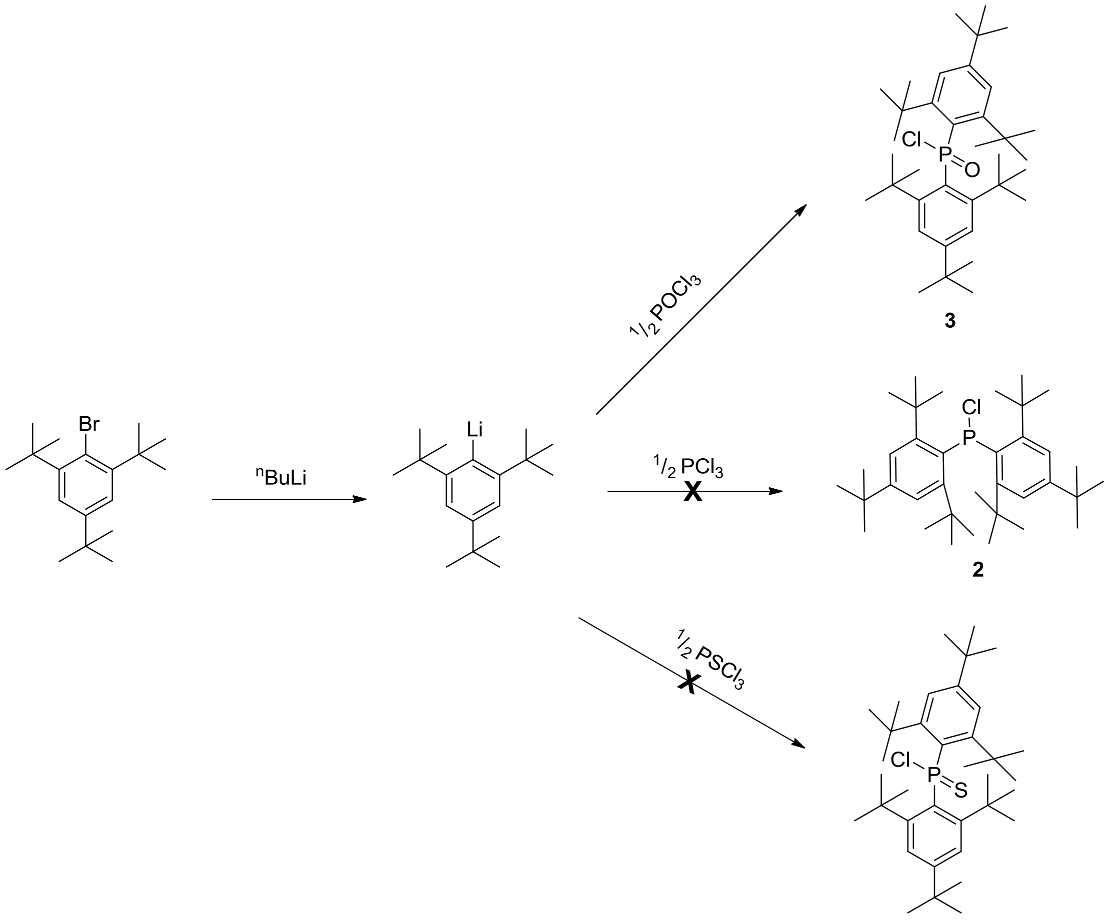
3 **4** **5**

Figure 24 The structures of **3**, **4** and **5**

A phosphonyl radical $Mes^*_2P\cdot(=O)$ has been made when **3** was irradiated with a UV light in the presence of electron rich olefins.[60,61] The same phosphonyl radical has also been made via the X-ray irradiation of a single crystal of **3**[62] or using the phosphine oxide Mes*$_2$P(=O)H **5** as a precursor instead,[61] see Figure 24. The propensity of Mes* for encapsulation has allowed the stability of this radical species to be studies in detail. Electron paramagnetic resonance (EPR) studies allowed detailed examinations of the phosphorus environment in this persistent radical.[63]

c. Other bis(supermesityl) substituted phosphorus compounds in the literature

The reaction of Mes*Li with POCl$_3$ to make **3** is at variance with the analogous reaction of two equivalents of Mes*Li with PCl$_3$; this does not bequeath the geminally disubstituted Mes*$_2$PCl **2**, instead Mes*PCl$_2$ **1** and Mes*P=PMes* were produced.[32] Following on from this two equivalents of Mes*Li were reacted with the sulfide counterpart PSCl$_3$, which did not result in the attainment of geminally disubstituted thiophosphinic chloride Mes*$_2$P(=S)Cl,[57] see Scheme 1. Data for single crystal X-ray diffraction of Mes*$_2$PH **6** has been deposited with CCDC[64] as part of a private communication, however no spectroscopic data or synthetic procedure has been reported as of yet. This would be the only known example of two 2,4,6-tritertbutylphenyl groups bonded to a single phosphorus(III) atom. The phosphinyl radical Mes*$_2$P· related to this structure was observed previously (by EPR) as part of a transitional pathway when **3** was photolysised.[63] This hints that Mes*$_2$PH **6** could be isolated and characterised.



Scheme 1 The reaction of Mes*Li with PCl_3, $POCl_3$ and $PSCl_3$

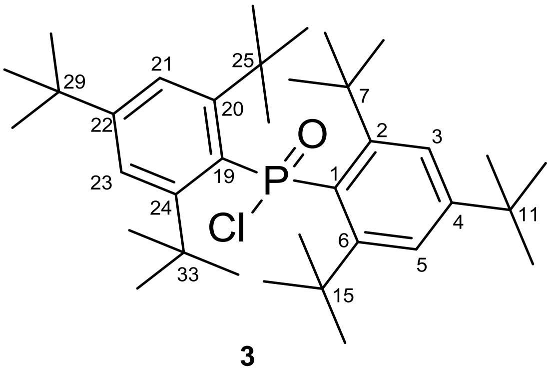
From the difference of reactivity between PCl_3, $POCl_3$ and $PSCl_3$ we must extrapolate that the oxygen double bonded to the phosphorus in $POCl_3$ has a striking influence on the electronics of the system by drawing electron density away from the phosphorus centre, thus increasing the electrophilicity of the phosphorus atom and allowing the double addition to occur. The phosphorus-sulfur double bond is much less polarised as sulfur has a greatly diminished eletronegitivity in relation to oxygen (2.58 vs. 3.44). The lone pair on trivalent phosphorus resides in a sp^3-orbital closer to the phosphorus nucleus which does not allow two Mes* substituents to be attached geminally to the central atom. This exemplifies how the attachment of bulky supermesityl substituents is affected by the electronic properties of the nuclei it interacts with.

Before the advent of the research undertaking described in this chapter the only other successful synthesis (other than the production of **3**) described in the literature of two Mes* groups geminally substituted on a phosphorus centre was the phosphaalkene Mes*-P=CH-P(Mes*)$_2$.[65] Reported spectroscopic data (^{31}P NMR spectra only) were incomplete and no specific synthetic procedure was provided. There is some limited ^{31}P NMR spectroscopic data for the phosphine oxide Mes*$_2$P(=O)H **5**, see Figure 24, however no procedure or other physical data were provided.[62]

d. Possible routes to phosphinyl radicals

With due regard to these literature examples we must conclude that Mes*$_2$P(=O)Cl **3** is the only available synthon for our investigation of the effects of sterically encumbered groups on phosphorus species. Thus, **3** became our principle starting material from which all work detailed in this chapter derives. It is the ability of extremely bulky groups to give a degree of persistence to normally reactive moieties which attracted us to using supermesityl in the first place. Of particular interest to us is the phosphinyl radical Mes*$_2$P·, which we envisaged would have a good level of stability if it could be isolated. As its desired chlorophosphine precursor Mes*$_2$PCl **2** could not be produced via double substitution on phosphorus trichloride,[32] we attempted to discover a circuitous route to **2**.

e. Structural and Spectroscopic characteristics of Mes*$_2$P(=O)Cl



3

Figure 25 Numbering scheme for Mes*$_2$P(=O)Cl **3**

Mes*$_2$P(=O)Cl **3** has been subjected to close theoretical scrutiny due to the idiosyncratic nature of its structure.[66,67] Its phenyl rings adopt a boat-like conformation with the *ipso*- and *para*-carbons displaced out the same side of the mean planes formed by C(2), C(3), C(5) & C(6) and C(20), C(21), C(23) & C(24) respectively, see Figure 25 and Table 1.[58] Furthermore the phosphorus centre is displaced ~1.12 Å out of the same mean planes. The *ortho*-positioned ^{t}Bu groups are bent in the opposite direction from *ipso*-carbons out of these same planes.

Table 1 Approximate displacement from mean planes (Å) for Mes*$_2$P(=O)Cl **3**[58]

Displacement from mean plane[a] (Å)		**Displacement from mean plane[b] (Å)**	
P	1.12	P	1.13
C(1)	0.22	C(19)	0.25
C(4)	0.12	C(22)	0.14
C(7)	0.40	C(25)	0.52
C(15)	0.42	C(33)	0.52

[a] Distance from the mean plane fitted through atoms C(2), C(3), C(5) and C(6)

[b] Distance from the phenyl mean plane fitted through atoms C(20), C(21), C(23) and C(24)

Such distortion calls in to question the true degree of aromaticity of these rings. The loss of planarity is likely to impede the orthogonal alignment of the p-orbitals associated with the ring carbon atoms. This distortion is a direct result of the presence of multiple bulky substituents on the aromatic rings which engenders intramolecular interactions with the phosphorus atom and the bulky groups on the other ring. Only by twisting out of planarity, can the two Mes* groups attach geminally to a single phosphorus centre. These structural attributes make $Mes^*_2P(=O)Cl$ **3** quite unlike most other phosphine oxides. The sheer magnitude of the conformational deformity that is seen in it is highly unusual. This was among the myriad of reasons why we decided to investigate its further chemistry.

We established that **3** could be synthesised via the literature method,[57,58] on a reasonably large scale (15 to 20 g) in yields of up to 65% after purification by column chromatography on silica. The spectroscopic work done previously by Yoshifuji et al. was limited by the low working frequencies which the NMR spectroscopic data was collected at (^1H at 90 MHz, ^{13}C at 25.2 MHz);[57] the aromatic literature peaks could not be catalogued individually. We performed NMR spectroscopic acquisitions at a much higher working frequencies (^1H at 300.1 MHz, ^{13}C at 75.5 MHz) and this higher quality data and its assignment is detailed in the experimental section of the chapter. We observed that both ^1H and ^{13}C NMR spectra of **3** are more complex than a cursory look at its structure might suggest due to the presence of a number of prochiral groups. Thus all four of the aromatic hydrogen atoms are anisochronous (δ_H 7.47, 7.36, 7.24 and 7.15) in the ^1H NMR spectra. There are no formal stereogenic centres in **3**, thus the anisochronicity of the prochiral groups must be the result of a large rotational barrier around both phosphorus-*ipso*-C bonds. This impediment or complete cessation of rotation on an NMR spectroscopy timescale allows each of the supposedly chemically and magnetically equivalent peaks to be recorded separately. Their magnetic inequivalence also allowed $^4J_{H-H}$ couplings of the *meta*-hydrogens to be present which further complicated the splitting patterns of peaks in the aromatic region of the ^1H NMR spectrum. The anisochronicity of aromatic hydrogen atoms as well as other groups became a common theme during our synthetic study of phosphorus centres with sterically encumbering groups.

2. *Reactivity of Mes*$_2$P(=O)Cl*

a. Reaction with organolithium

We decided to conduct a reactivity study of Mes*$_2$P(=O)Cl **3**. Normally, phosphorus-chlorine bonds are labile to nucleophilic attack by organometallics. It has been long established that phosphinic chlorides $R_2P(=O)Cl$ react with organolithiums (R'Li) or organo-Grignard reagents (R'MgX) to produce the corresponding tertiary phosphine oxides $R_2R'P(=O)$, in respectable but not spectacular yields.[68,69] In contrast, when we reacted **3** with methyllithium, first at low temperature and eventually in refluxing hexane for 90 minutes, it was judged by ^{31}P NMR spectroscopy that no transformation had taken place and the desired product Mes*$_2$P(=O)Me **8** was not obtained. This somewhat surprising result set the tone for our investigation into the reactivity of **3**.

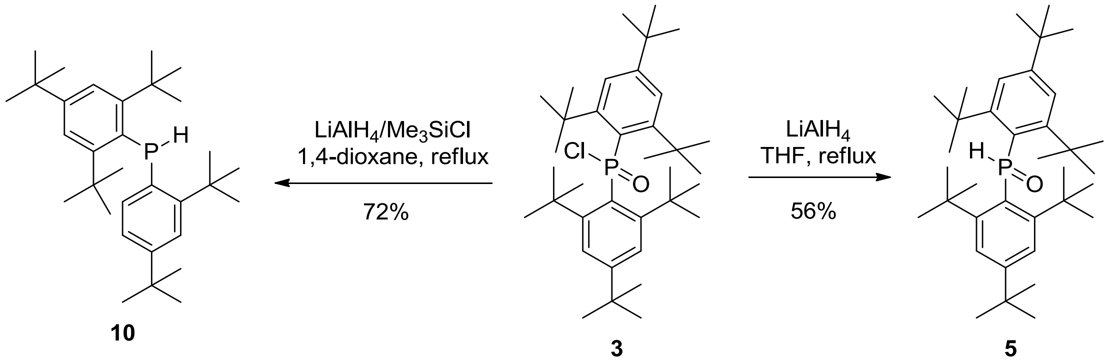
b. Reduction of Mes*$_2$P(=O)Cl

We then turned our attention to the reduction of **3**. To achieve this, a range of hydridic reducing reagents were probed with a view to the production of the corresponding phosphorus(III) species Mes*$_2$PH **6**. These efforts are documented in Table 2. It was our desire to achieve this transformation using the least harsh reaction conditions available which would still allow the desired product to be isolated in an acceptable yield. To this end, portions of **3** were treated with $LiAlH_4$, $[i\text{Bu}_2AlH]_2$ (DIBAL) or $LiBEt_3H$ (Superhydride) in THF at room temperature for several hours. In all cases, when an aliquot of the reaction mixture was taken and analysed via ^{31}P NMR spectroscopy, it was abundantly clear that no reaction had occurred. We then moved to reaction condition which involved heating the reaction mixture; samples of **3** were heated under reflux in THF with Ph_3SiH, $NaBH_4$ or NaH which resulted in the recovery of starting material exclusively. On the same note, the heating of **3** with $HSiCl_3$/Et_3N under reflux in toluene also resulted clearly in no reaction occurring. This was particularly interesting as $HSiCl_3$/R_3N is a widely employed reducing reagent for phosphine oxides.[70] This inertia towards these milder reduction conditions convinced us that a new approach might be needed. It was for this reason that a sample of **3** in THF was heated under reflux with $LiAlH_4$. Slow reaction was observed under these conditions affording the corresponding secondary phosphine oxide Mes*$_2$P(=O)H **5**. The reaction was carefully monitored via $^{31}P\{^1H\}$ NMR spectroscopy. The reaction was deemed to be complete when all the starting material had been consumed to be replaced with a transient (presumably aluminium complex) compound (δ_P 102.4). After careful hydrolysis with water, **5** (δ_P 12.9, $^1J_{PH} = 483.0$ Hz) was recovered as part of a crude product mixture which also contained significant amounts of phosphorus-carbon bond cleavage compounds Mes*H, Mes*PH_2 (δ_P -129.9 (t, $^1J_{PH} = 210.1$ Hz))[71] and Mes*P(=O)H_2 (δ_P -11.3 (t, $^1J_{PH} = 482.4$ Hz)).[72] Column chromatography on silica was used to purify **5**, which was recovered in moderate yields of 35 to 56 %, see Scheme 2. In addition to ^{31}P, ^1H and ^{13}C NMR spectroscopy, Mes*$_2$P(=O)H **5** was fully characterised by IR, Raman and ES MS, and its purity was verified by microanalyses. It has also been characterised by a single crystal X-ray diffraction study, see Figure 27 and Table 3. Further examination of this reaction revealed that the reaction can be accelerated by the addition of an excess of Me_3SiCl or by replacing the THF solvent with (higher boiling) 1,4-dioxane. What did not accelerate the reaction was the use of a THF solution of $LiAlH_4$ (rather than the solid form), nor did it lead to an improvement in yields. The production of phosphorus-carbon bond cleavage co-products seems unavoidable.

c. Synthesis of Mes*(2,4-*t*$Bu_2C_6H_3$)PH

Although, the synthesis of **5** offered a fascinating insight into the inertia of Mes*$_2$P(=O)Cl **3** towards what would normally be described as harsh reduction conditions, it did not satisfy our desired to produce new, sterically encumbered phosphorus(III) compounds. It was in this regard that **3** was reacted with mixed reducing reagent systems $LiAlH_4$/Me_3SiCl or $LiAlH_4$/$AlCl_3$ in the high boiling point (101 °C) ethereal solvent 1,4-dioxane. These reactions were monitored via $^{31}P\{^1H\}$ NMR spectroscopy and over a sufficient period of time the starting material peak decayed and a signal corresponding to trivalent phosphorus species (δ_P -67.1 (d, $^1J_{PH}$ = 237.3)) was detected. To our astonishment, the major product to emerge was not the expected secondary phosphine Mes*$_2$PH **6** but a new trivalent phosphorus species Mes*(2,4-*t*$Bu_2C_6H_3$)PH **10**. This is obviously the result of the loss of one of the flanking ^{t}Bu groups on the aromatic ring, which could be formally described as a reverse-Friedel-Crafts reaction, see Scheme 2. This kind of carbon-carbon bond cleavage is quite rare, even in the presence of a powerful Lewis acid. The loss of one *ortho*-substituted *t*Bu group allows a significant relaxation of the steric crowding within the molecule of **10,** which is likely to be the driving force behind this bond cleavage, see Figure 34 and Table 6.

The use of Me_3SiCl was preferred over $AlCl_3$ as the reductive additive as less Al_2O_3 is formed on hydrolysis. The crude solid obtained was contaminated with Mes*H, Mes*PH_2 and Mes*P(=O)H_2, however these were removed via column chromatography on silica; the pure product **10** was generated in good yields of 55 to 72% (from the $LiAlH_4$/Me_3SiCl reaction). The phosphorus centre in **10** is still strongly shielded despite the loss of the *tert*-butyl group, with a significant difference between its chemical shift (δ_P -67.1) and that of the non-crowded Ph_2PH (δ_P -39.9 (dquint, $^1J_{PH}$ = 216, d, $^3J_{PH}$ = 7)).[73] Mes*(2,4-tBu$_2$C$_6$H$_3$)PH **10** was fully characterised by ^{31}P, ^1H and ^{13}C NMR spectroscopy, IR, Raman and ES MS; its purity was verified by microanalyses. It has also been characterised by a single crystal X-ray diffraction, see Table 6.



Scheme 2 The reaction of **3** under different reductive conditions

d. Reduction conditions

It is noteworthy that the reaction conditions needed to produce both **5** and **10** would be considered harsh by general synthetic standards, particularly when compared to the analogous conditions needed to reduce less sterically hindered secondary phosphine oxides. Examples of this can be seen in the transformation of $Ph_2P(=O)H$ to the corresponding phosphine Ph_2PH, which is achieved by adding [iBu$_2$AlH]$_2$ (DIBAL) to a THF solution of $Ph_2P(=O)H$ at room temperature, which gives a very high yield of 86% after workup.[74] There are many literature examples of high yielding transformation of phosphine oxides to the respective phosphines using reducing reagents which we have attempted to utilise such as DIBAL[75] or $LiAlH_4$ at ambient temperature,[76,77] see Table 2.

Table 2 Reaction conditions for reduction of Mes*$_2$P(=O)Cl **3**

Reducing Agent	Solvent	Temperature (^{o}C)	Time (hours)	Major Product
$LiAlH_4$	THF	RT	10	No reaction
[iBu$_2$AlH]$_2$	THF	RT	10	No reaction
$LiBEt_3H$	THF	RT	10	No reaction
$NaBH_4$	THF	65 (reflux)	6	No reaction
NaH	THF	65 (reflux)	6	No reaction
Ph_3SiH	THF	65 (reflux)	6	No reaction
$HSiCl_3/Et_3N$	Toluene	110 (reflux)	4	No reaction
$LiAlH_4$	THF	65 (reflux)	6 to 9	Mes*$_2$P(=O)H **5**
$LiAlH_4$ + Me_3SiCl	THF	65 (reflux)	5	Mes*$_2$P(=O)H **5**
$LiAlH_4$	1,4-Dioxane	101 (reflux)	6	Mes*$_2$P(=O)H **5**
$LiAlH_4$ + $AlCl_3$	1,4-Dioxane	101 (reflux)	7 to 9	Mes*(2,4-^{t}Bu$_2$C$_6$H$_3$)PH **10**
$LiAlH_4$ + Me_3SiCl	1,4-Dioxane	101 (reflux)	5	Mes*(2,4-^{t}Bu$_2$C$_6$H$_3$)PH **10**
$LiAlH_4$ + $CeCl_3$	1,4-Dioxane	101 (reflux)	6	Mes*PH$_2$

There has been literature mention of using the mixed reductive system $LiAlH_4/NaBH_4/CeCl_3$ as a means of achieving the reduction of secondary phosphine oxides $R_2P(=O)H$ to secondary phosphine-borane adducts $R_2PH{\cdot}BH_3$. These reactions were accomplished at room temperature in good yields.[78,79] With this in mind, we strived to reduce **3** using a $LiAlH_4/CeCl_3$ mixed reducing reagent in 1,4-dioxane. Starting material was the exclusive product which was obtained when this reaction was conducted at room temperature, whereupon the heating of this reaction mixture to reflux for a significant length of time led to excessive cleavage of bonds and the recovery of Mes*PH$_2$ as the major product, see Table 2.

3. The Structural and spectroscopic characteristics of $Mes^*_2P(=O)H$ and its further reactions

a. Spectroscopic study of $Mes^*_2P(=O)H$

As has been mentioned before, **5** was used as a precursor to the phosphonyl radical $Mes^*_2P\cdot(=O)$.[61] However, no spectroscopic details or synthetic method of preparation was presented besides the magnitude of the $^1J_{PH}$ coupling (478 Hz)[61] of **5**. This is in good agreement with the characterisation data which we now report (δ_P 12.9, $^1J_{PH}$ = 483.0 Hz). When **5** was compared to the related non-crowded phosphine oxide $Ph_2P(=O)H$ (δ_P 21.5, $^1J_{PH}$ = 480.6 Hz),[80] it was revealed that the phosphorus atom in $Mes^*_2P(=O)H$ is only slightly more shielded as indicated by the closeness of their δ_P values and also that the magnitude of their $^1J_{PH}$ splitting is very similar. The ^1H and ^{13}C NMR spectra of **5** show significant broadening of all spectral lines at room temperature. The likely cause of this is hindered rotation around the phosphorus-carbon bonds at a rate comparable to NMR spectroscopy timescale. Upon cooling of a concentrated sample of **5** in CD_2Cl_2 to -60 °C all of the signals in both the aliphatic and aromatic regions of ^1H NMR spectrum sharpened significantly. At this temperature the four *ortho t*Bu groups become distinctly anisochronic, while three distinct singlets (1:2:1 intensity ratio) are observed for the four aromatic protons. The results of these changes can be seen in Figure 26 and are detailed more explicitly in the experimental section of this chapter.

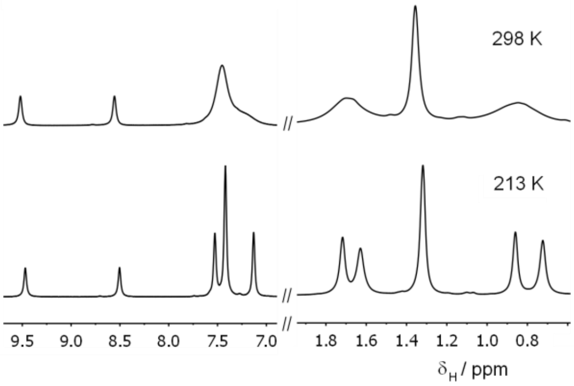


Figure 26 ^{1}H NMR spectra of **5** at 298 K (top) and 213 K (bottom) showing fluxional character of aromatic (left) and aliphatic (right) signals. The doublet with large coupling constant on the extreme left is due to the P-H hydrogen atom. Intensity of the left part of spectra was increased for clarity. CD_2Cl_2 was used as a solvent, working frequency was 499.9 MHz.

b. Deprotonation of Mes*$_2$P(=O)H 5

Having isolated and characterised **5**, we decided to explore its reactivity. One obvious route to further reaction is to deprotonate **5** with a suitable base. A THF solution of **5** was cooled to -78 °C and one equivalent of *n*BuLi was added slowly. When the solution was maintained at this temperature no reaction occurred as indicated by the starting material being the only peak present when an aliquot was tested via ^{31}P NMR spectroscopy. However, when the reaction mixture was allowed to warm up slowly, a colour change from colourless to rusty-red manifested just below 0 °C. The formation of the corresponding phosphinite Mes*$_2$P(=O)$^-$ **7** was confirmed by the ^{31}P NMR spectroscopy, which showed that the starting material had been replaced with a new high frequency signal (δ_P 106.4). All further reactions were performed at 0 °C, where deprotonation was shown via ^{31}P NMR spectroscopy to be quantitative 10 minutes after the addition of *n*BuLi, see Scheme 3.

c. Reaction of phosphinite 7 with alkyl halides

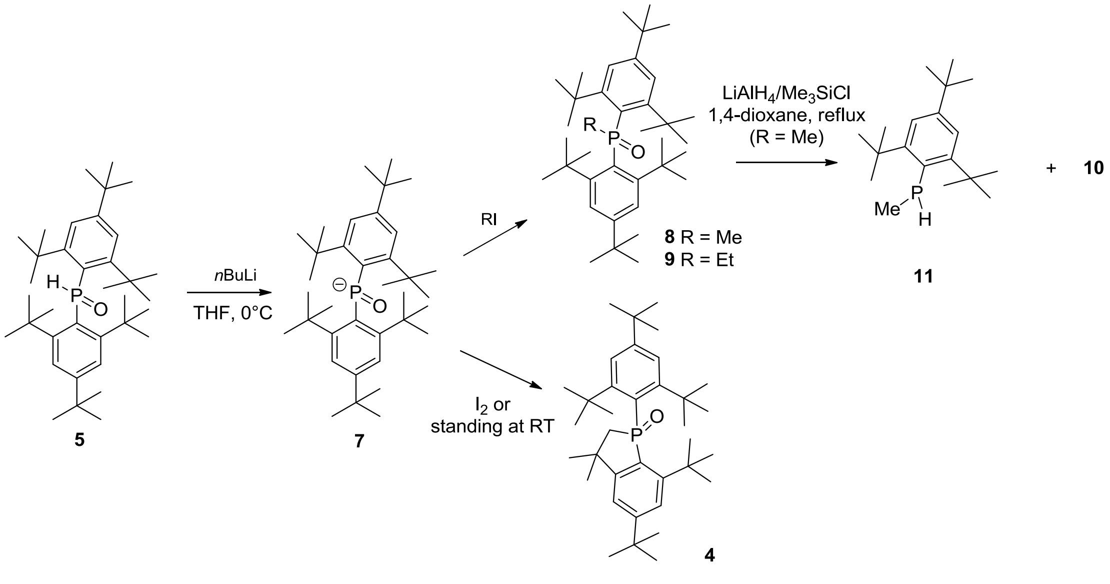
With confirmation of the formation of our desired phosphinite **7**, we decided to investigate its reactivity towards a range of electrophiles. Ergo, we added methyl iodide to a THF solution of **7** and allowed the reaction mixture to rise to ambient temperature; the formation of the desired tertiary phosphine oxide $Mes^*_2P(=O)Me$ **8** was monitored visually by virtue of a colour change from rusty red to colourless/pale yellow. The related reaction with ethyl iodide to produce $Mes^*_2P(=O)Et$ **9** needed some gentle heating to 50 °C to be driven to completion, at which point the dark solution gave way to a light yellow one. When attempts were made to react **7** with more sterically demanding alkyl halides such as benzylbromide, *i*PrBr and *t*BuCl in identical conditions as used before, our reactions were less successful. The ^{31}P NMR spectra of the mixtures obtained at the conclusion of these reactions revealed a complex mixture of phosphorus containing compounds were formed in each case. Full characterisation of **8** and **9** was conducted with ^{31}P, ^{1}H and ^{13}C NMR spectroscopy, IR, Raman and ES MS; their purity was verified by microanalyses. However, the yields of analytically pure materials obtained via recrystallisation in acetonitrile were disappointing. ^{31}P NMR spectroscopic analysis of the crude product solids obtained showed that the conversions of **7** to **8** or **9** were almost quantitative; recrystallisation gave only moderate to poor yields (50 and 7%, respectively). Both **8** and **9** were characterised by a single crystal X-ray diffraction, see Figure 28, Figure 30 and Table 3.

d. Reaction of phosphinite 7 with halogens

We also investigated the halogenation of **7** with elemental bromine and iodine, which we hoped would form the corresponding phosphinic bromide Mes*$_2$P(=O)Br or iodide Mes*$_2$P(=O)I respectively. We found that these reactions did not proceed as anticipated, however the reaction of **7** with I_2 did produce the phosphindole **4** almost exclusively (as indicated by ^{31}P NMR spectroscopy) which was isolated as a colourless solid in good yield (70%). A retrospective analysis of our previous reactions revealed that **4** was present in the product mixtures obtained from all of the reactions involving larger electrophiles, see Scheme 3. We therefore allowed a THF solution of **7** to stir at room temperature in the absence of an electrophile for several hours. Subsequent analysis by ^{31}P NMR spectroscopy confirmed **4** was formed through intramolecular quenching. A review of the relevant literature revealed that an attack of a proximate *t*Bu group in Mes* resulting in cyclisation has been reported previously for a number of similar systems.[32,81,82] The particular phosphindole **4** which we recovered has been synthesised before from the intramolecular dehydrohalogenation of Mes*$_2$P(=O)Cl **3** in pyridine/DMF.[59] The data we obtained for **4** (δ_P 54.9) was in good agreement with the literature values reported.[59] Furthermore, we have obtained a single crystal X-ray diffraction structure for **4** which has not been detailed until now, see Table 3, Figure 32 and Figure 33.

e. Reduction of Mes*$_2$P(=O)Me 8

With the moderate success we had with making tertiary phosphines oxides **8** and **9**, we turned our attention to their potential for reduction to phosphorus(III) species. The reduction of **8** was examined using identical hydridic reducing condition as had been used previously in the production of Mes*(2,4-*t*$Bu_2C_6H_3$)PH **10**. A stirred 1,4-dioxane suspension of $LiAlH_4$/Me_3SiCl and **8** was heated under reflux for a significant length of time; the reaction was monitored via ^{31}P NMR spectroscopy. Upon completion of the reaction a spectroscopic investigation showed that the expected product Mes*$_2$PMe (or possibly Mes*(2,4-$^tBu_2C_6H_3$)PMe) was not obtained. The compounds reaped were the secondary phosphine Mes*MePH **11** as the major product (isolated in 42 to 67% yield after column chromatography) and an appreciable amount of **10**, see Scheme 3. The ^{31}P, ^1H and ^{13}C NMR spectroscopy confirmed the identities of both **10** and **11**. In addition to that, a single crystal X-ray diffraction structure of **11** proved beyond doubt our assignment. Mes*MePH **11** had been synthesised and well characterised before, albeit by a different route.[83,84] The ^{31}P NMR spectroscopy data reported [δ_P -91.4 (dquart, $^1J_{PH}$ = 222.9, $^2J_{HP}$ = 5.1 Hz)][84] was in good agreement with the data which we collected [δ_P (^1H coupled, $CDCl_3$) -91.3 (dquart, $^1J_{HP}$ = 225.8, $^2J_{HP}$ = 5.0 Hz)].



Scheme 3 The reactions of the phosphine oxide Mes*$_2$P(=O)H **5** with *n*BuLi and electrophiles

f. X-ray discussion of 4, 5, 8 and 9

The X-ray crystal structures of **4**, **5**, **8** and **9** are shown in Table 3 and Figure 32, Figure 27, Figure 28 and Figure 30 respectively. Crystals were grown via the slow evaporation of a concentrated dichloromethane solution. Compound **9** co-crystallised with one molecule of DCM; no solvent molecules were present in the crystals of **4**, **5** or **8**.

Table 3 Bond distances (Å), bond angles (°), torsion angles (°) and displacements from mean phenyl planes (Å) in compounds **4**, **5**, **8** and **9**.

Bond lengths (Å)	**4**	**5**	**8**	**9**
P(1)-O(1)	1.411(7)	1.518(4)	1.525(4)	1.4888(13)
P(1)-C(1)	1.854(9)	1.809(4)	1.861(5)	1.892(3)
P(1)-C(19)	1.824(11)	1.858(4)	1.854(4)	1.864(3)
P(1)-C(37)/C(36)[a]	1.807(11)	-	1.735(6)	1.840(3)
Bond angles (°)				
C(1)-P(1)-C(19)	108.6(5)	114.57(17)	111.5(2)	109.54(10)
O(1)-P(1)-C(1)	111.7(5)	110.89(18)	109.37(19)	111.55(9)
O(1)-P(1)-C(19)	111.5(5)	111.49(18)	112.12(19)	112.20(8)
O(1)-P(1)-C(37)/C(36)[a]	112.9(5)	-	110.8(3)	110.44(10)
C(1)-P(1)-C(37)/C(36)[a]	114.8(5)	-	106.2(3)	107.04(10)
C(19)-P(1)-C(37)/C(36)[a]	96.3(5)	-	106.7(2)	105.79(11)
C(2)-C(1)-C(6)	117.2(8)	118.1(4)	115.7(4)	116.52(19)
C(20)-C(19)-C(24)	117.8(10)	117.8(4)	116.1(4)	115.75(19)
C(1)-C(2)-C(7)	127.0(9)	129.4(4)	128.4(4)	129.7(2)
C(1)-C(6)-C(15)	127.7(9)	127.4(3)	127.4(4)	132.1(2)
C(19)-C(20)-C(25)	128.7(9)	126.6(4)	124.9(4)	126.74(17)
C(19)-C(24)-C(33)	114.5(9)	125.8(4)	127.1(4)	126.32(17)
Dihedral angles (°)				
C(1)-C(2)-C(3)-C(4)	2.9(17)	2.4(6)	7.1(7)	8.8(3)
C(1)-C(6)-C(5)-C(4)	1.6(16)	5.6(6)	2.8(7)	2.0(4)
C(2)-C(3)-C(4)-C(5)	14.5(16)	9.0(6)	9.3(7)	5.5(3)
C(3)-C(4)-C(5)-C(6)	15.2(16)	7.3(6)	11.5(7)	11.2(4)
C(3)-C(2)-C(1)-C(6)	20.5(14)	15.5(5)	20.9(6)	17.6(3)
C(2)-C(1)-C(6)-C(5)	19.9(13)	17.0(5)	18.9(6)	12.5(3)
C(19)-C(20)-C(21)-C(22)	0.3(15)	2.8(6)	1.6(7)	9.0(3)
C(19)-C(24)-C(23)-C(22)	4.0(16)	6.5(6)	10.0(7)	4.1(3)
C(20)-C(21)-C(22)-C(23)	3.7(15)	12.3(6)	12.8(7)	10.9(3)
C(21)-C(22)-C(23)-C(24)	5.8(15)	10.3(6)	8.4(7)	13.5(3)
C(21)-C(20)-C(19)-C(24)	2.3(14)	20.0(5)	20.2(6)	26.2(3)
C(20)-C(19)-C(24)-C(23)	0.3(15)	21.8(5)	24.1(6)	23.8(3)

Displacement from mean phenyl plane[b] (Å)				
P(1)	1.205	0.658	0.976	0.745
C(1)	0.145	0.106	0.132	0.101
C(4)	0.119	0.074	0.095	0.074
C(7)	0.473	0.367	0.491	0.452
C(15)	0.527	0.366	0.564	0.290
C(11)	0.354	0.255	0.323	0.227
Displacement from mean phenyl plane[c] (Å)				
P(1)	0.117	1.076	1.001	1.076
C(19)	0.017	0.137	0.146	0.164
C(22)	0.028	0.100	0.100	0.113
C(25)	0.178	0.517	0.603	0.715
C(33)	0.187	0.532	0.684	0.625
C(29)	0.085	0.351	0.350	0.345

[a] C(37) for **8** and **9**, C(36) for **4**

[b] Distance from the phenyl mean plane fitted through atoms C(1) to C(6)

[c] Distance from the phenyl mean plane fitted through atoms C(19) to C(24)

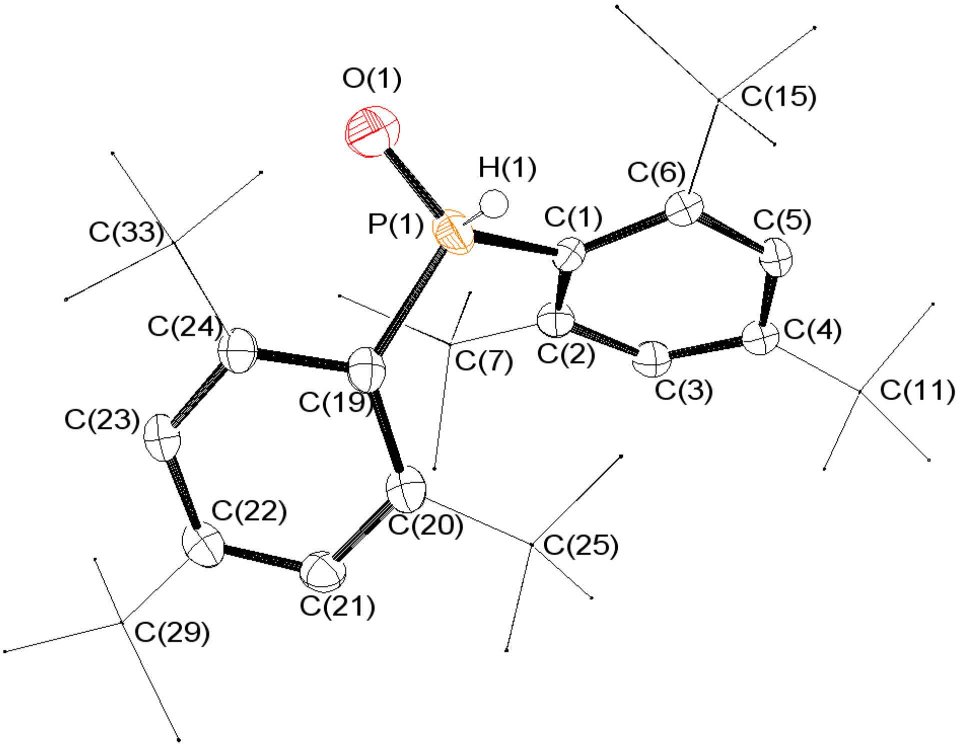


Figure 27 Molecular structure of **5**. Thermal ellipsoids are set at 50% probability, all hydrogen atoms except H(1) are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

In the molecule of **5,** the bond angles around the central phosphorus atom are all larger than the ideal tetrahedral value, with the C(1)-P(1)-C(19) angle (114.57(17)°)

being larger than those present in **4**, **8** & **9**. The small size of hydrogen atom positioned on the phosphorus centre allows the other bond angles to widen. The phosphorus atom is displaced significantly from the mean aromatic planes by 0.65 and 1.07 Å. The *ortho*-positioned *tert*-butyl groups display significant in-plane bending with distortions between 5.8(4) to 9.4(4)° away from the idealised sp^2 hybridized carbon angle of 120°. Their quaternary carbon centres are also bent out of the mean aromatic planes to the tune of between 0.18 to 0.53 Å. The phenyl rings themselves display a deviation from planarity by adopting a boat conformation with the *ipso* and *para* carbon atoms lying 0.11 & 0.14 Å and 0.07 & 0.11 Å out the same side of the mean aromatic planes respectively, as seen in Table 3. The distortion also manifests itself by large torsion angles within the phenyl rings. The aromatic groups are positioned in such a manner that the angle between the two mean phenyl planes is 33.0°. This all goes to show that **5** is an incredibly crowded structure, as seen from Figure 27.

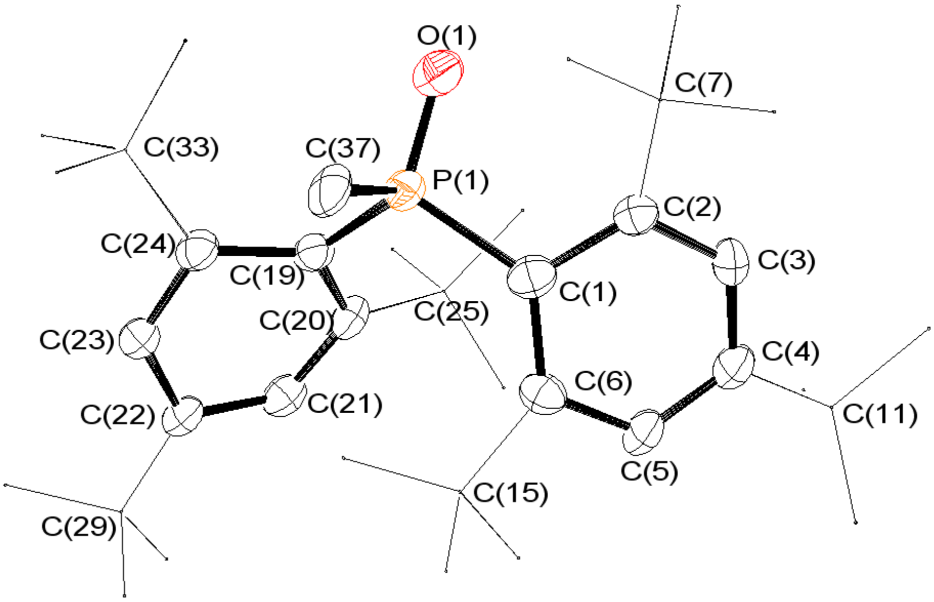


Figure 28 Molecular structure of **8**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

Figure 28 and Table 3 show that the addition of the methyl group onto the phosphorus in **8** results in the bond angles observed around the phosphorus becoming marginally more acute, all of these are around the idealised tetrahedral angle value. The phosphorus atom lies about 1.00 Å out of the mean phenyl planes as illustrated in Figure 29. The *ortho*-^{t}Bu groups are bent out the opposite side of these aromatic planes, with their quaternary carbon atoms displaced 0.49 and 0.68 Å from the mean phenyl ring plane. They also experience considerable in-plane distortion with bond angles which are between 4.9(4) and 8.4(4)° away from the ideal geometry.

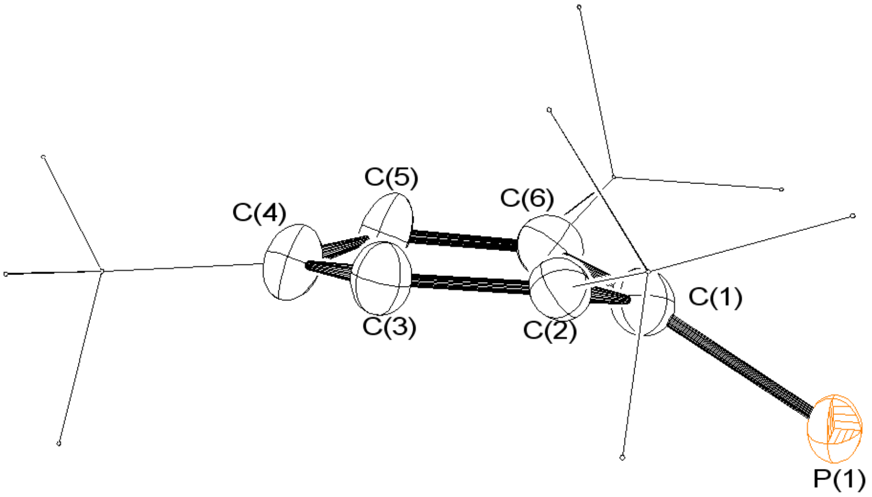


Figure 29 Alternative view of the structure of **8** showing the displacement of the phosphorus atom and the ^{t}Bu groups out of the mean aromatic plane. Thermal ellipsoids are set at 50% probability; hydrogen atoms, second Mes* ring, oxygen atom and methyl group are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

Boat-like buckling of the phenyl rings is also observed with the *ipso*-C and *para*-C atoms lying about 0.14 Å and 0.10 Å, respectively, out of the mean aromatic plane, see Figure 29 and Table 3. Significant distortion is also indicated by the large dihedral angles within the aromatic rings, the mean planes of which make an angle of 21.3° with each other.

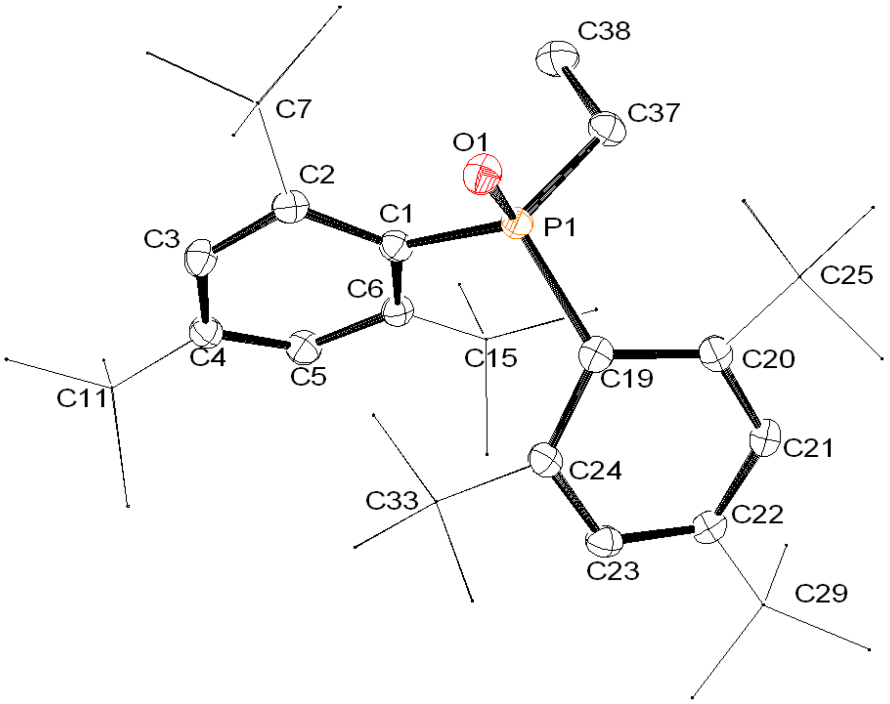


Figure 30 Molecular structure of **9**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and solvated molecule of CH_2Cl_2 are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

Compound **9** displays many of the same structural motifs as **5** and **8**, see Figure 30 and Figure 31. The phosphorus atom is displaced by 0.745 and 1.076 Å from the mean phenyl planes and the angles around this central phosphorus are close to the standard tetrahedral value.

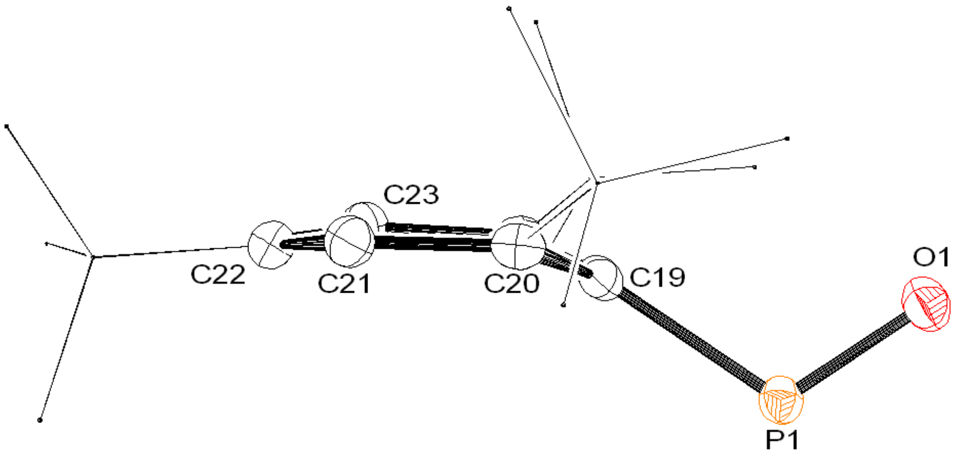


Figure 31 Alternative view of the structure of **9** showing the displacement of the phosphorus atom and the ^{t}Bu groups out of the mean aromatic plane. Thermal ellipsoids are set at 50% probability, hydrogen atoms, second Mes* ring, solvated molecule of CH_2Cl_2 and ethyl group are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

The *ortho*-^{t}Bu groups in **9** have a larger in-plane bending than those present in **5** or **8**, with the *o*-^{t}Bu groups bending between 6.32(17) and 12.1(2)° away from the idealized 120° angle. The out of plane bending of these *ortho*-substituted groups (between 0.290 and 0.715 Å) is broadly similar to that observed for **3** and **6**.

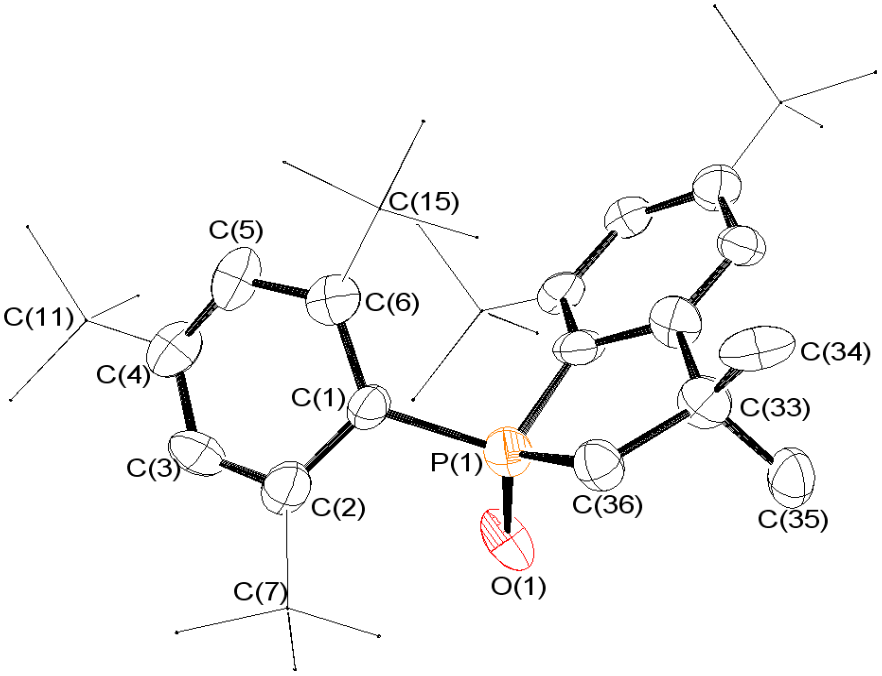


Figure 32 Molecular structure of phosphindole **4**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

Figure 32 and Table 3 show that the X-ray structure of the phosphindole **4** displays significant differences from **5**, **8** and **9**. The angles around the central phosphorus atom vary considerable from 96.3(5)° for C(19)-P(1)-C(36) in the five-membered ring to 108.6(5)° for the C(1)-P(1)-C(19). It is also interesting to note that the P(1)=O(1) bond length in **4** (1.411(7) Å) is the shorter than those seen in **5**, **8** or **9**. This is particularly noticeable when it is juxtaposed with the related phosphorus-oxygen bond length in the non-crowded phosphine oxide $Ph_2P(O)Me$ (1.494(2) Å).[85] The five-membered ring moiety within **4** is remarkably planar, with C(33) deviating the furthest from this mean 5-five-membered ring plane with a displacement of 0.133 Å, see Figure 33.

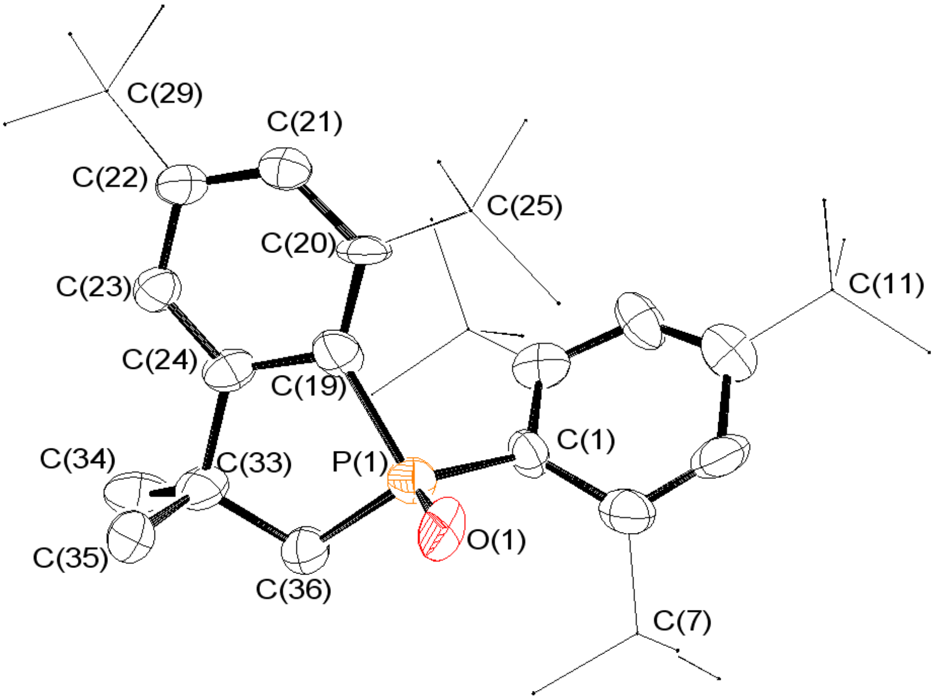


Figure 33 Alternative view of the structure of **4** showing the phosphindole ring more clearly. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

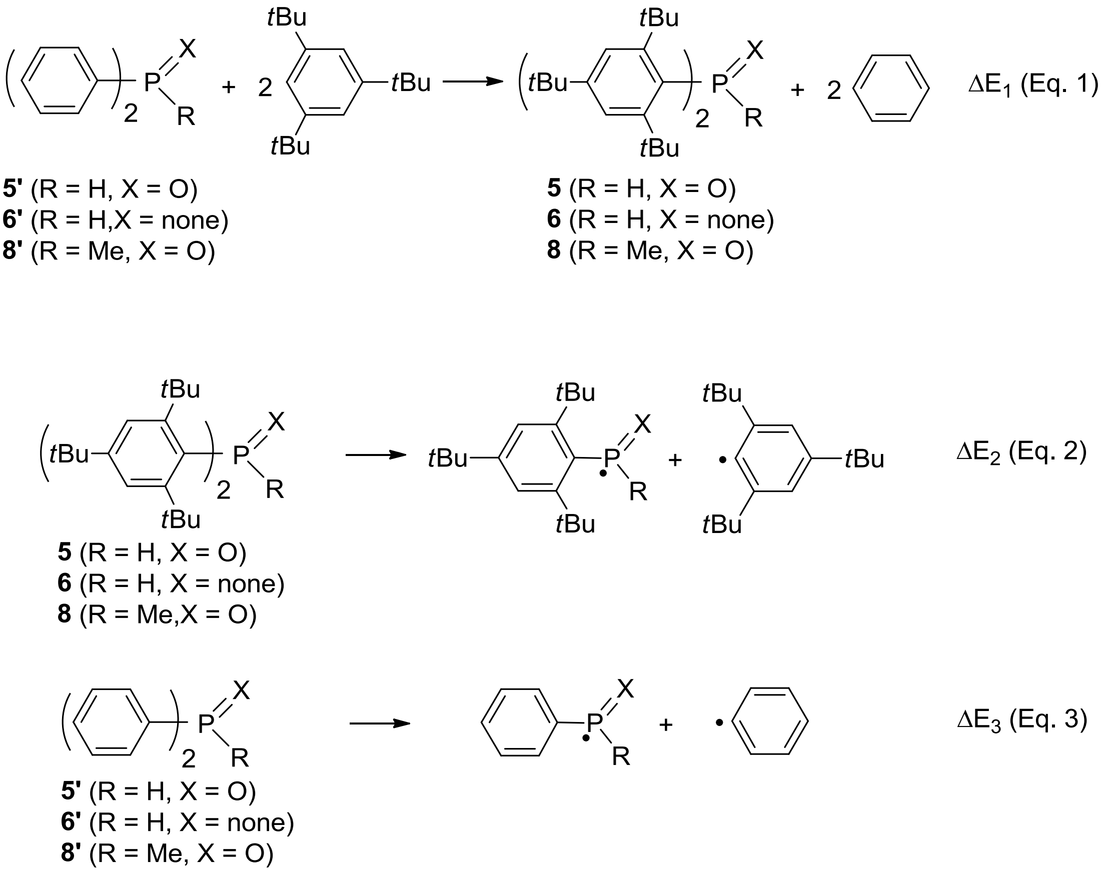
The Mes* ring [C(1) to C(6)] in **4** is again heavily distorted; C(1) and C(4) sit 0.145 and 0.119 Å, respectively, out of the mean aromatic plane, which adopts a boat conformation. This phenyl ring is even more buckled than those present in **5**, **8** or **9**. This is also illustrated by the large torsion angles within the aromatic ring. These contrast hugely with the phosphindole ring component, which has very little distortion. The majority of the strain is found within the Mes* ring. The phosphorus centre is bent 1.205 Å out of the Mes* phenyl plane, which is again the largest divergence seen amongst these comparable compounds (**5**, **8** and **9**). The phenyl plane makes an interplanar angle of 44.2° with the fused aromatic plane, similar to the angles seen for **5**, **8** and **9**. The *ortho*-^{t}Bu groups on the Mes* substituent both display in-plane bending of between 7.0(9) and 7.7(9)° away from the standard sp^2 hybridized carbon value and out of plane distortion with the tertiary carbon atoms lying 0.47 and

0.53 Å in the opposite direction from the phosphorus, see Table 3. These resemble the values seen for the compounds **5**, **8** and **9**.

g. Computational discussion

In order to gain further insight into the physical and structural properties of these sterically encumbered phosphorus centres we commissioned DFT calculations for **5**, **8** and model compounds for comparison. These calculations were preformed by Prof. Michael Bühl. The results of these calculations are summarised in Table 4. Mes*$_2$P(=O)Cl **3** has been the subject of theoretical study before;[66,67] This study was done at a lower theoretical, Hartree–Fock (HF) level, and dispersion interactions were not accounted for. The starting point was to optimise the structures at the B3LYP or M06-2X level starting from the X-ray crystal structures. The contortion of the benzene rings were overall largely preserved in the gas-phase equilibrium geometries.

The strain was evaluated as per equations in Scheme 4 and the main results of these calculations are tabulated in Table 4.



5' (R = H, X = O)
6' (R = H,X = none)
8' (R = Me, X = O)

5 (R = H, X = O)
6 (R = H, X = none)
8 (R = Me, X = O)

5 (R = H, X = O)
6 (R = H, X = none)
8 (R = Me,X = O)

5' (R = H, X = O)
6' (R = H, X = none)
8' (R = Me, X = O)

Scheme 4 Isodesmic equation (**1**) and bond dissociation equations (**2**, **3**) used in computations.

Equation **1** in Scheme 4 chronicles the transfer of the *tert*-butyl groups from two Mes*H groups on to the unconstrained phosphorus models **5'**, **6'** and **8'**. The energy associated with this reaction is ΔE_1. Equations **2** and **3** show the effects of phosphorus-carbon bond dissociation on two systems; one the sterically bulky compounds produced during our synthetic work (Eq. 2), the other a related uncrowded system (Eq. 3). The difference in the bond dissociation energies (BDEs, D_0 values) associated with these systems were then calculated ($\Delta E_2 - \Delta E_3$). This difference is largely due to the strain in the phosphorus structure with two geminally bonded Mes* motifs. It should be noted however that there are electronic effects, such as the difference in stabilization of the phosphorus or carbon-centred radicals from the electron-rich 2,4,6-tri-*tert*-butylphenyl groups, which may contribute as well. The results of the calculations are shown in Table 4.

Table 4 Energies in kJ mol^{-1} for compound **5**, its trivalent analogue **6** and the methylated compound **8** evaluated at the B3LYP-D3 level (in parentheses: M06-2X), both including zero-point energies.

Compound	ΔE_1 ^{a}	ΔE_2 ^{a}	ΔE_3 ^{a}	$\Delta E_4 = \Delta E_3 - \Delta E_2$
5	183 (186)	230 (240)	358 (379)	127 (139)
6	180	196	307	111
8	249	170	352	182

^{a} For definition see equations **1**, **2** and **3** in Scheme 4

At both B3LYP-D3 and M06-2X levels, the total strain (ΔE_1) for compound **5** is greater than 180 kJ mol^{-1}. It is worth noting that the strain in **5**, when calculated via ΔE_1, is significantly higher (266.2 kJ mol^{-1} vs. 183.1 kJ mol^{-1} at B3LYP+ZPE) when dispersion interactions are not accounted for. This shows that weak interactions play an important role in determining the structure of this compound, which contains a large number of sub-van der Waals contacts.

We have demonstrated crystallographically that when the hydrogen atom directly bonded to the phosphorus centre on **5** is replaced by a methyl group to make **8**, the C(1)-P(1)-C(19) bond angle becomes slightly more acute [114.57(17)° (B3LYP 114.0°) to 111.5(2)° (B3LYP 111.9°)] and thus the Mes* rings are pushed closer to one another. This further distorts the aromatic rings (as seen from the torsion angles in the X-ray diffraction data) and the total strain of the system is increased to slightly below 250 kJ mol^{-1}, see ΔE_1 value in Table 4. From what we know about the influence of sterically hindering groups on molecular systems, this increase in strain did not come as a surprise to us.

A crystal structure of Mes*$_2$PH **6** has been deposited with CSDS[64] but no other data were reported for this compound. In order to investigate the differences between the strain present in phosphines and phosphine oxides, computations were performed for **6**. We expected to see a contraction of the equivalent of the C(1)-P(1)-C(19) angle and thus an increase in the repulsion between Mes* groups. Indeed, the B3LYP optimized C-P-C angle was reduced on going from 114.0° in **5** to 111.1° in **6**. There are two independent molecules in the crystal structure of **6** and the C-P-C angles measured were 109.48(16) and 111.65(19)°. These experimental and calculated values contrast greatly with the X-ray diffraction data for the closely related phosphine **10** which has a C(1)-P(1)-C(19) angle of 104.00(10)°, see Table 6. There is also very little difference in strain calculated for **6** compared with **5**, see ΔE_1 values in Table 4. This is again at complete odds with the obstacles which we encountered in our synthetic endeavours where we found that **6** was not a product of the forceful reduction of Mes*$_2$P(=O)Cl **3**. It is perhaps the lower bond dissociation energies (BDE) of the phosphorus-carbon bond in **6** compared with **5** which is the reason for this inconsistency, see ΔE_2 values in Table 4.[86] In spite of this, the tertiary phosphine oxide **8** was isolated without great difficulty even though the P-C$_{Ar}$ BDE for this was predicted to be lower again. From this we come to the conclusion that the difficulty in acquiring **6** may hinge on other steric or kinetic factors which could not be properly taken into account when the calculations were done.

To look at the theoretical effects of replacing the hydrogen atom bonded to the phosphorus centre on **5** with an even bulkier alkyl group, Mes*$_2$P(=O)^{t}Bu (which could not be produce by our synthetic methodology) was optimised. The steric bulk of the ^{t}Bu group pushes the aromatic rings even closer together (C$_{Ar}$-P-C$_{Ar}$ bond angle of

109.7°) which would put a huge distortion on the P(Mes*)$_2$ moiety compared with **5** or **8**. It was found that the optimised P-C$_{Ar}$ and P-C$_{Alk}$ bond distances in Mes*$_2$P(=O)^{t}Bu where greater than 1.9 Å and 2.0 Å respectively, this compares to 1.861(5) and 1.735(6) Å in **8**. The calculated strain predicted for this molecule is incredibly high, 359 kJ mol^{-1} for Eq. **1** (B3LYP-D3 level) which would illustrate why Mes*$_2$P(=O)^{t}Bu was not made during our experimental work.

4. *The structure of Mes*(2,4-tBu$_2$C$_6$H$_3$)PH and its further reactions*

a. Production and potential deprotonation of Mes*(2,4-*t*Bu$_2$C$_6$H$_3$)PH 10

When Mes*$_2$P(=O)Cl **3** was reacted with the mixed reducing reagents LiAlH$_4$/Me$_3$SiCl or LiAlH$_4$/AlCl$_3$ in refluxing 1,4-dioxane (boiling point 101 °C) for a sufficient length of time, the phosphorus(III) species Mes*(2,4-*t*Bu$_2$C$_6$H$_3$)PH **10** was obtained in good yields (55 - 72 %). The implications of this loss of a flanking ^{t}Bu group are examined in X-ray discussion below, see Table 6. The phosphorus centre in **10** is still heavily shielded despite this carbon-carbon bond cleavage so we decided to conduct an investigation into the reactivity of **10**.

Literature examples have shown that secondary phosphines can be deprotonated by *n*BuLi[87] or other strong bases[88] and that the resulting phosphido anions can then be reacted with electrophiles to obtain a vast array of tertiary phosphines.[89,90] The transformation of **10** into a phosphido anion was therefore a significant goal of ours. Consequently, it came as a disappointment to us that no reaction was observed by ^{31}P NMR spectroscopy when **10** was heated with *n*BuLi in hexane under reflux for 2 hours. Analogously, no deprotonation was detected via ^{31}P NMR spectroscopy upon treating **10** with LDA or *s*BuLi at room temperature in ethereal solvents. It was in view of these results that a hexane solution of **10** was treated with a *t*BuLi solution at room temperature. A ^{31}P NMR spectrum of the resultant mixture revealed that a complex mixture of phosphorus containing products had been obtained. Previous work which has been carried out in relation to the deprotonation of sterically encumbered secondary phosphines have made similar observation as us;[84] when *n*BuLi was used to deprotonate Mes*RPH (where R = Me, *i*Pr or Ph) at -78°C, this reaction progressed readily. In contrast, when Mes*MesPH was treated with *n*BuLi, it did not undergo deprotonation, even at room temperature.

b. Chlorination of Mes*(2,4-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$)PH 10

We henceforth turned our attention to replacing the hydrogen directly bonded to the phosphorus centre via a different method. It has been documented[63] that extremely crowded chlorophosphines (R_2PCl) are good precursors for phosphinyl radicals ($R_2P\cdot$) via one electron reductions. It was our desire to produce the chlorophosphine derivative of **10** (Mes*(2,4-$^t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$)PCl **12**) and so we examined a range of potential chlorinating reagents and conditions, see Table 5. Portions of **10** were placed in NMR spectroscopy tubes and neat chloroform, tetrachloromethane or 1,1,2,2-tetrachloroethane were added. There sample tubes were exposed to sunlight for several weeks and tested periodically with ^{31}P NMR spectroscopy. We found that no discernable reaction occurred which led us to the conclusion that more forceful chlorination reagents or higher temperatures might be needed. No reaction was recorded when a toluene solution of **10** was heated with PCl_3 for several hours. A toluene solution of **10** was stirred at room temperature with phosgene (as a toluene solution) whereupon no reaction was observed, however when this solution was heated to 110°C under reflux for 5 hours, the dichlorophosphine (2,4-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$)$PCl_2$ **13** was recovered as the majority phosphorus containing product, see Scheme 5. This is a previously reported compound and our ^{31}P NMR spectroscopic data was in good agreement with the literature value (δ_P 166.9ppm in $CDCl_3$, literature value δ_P 167.2 in C_6D_6).[91] Crystals suitable for X-ray diffraction work were grown and we obtained the (previously unpublished) single crystal X-ray diffraction data of **13**. We have only been able to grow relatively small crystals; hence our structural data are rather poor. However they are adequate to demonstrate connectivity and support assignment of the structure. Attempts were made to produce **12** via reactions of **10** with phosgene in the presence of triethylamine or using thionyl chloride at room temperature. In both cases, a complex mixture of phosphorus containing products was generated, none of which could be identified as **12**.

Table 5 Reaction conditions used in attempted chlorination of **10**.

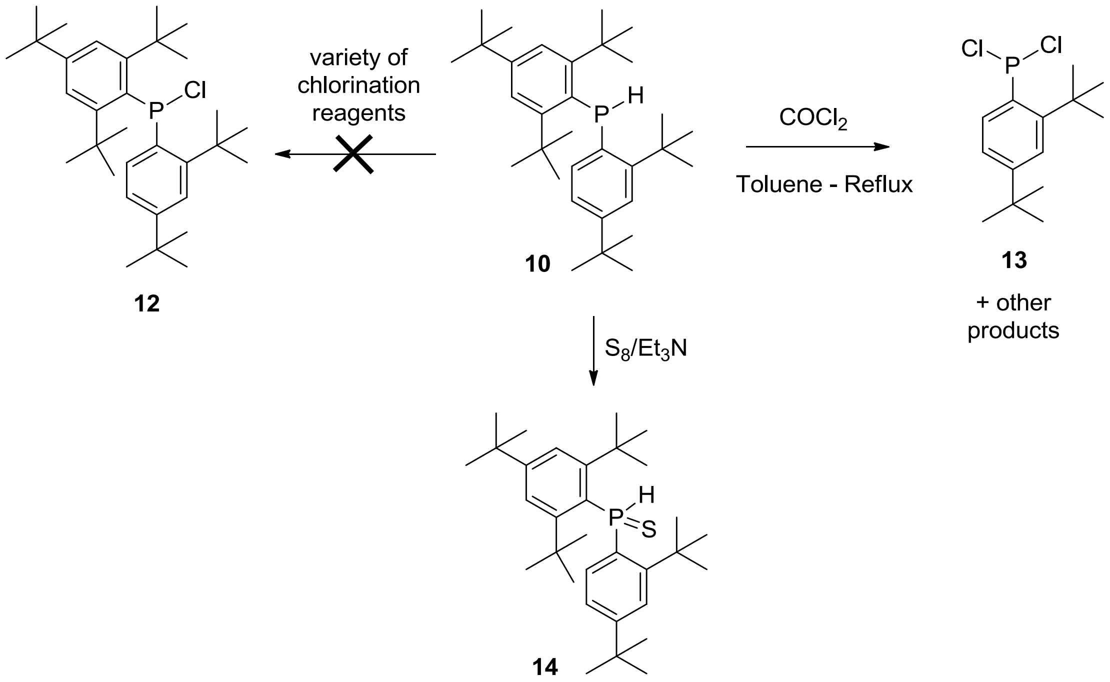
Chlorination agent	Solvent	Temperature (°C)	Time	Major Product
$CHCl_3$	Neat	RT	Weeks	No reaction
CCl_4	Neat	RT	Weeks	No reaction
$Cl_2HC\text{-}CHCl_2$	Neat	RT	Weeks	No reaction
PCl_3	Toluene	110 (reflux)	5 hours	No reaction
$Cl_2C{=}O$	Toluene	RT	5 hours	No reaction
$Cl_2C{=}O$	Toluene	110 (reflux)	5 hours	(2,4-*t*$Bu_2C_6H_3$)PCl_2 **13**
$Cl_2C{=}O + NEt_3$	Toluene	RT	1 hour	Complex mixture
$Cl_2S{=}O$	Toluene	RT	1 hour	Complex mixture

c. Boronation, thionation and selenation of Mes*(2,4-*t*$Bu_2C_6H_3$)PH 10

Due to our lack of success in replacing the hydrogen atom on the phosphorus centre on **10**, we altered the focus of our reactivity study to examining its potential as a Lewis base, see Scheme 5. With that in mind a THF solution of **10** was treated with a borane dimethyl sulfide complex (in Et_2O) with a view to making a borane adduct. After stirring at room temperature for 2 hours a ^{31}P NMR spectrum of the reaction mixture showed that no reaction had occurred. No reaction was also observed when a toluene solution of **10** was heated under reflux with the same borane complex. This lack of affinity for borane was flabbergasting as the production of borane adducts of phosphorus(III) structure is easily achieved with less sterically hindered compounds such as $Mes_2HP{\cdot}BH_3$.[92]

In light of this, we were somewhat surprised by the clean reaction of **10** with elemental sulfur. The desired secondary phosphine sulfide (Mes*(2,4-$^tBu_2C_6H_3$)P(=S)H **14**) was produced in rather forceful conditions by heating **10** with one equivalent of powdered S_8 under reflux in toluene with the addition of an excess of Et_3N, see Scheme 5. The pure product **14** was isolated in 45 % yield after column chromatography and was fully characterised by ^{31}P, ^1H and ^{13}C NMR spectroscopy, IR, Raman and ES MS (including exact mass determination); its purity was verified by microanalyses. It is interesting to note that the phosphorus-hydrogen stretching bands in both IR and Raman of **14** are extremely weak, much more so than in **10**. A crystalline sample of **14** was also prepared and this was characterised by a single crystal X-ray diffraction, see Table 6. When **14** is compared to the less sterically encumbered sulfide $Ph_2P(=S)H$ it was shown that they have very similar phosphorus chemical shifts (δ_P 17.3 for **14**, δ_P 23.4 for $Ph_2P(=S)H$).[93]

In contrast, when **10** was treated with grey selenium and an excess of Et_3N in boiling toluene, starting material was recovered exclusively. This outcome was not surprising for us as selenations generally requires more forcing conditions than related thionations.



Scheme 5 The chlorination and thionation reactions of the secondary phosphine **10**.

d. X-ray discussion of the novel compounds 10, 13 and 14

The X-ray crystal structures of **10**, **13** and **14** are shown in Table 6 and Figure 34, Figure 35 and Figure 36 respectively. Crystals of **10** and **14** were grown via the slow evaporation of a concentrated dichloromethane solution. Crystals of **13** were obtained from evaporating toluene solution under reduced pressure. The structural date for **13** is poor so the aromatic ring C(1) to C(6) is fixed as being planer.

Table 6 Bond distances (Å), bond angles (°), torsion angles (°) and displacements from mean phenyl planes (Å) in compounds **10**, **13** and **14**.

Bond lengths (Å)	**10**	**13**	**14**
P(1)-C(1)	1.853(2)	1.828(10)	1.838(7)
P(1)-C(19)/Cl(1)	1.868(3)	2.072(3)	1.852(8)
P(1)-S(1)/Cl(2)	-	2.072(3)	1.959(4)
Bond angles (°)			
C(1)-P(1)-C(19)	104.00(10)	-	110.3(4)
C(1)-P(1)-S(1)/Cl(1)	-	99.9(3)	114.9(3)
Cl(1)-P(1)-Cl(2)	-	99.0(2)	-
C(19)-P(1)-S(1)	-	-	119.4(3)
C(2)-C(1)-C(6)	118.94(18)	120.2(8)	118.5(6)
C(20)-C(19)-C(24)	117.7(2)	-	119.2(8)
C(1)-C(2)-C(7)	124.66(19)	124.4(8)	126.8(6)
C(1)-C(6)-C(15)	125.13(18)	-	129.1(7)
C(19)-C(20)-C(25)	124.06(19)	-	127.3(7)
Dihedral angles (°)			
C(1)-C(2)-C(3)-C(4)	2.9(3)	0	0.5(13)
C(1)-C(6)-C(5)-C(4)	1.5(3)	0	1.6(14)
C(2)-C(3)-C(4)-C(5)	3.5(3)	0	0.8(13)
C(3)-C(4)-C(5)-C(6)	4.2(3)	0	0.3(14)
C(3)-C(2)-C(1)-C(6)	8.6(3)	0	0.9(12)
C(2)-C(1)-C(6)-C(5)	8.0(3)	0	1.8(12)
C(19)-C(20)-C(21)-C(22)	1.1(3)	-	3.2(13)
C(19)-C(24)-C(23)-C(22)	0.9(4)	-	3.6(14)
C(20)-C(21)-C(22)-C(23)	0.6(3)	-	3.3(13)
C(21)-C(22)-C(23)-C(24)	0.4(3)	-	6.6(13)
C(21)-C(20)-C(19)-C(24)	0.6(3)	-	6.3(12)
C(20)-C(19)-C(24)-C(23)	0.3(3)	-	3.2(13)
Displacement from mean phenyl plane[a] (Å)			
P(1)	0.351	0	0.251
C(1)	0.053	0	0.008
C(4)	0.036	0	0.004
C(7)	0.221	0	0.017
C(15)	0.175	-	0.040
C(11)	0.108	0	0.058
Displacement from mean phenyl plane[b] (Å)			
P(1)	0.043	-	0.186
C(19)	0.001	-	0.036
C(22)	0	-	0.035
C(25)	0.078	-	0.151
C(29)	0.015	-	0.145

[a] Distance from the phenyl mean plane fitted through atoms C(1) to C(6)

[b] Distance from the phenyl mean plane fitted through atoms C(19) to C(24)

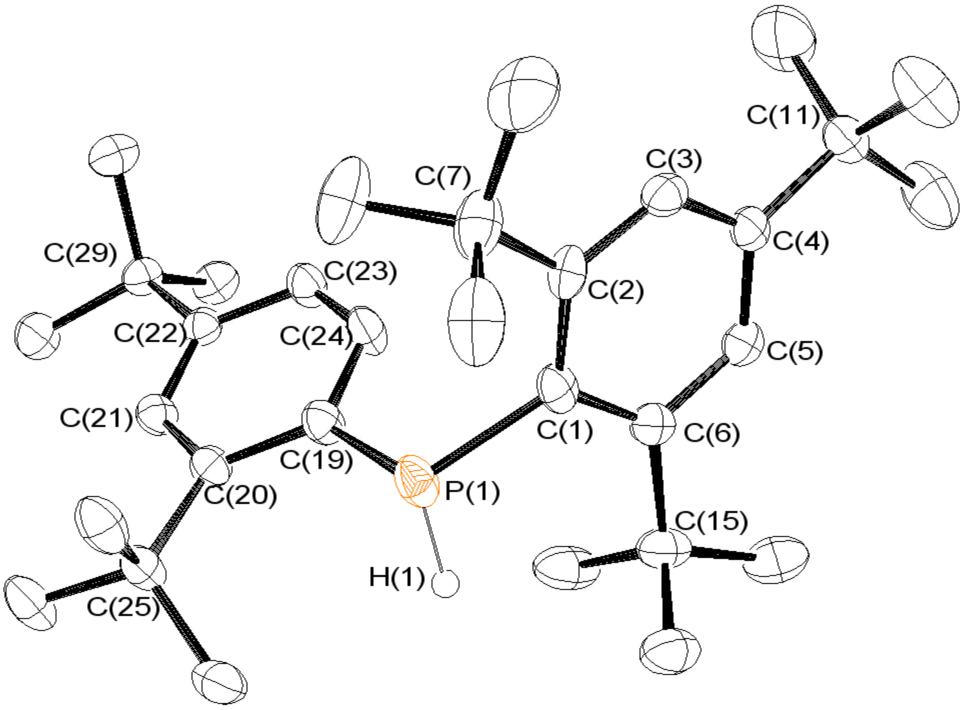


Figure 34 Molecular structure of **10**. Thermal ellipsoids are set at 50% probability, all hydrogen atoms except H(1) are omitted for clarity.

Table 6 displays the crystallographic data for **10**, which shows that **10** adopts a more relaxed geometry than Mes*$_2$P(=O)H **5** with much decreased torsion angles and the phosphorus centre much closer to the mean aromatic planes (0.043 and 0.351 Å displacements for **10** vs. 0.658 and 1.076 Å for **5**). The mean phenyl planes are for all practical purposes perpendicular to each other (88.6°). This helps to prevent the *ortho*-^{t}Bu groups from interacting sterically with one another. The decrease in ring distortion is mirrored by less out of plane twisting of the flanking *tert*-butyl groups, the quaternary carbons of which lie between about 0.078 and 0.221 Å out of their respective mean aromatic planes. The in-plane bending observed shows these groups are positioned between 4.06(19) and 5.13(18)° away from the idealized trigonal planar molecular geometry, which is notably less than the angles seen in **5**, **8** and **9**. The C(1)-P(1)-C(19) angle in **10** is significantly sub-tetrahedral (104.00(10)°). This concurs with our view that as the lone pair lies closer to the phosphorus atomic centre than the electron density in a P=O bond that there be a significant narrowing of angles compared with P(V) structures **5**, **8** and **9**.

As was alluded to before, crystal data for the secondary phosphine Mes*$_2$PH **6** has been deposited with CSDS.[64] No auxiliary information, either synthetic or physical has been offered as yet to support this structure. There are two molecules in the unit cell of **6** and the C(1)-P(1)-C(19) equivalent angles are 109.48(16) and 111.65(19)°, the phosphorus centres are displaced between 0.69 and 0.80 Å from the respective phenyl planes. The phenyl rings in **6** are significantly more twisted than those in **10** with a large increase in torsion angles and displacements of the *ipso*-carbon atoms from the mean aromatic planes. This clearly demonstrates the effect that the loss of an *ortho*-positioned *tert*-butyl group has on the system, **10** being much less deformed than other examples such as **5, 8** and **9**.

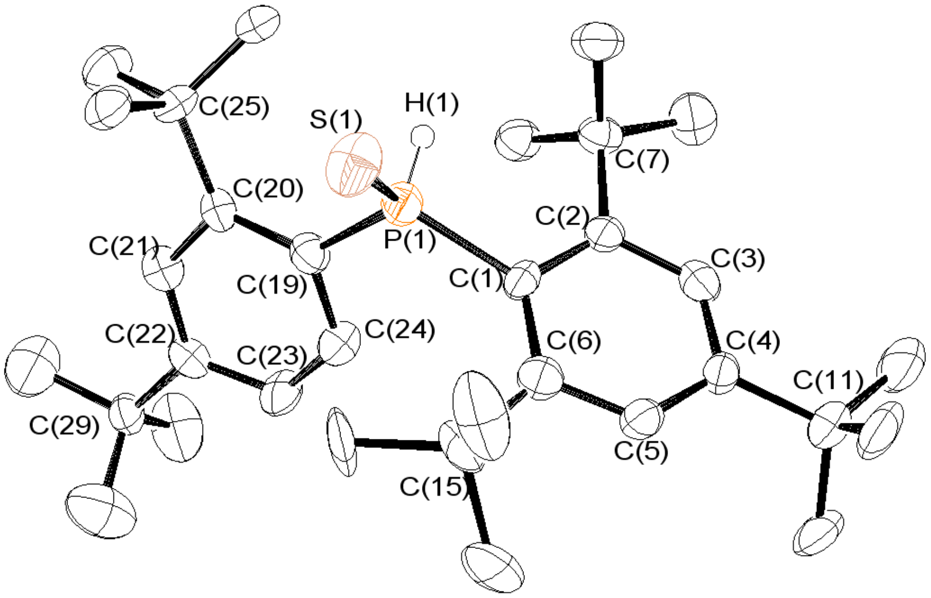


Figure 35 Molecular structure of the sulfide **14**. Thermal ellipsoids are set at 50% probability, hydrogen atoms except H(1) are omitted for clarity.

X-ray structure of sulfide **14** is shown in Figure 35 and Table 6. The C(1)-P(1)-C(19) angle (110.3(4)°) in **14** is much closer to the standard tetrahedral value. The Mes* group is close to being planar, with C(1) being displaced only 0.008 Å from the mean aromatic plane and limited contortion of the ring. The phenyl ring within the 2,4-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$ group is twisted very slightly into a boat conformation, but this twisting is decidedly less than the distortion seen in **5**, **8** and **9**. The mean phenyl planes lie almost perpendicular in relation to each other (71.9°) and phosphorus centre is displaced 0.186 and 0.251 Å out of these mean aromatic planes. This shows there is still some significant steric hindrance present in the system but unambiguously less than in the structure with two whole supermesityl groups. The flanking *tert*-butyl groups display virtually no bending out of their respective mean aromatic planes, however they are still considerably contorted away from the ideal 120° angles (between 6.8(6) and 9.1(7)°). The P(1)-S(1) bond length in **14** (1.958(2) Å) is almost identical with that of the similarly crowded bis(alkyl) phosphine sulfide $(t\mathrm{Bu})_2\mathrm{P({=}S)H}$ (1.9666(6) Å).[94]

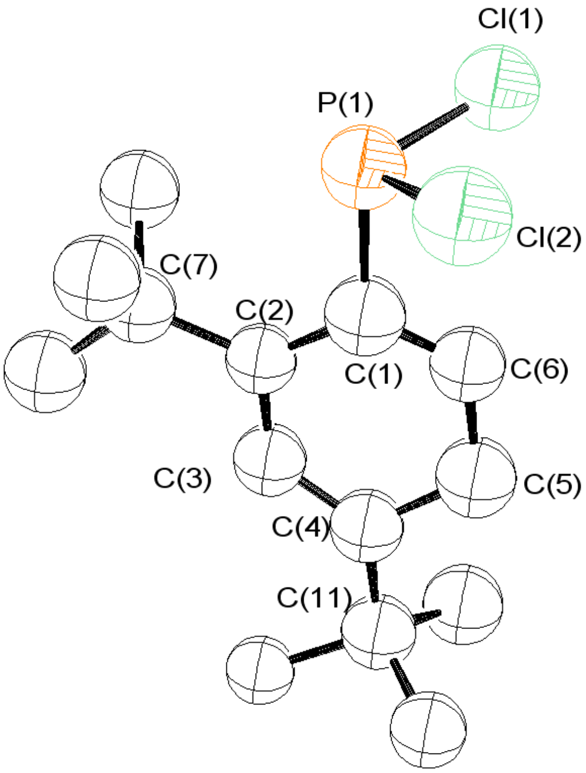


Figure 36 Molecular structure of **13**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

X-ray structure of (2,4-*t*Bu$_2$C$_6$H$_3$)PCl$_2$ **13** is shown in Figure 36 and Table 6. The structure of **13** can be considered as a product of a formal replacement of one Mes* group in **12** with a Cl atom. This causes the phenyl ring within the 2,4-*t*Bu$_2$C$_6$H$_3$ group to relax to become perfectly planar, which results in this structure possessing crystallographic C_s symmetry. The lone pair has a gargantuan influence on the molecular geometry around the central phosphorus atom with carbon-phosphorus-chlorine bond angles being 99.9(3)°. When compared to the analogous aryldichlorophosphine Mes*PCl$_2$ **1**,[95] (2,4-*t*Bu$_2$C$_6$H$_3$)PCl$_2$ **13** is demonstrably more relaxed with the C(2)-C(1)-C(6) angle of 120.2(8)° compared with 113.9(10)° for **1**. The angles P(1)-C(1)-C(2) (122.1(8)°) and P(1)-C(1)-C(6) (117.6(7)°) in **13** are in significant contrast with the corresponding angles 130.8(9) and 111.9(9)° in Mes*PCl$_2$ **1**.

5. Experimental

General notes

All experiments were carried out in standard Schlenk glassware or in a glove box with strict exclusion of air and moisture, using a nitrogen or argon atmosphere. Solvents were dried on an MBraun solvent purification system. Column chromatography was performed in air with non-degassed solvents. The 2-bromo-1,3,5-tri-*t*-butylbenzene (Mes*Br) starting material was made according to literature procedures in two steps from benzene.[29,30] Unless stated otherwise, the new compounds were fully characterized by $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, including measurement of $^{1}H\{^{31}P\}$, ^{31}P (^{1}H coupled), H–H DQF COSY , H–P HSQC and H–C HSQC experiments. Measurements were performed at 25 °C unless said otherwise; 85% H_3PO_4 was used as external standard in ^{31}P. ^{1}H and ^{13}C NMR spectroscopy chemical shifts are relative to TMS, which was used as internal standard, or residual solvent peaks were used for calibration ($CHCl_3$ δ_H 7.26, δ_C 77.2 ppm). *J* values are given in Hz.

Mes*$_2$P(=O)Cl 3. A solution of Mes*Br (15.27 g, 46.9 mmol) in THF (200 ml) was cooled to -78 °C. A hexane solution of *n*-butyllithium (20 ml of 2.5M solution, 50 mmol) was added over 30 minutes and the solution was then stirred for a further 30 minutes at -78 °C. Phosphoryl chloride (5.0 ml, 51.9 mmol) was added over 20 minutes. The resulting solution was maintained at -78 ^{o}C for 2 hours and was then allowed to rise to ambient temperature overnight. The solvent and excess phosphoryl chloride were removed *in vacuo*. The yellow solid residue was taken up in dichloromethane and washed with 3 × 100 ml of water. The organic layer was separated and dried over anhydrous magnesium sulfate. The volatiles were removed *in vacuo* and the resultant yellow solid was chromatographed on silica gel. Elution with hexane gave the by-product 1,3,5-tri-*t*-butylbenzene as the first band. The eluent was then changed to 97:3 hexane:ethyl acetate which furnished **3** as a white solid (yield range 7.26-8.74 g, 54-65%); mp 206-210 ºC; (Found: C, 75.24; H, 10.15. Calc. for $C_{36}H_{58}ClOP$: C, 75.42; H, 10.20); IR (KBr disk) υ_{max}/cm^{-1} 2962vs (υ_{CH}), 2908s (υ_{CH}), 1583m, 1236s ($\upsilon_{P=O}$), 614s, 205s; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2967vs (υ_{CH}), 2911vs (υ_{CH}), 1584m, 1238m ($\upsilon_{P=O}$), 821s, 267s; δ_H (300.1 MHz; $CDCl_3$) 7.47 (1H, dd, $^4J_{PH}$ = 4.8, $^4J_{HH}$ = 1.8, ArH), 7.36 (1H, dd, $^4J_{PH}$ = 4.6, $^4J_{HH}$ = 1.9, ArH), 7.24 (1H, dd, $^4J_{PH}$ = 5.8, $^4J_{HH}$ = 2.0, ArH), 7.15 (1H, dd, $^4J_{PH}$ = 6.0, $^4J_{HH}$ = 2.1, ArH), 1.55 (9H, s, *o*-*t*Bu), 1.50 (9H, s, *o*-*t*Bu), 1.23 (18H, s, 2 × *p*-*t*Bu), 0.69 (9H, s, *o*-*t*Bu), 0.66 (9H, s, *o*-*t*Bu); δ_C (75.5 MHz, $CDCl_3$) 161.7 (d, $^2J_{PC}$ = 9.9, *o*-C), 159.3 (d, $^2J_{PC}$ = 7.1, *o*-C), 155.1 (d, $^2J_{PC}$ = 12.7, *o*-C), 153.3 (d, $^2J_{PC}$ = 11.9, *o*-C), 151.1 (d, $^4J_{PC}$ = 4.5, *p*-C), 150.9 (d, $^4J_{PC}$ = 5.0, *p*-C), 131.5 (d, $^1J_{PC}$ = 126.0, *ipso*-C), 127.7 (d, $^1J_{PC}$ = 134.5, *ipso*-C), 126.1 (d, $^3J_{PC}$ = 15.7, *m*-C), 125.6 (d, $^3J_{PC}$ = 15.7, *m*-C), 124.2 (d, $^3J_{PC}$ = 16.1, *m*-C), 123.3 (d, $^3J_{PC}$ = 17.1, *m*-C), 42.1 (s, *o*-$\underline{C}(CH_3)_3$), 42.0 (s, *o*-$\underline{C}(CH_3)_3$), 41.7 (s, *o*-$\underline{C}(CH_3)_3$), 41.6 (s, *o*-$\underline{C}(CH_3)_3$), 41.1 (d, $^5J_{PC}$ = 3.1, *p*-$\underline{C}(CH_3)_3$), 41.0 (d, $^5J_{PC}$ = 4.0, *p*-$\underline{C}(CH_3)_3$), 33.4 (s, *o*-$C(\underline{C}H_3)_3$), 33.0 (s, *o*-$C(\underline{C}H_3)_3$), 32.5 (s, *o*-$C(\underline{C}H_3)_3$), 31.7 (s, *o*-$C(\underline{C}H_3)_3$), 29.9 (broad s, 2 × *p*-$C(\underline{C}H_3)_3$); δ_P (121.5 MHz, $CDCl_3$) 45.3 (s); MS (ES+) *m/z* 573.36 (M+H$^+$).

Mes*$_2$P(=O)CH$_3$ 8. A hexane (10 ml) solution of **3** (0.125 g, 0.218 mmol) was cooled in ice. Methyllithium (0.2 ml of 1.6 M solution in hexane, 0.32 mmol) was added to this dropwise. This was stirred and allowed to rise to room temperature. A $^{31}P\{^1H\}$ NMR spectroscopy investigation showed that only starting material was present. The solution was then heated to reflux and maintained at that temperature for 90 minutes. Upon cooling the mixture was reassessed and it was shown that the starting material was the only phosphorus containing compound present. $\delta_{P\{^1H\}}$ (121.5 MHz, $CDCl_3$) 45.9 (s)

Mes*$_2$P(=O)H 5. A suspension of lithium aluminium hydride (2.00 g, 52.8 mmol) in THF (100 ml) was cooled in ice. To this powdered **3** (3.56 g, 6.22 mmol) was added in small batches with stirring. The suspension was heated under reflux; samples of reaction mixture were taken periodically and investigated by ^{31}P NMR spectroscopy. The reaction was deemed complete when the starting material vanished from spectrum to be replaced by a transient (presumably aluminium) complex of compound **5** (s, δ_P 102.4). The time needed to drive reaction to completion varied from 6 to 9 hours. The mixture was cooled in ice and then water (5 mL) was added very slowly to hydrolyse remaining hydride with evolution of H_2 gas. The resulting suspension was filtered using glass sinter (porosity S3) and the solid collected on the filter was washed through with dichloromethane (3 × 30 ml). The volatiles were evaporated *in vacuo*. The yellow residue was then taken up with more dichloromethane and washed with water (3 × 100 ml). The organic layer was separated and dried with anhydrous magnesium sulfate. The volatiles were then removed *in vacuo*. The yellow solid obtained was chromatographed on silica gel. Elution with hexane gave the by-products 1,3,5-tri-*t*-butylbenzene and 2,4,6-tri-*t*-butylphenylphosphine [δ_P -129.9 (t, $^1J_{PH}$ = 210.1 Hz)].[71] The eluent was then altered to 97:3 hexane:ethyl acetate. The by-product 2,4,6-tri-*t*-butylphenylphosphine oxide [δ_P -11.3 (t, $^1J_{PH}$ = 482.4 Hz)][72] emerged slightly ahead of the desired product **5** (δ_P 12.9 (d, $^1J_{HP}$ = 483.0 Hz)), so the first few fractions were tested by ^{31}P NMR spectroscopy until the first uncontaminated fraction egressed. After combining the uncontaminated fractions and evaporation of volatiles in vacuo **5** was obtained as a white powder (yield range 1.27-1.87 g, 38-56%); mp 179-181 °C; (Found: C, 79.91; H, 11.36. Calc. for $C_{36}H_{59}OP$: C, 80.25; H, 11.04); IR (KBr disk) υ_{max}/cm^{-1} 2965vs (υ_{CH}), 2909vs (υ_{CH}), 1586m, 1191s ($\upsilon_{P=O}$), 982s, 614s; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2969vs (υ_{CH}), 2909vs (υ_{CH}), 1595m, 1192s ($\upsilon_{P=O}$), 822s, 567s; δ_H (300.1 MHz; $CDCl_3$) 8.91 (1H, d, $^1J_{PH}$ = 482.8, P-H), 6.70-7.70 (4H, br s, 4 × ArH), 1.80-1.40 (18H, br m, 2 × o-*t*Bu), 1.21 (18H, s, 2 × p-*t*Bu), 1.00-0.40 (18H, broad s, 2 × o-*t*Bu); δ_C (100.6 MHz, $CDCl_3$) 155.0-156.6 (br m, C_q), 150.4-152.2 (br m, C_q), 121.9-127.8 (br m, 4 × CH), 37.6-43.2 (br m, 4 × o-$\underline{C}(CH_3)_3$), 34.5 (s, 2 × *p*-$\underline{C}(CH_3)_3$), 32.1-34.0 (br m, 4 × o-$C(\underline{C}H_3)_3$), 30.4-31.7 (br s, 2 × p-$C(\underline{C}H_3)_3$); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 12.9 (s); δ_P (121.5 MHz, $CDCl_3$) 12.9 (d, $^1J_{HP}$ = 483); δ_H (499.9 MHz; CD_2Cl_2; 213 K) 8.99 (1H, d, $^1J_{PH}$ = 483.3, P-H), 7.53 (1H, br s, ArH), 7.42 (2H, br s, 2 × ArH), 7.13 (1H, br s, ArH), 1.72 (9H, s, o-*t*Bu), 1.63 (9H, s, o-*t*Bu), 1.32 (18H, s, 2 × p-*t*Bu), 0.86 (9H, s, o-*t*Bu), 0.72 (9H, s, o-*t*Bu); δ_C (125.7 MHz, CD_2Cl_2; 213 K) 161.4 (s, *o*-C), 155.8 (d, $^2J_{PC}$ = 3.4, *o*-C), 155.6 (d, $^2J_{PC}$ = 11.1, *o*-C), 154.8 (d, $^2J_{PC}$ = 6.1, *o*-C), 151.8 (s, *p*-C), 150.8 (s, *p*-C), 129.9 (d, $^1J_{PC}$ = 106.2, *ipso*-C), 128.1 ($^1J_{PC}$ = 96.6, *ipso*-C), 126.6 (d, $^3J_{PC}$ = 11.7, *m*-C), 124.6 (d, $^3J_{PC}$ = 11.3, *m*-C), 124.5 (d, $^3J_{PC}$ = 13.3, *m*-C), 123.3 (d, $^3J_{PC}$ = 11.1, *m*-C), 40.8 (s, *o*-$\underline{C}(CH_3)_3$), 40.1 (d, $^3J_{PC}$ = 3.1, *o*-$\underline{C}(CH_3)_3$), 39.9 (s, *o*-$\underline{C}(CH_3)_3$), 39.3 (s, *o*-$\underline{C}(CH_3)_3$), 34.8 (s, o-$C(\underline{C}H_3)_3$), 34.5 (s, 2 × *p*-$\underline{C}(CH_3)_3$), 33.1 (s, o-$C(\underline{C}H_3)_3$), 32.9 (s, o-$C(\underline{C}H_3)_3$), 31.2 (s, o-$C(\underline{C}H_3)_3$), 30.9 (s, 2 × p-$C(\underline{C}H_3)_3$); MS (ES+) *m/z* 539 (M+H$^+$), 561 (M+Na$^+$).

Mes*$_2$P(=O)H 5. Triethyl amine (1.4 ml, 10.1 mmol) was added to a solution of **3** (0.56g, 0.98 mmol) in toluene (20 ml). This stirred mixture was cooled in ice and trichlorosilane (1 ml, 9.9 mmol) was added dropwise. Upon completion of addition, the mixture was allowed to return to room temperature and then heated to reflux for four hours. It was then allowed to cool and it was investigated via $^{31}P\{^1H\}$ NMR spectroscopy. The mother liquor revealed the presence of starting material almost exclusively. $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 45.9 (s)

Mes*$_2$P(=O)H 5. A THF (30ml) solution of Mes*$_2$P(=O)Cl **3** (0.31g, 0.54 mmol) was cooled in ice. To this was added dropwise lithium triethylborohydride (5 ml of 1.0M solution in THF, 5 mmol) or diisobutylaluminium hydride (5 ml of 1.0M solution in THF, 5 mmol). The mixture was allowed to stir and rise to room temperature overnight. An aliquot of the reaction mixture was evaluated via $^{31}P\{^1H\}$ NMR spectroscopy. It was found in both cases to contain only starting material. $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 45.9 (s)

Mes*$_2$P(=O)H 5. The starting material **3** (0.24g, 0.42 mmol) was placed in a flask with either (a) sodium hydride (0.2g of 60% (w/w) in mineral oil, 5mmol) (b) sodium borohydride (0.2g, 5.3 mmol) or (c) Triphenylsilane (1.3g, 4.9 mmol). This was cooling in ice and THF (30 ml) was added. The stirred mixture was allowed to return to room temperature overnight. When a $^{31}P\{^1H\}$ NMR spectroscopic investigation divulged only starting material in these mixtures they were heated to reflux for 6 hours. Upon cooling the mixture were again assessed to reveal that no reaction had occurred in all cases

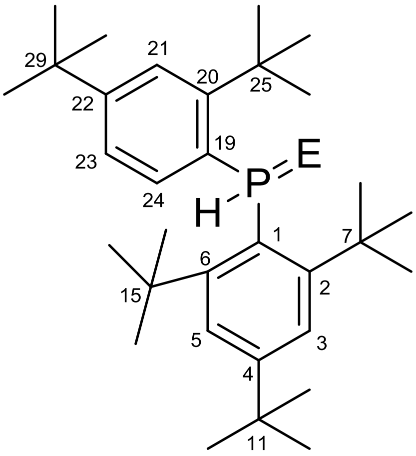


Figure 37 NMR spectroscopy numbering scheme for **10** and **14**. E = none or S

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH 10.

Method 1: A suspension of lithium aluminium hydride (2.50 g, 65.8 mmol) in 1,4-dioxane (100 ml) was cooled in ice. To this trimethylsilyl chloride (9.2 ml, 72.0 mmol) was added slowly, followed by powdered **3** (3.73 g, 6.51 mmol). The flask was fitted with a reflux condenser and heated to 100 °C. Samples of the reaction mixture were taken periodically and investigated by ^{31}P NMR spectroscopy, the heating was continued until all the starting material was consumed, typically 5 hours. The mixture was cooled in ice and then water (5 ml) was added very slowly to hydrolyse the remaining hydride with evolution of H$_2$ gas. The resulting suspension was filtered using glass sinter (porosity S3) and the solid collected on the filter was washed through with dichloromethane (3 × 30 ml). The volatiles were evaporated *in vacuo*. The yellow residue was then taken up with fresh dichloromethane and washed with water (3 × 100 ml). The organic layer was separated and dried with anhydrous magnesium sulfate. The volatiles were then removed *in vacuo*. The yellow solid obtained was chromatographed on silica gel using hexane as eluent. The by-product 2,4,6-tri-*t*-butylphenylphosphine [(δ_P -129.9 (t, $^1J_{PH}$ = 210.1 Hz)][71] emerged only slightly ahead of **10**, so the first few fraction were tested by ^{31}P NMR spectroscopy.

The uncontaminated fractions were combined and after evaporation of volatiles *in vacuo* **10** was obtained as a white powder (yield range 1.67-2.19 g, 55-72%).

Method 2:

A stirred suspension of lithium aluminium hydride (0.52 g, 13.7 mmol) and aluminium trichloride (2.01 g, 15.2 mmol) in 1,4-dioxane (40 ml) was cooled in ice. Powdered **3** (0.93 g, 1.62 mmol) was added in small batches. The suspension was heated under reflux; the progress of the reaction was monitored by ^{31}P NMR spectroscopy. When all the starting material was consumed (typically 7-9 hours) the reaction was cooled in ice and water (~ 5 ml) was added slowly to hydrolyse the remaining hydride with evolution of H_2 gas. The same workup procedure including chromatography purification was used as in Method 1 above. After combining the uncontamined fractions and evaporation of volatiles *in vacuo* **10** was obtained as a white powder (yield range 0.19-0.23 g, 26-30%); see Figure 37 for NMR spectroscopy numbering scheme; mp 158-162 ºC; (Found: C, 82.13; H, 11.39. Calc. for $C_{32}H_{51}P$: C, 82.35; H, 11.01); IR (KBr disk) υ_{max}/cm^{-1} 2963vs (υ_{CH}), 2867vs (υ_{CH}), 2427w (υ_{PH}), 1597m, 1473m, 1390m, 1393m, 1361m, 1237m, 879s; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2967vs (υ_{CH}), 2906vs (υ_{CH}), 2429w (υ_{PH}), 1597s, 1460m, 1202s, 1048m, 925s, 823s, 685s; δ_H (300.1 MHz; $CDCl_3$) 7.47 (1H, br s, H3 or H5), 7.41 (1H, br d, $^4J_{PH}$ = 2.6, H3 or H5), 7.28 (1H, dd, $^4J_{PH}$ = 4.4, $^4J_{HH}$ = 2.1, H21), 6.69 (1H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.1, H23), 6.05 (1H, d, $^1J_{PH}$ = 236.5, P-H), 5.77 (1H, dd, $^3J_{HH}$ = 8.1, $^3J_{PH}$ = 5.1, H24), 1.52 (9H, s, 25-Me_3), 1.40 (9H, s, 7-Me_3 or 15-Me_3), 1.37 (9H, s, 7-Me_3 or 15-Me_3), 1.29 (9H, s, 29-Me_3), 1.14 (9H, s, 11-Me_3); δ_C (75.5 MHz, $CDCl_3$) 155.6 (d, $^2J_{PC}$ = 21.6, C2 or C6), 154.5 (s, C2 or C6), 149.7 (d, $^2J_{PC}$ = 17.4, C20), 149.2 (s, C4 or C22), 148.3 (s, C4 or C22), 133.2 (s, C24), 132.9 (d, $^1J_{PC}$ = 28.3, C19), 128.4 (d, $^{1}J_{PC}$ = 29.9, C1), 121.6 (s, C3 or C5), 121.5 (s, C3 or C5), 121.4 (s, C21), 121.2 (s, C23), 37.4 (s, C7 or C15), 37.2 (s, C7 or C15), 36.3 (s, C25), 34.1 (s, C11), 33.5 (s, C29), 32.5 (s, 25-Me_3), 32.3 (s, 7-Me_3 or 15-Me_3), 32.1 (s, 7-Me_3 or 15-Me_3), 30.3 (s, 29-Me_3), 30.1 (s, 11-Me_3); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) -67.1 (s); δ_P (121.5 MHz, $CDCl_3$) -67.1 (d, $^{1}J_{HP}$ = 237.3); MS (ES+) *m/z* 467 ($M+H^+$), 505 ($M+O+Na^+$), 988 [$(M+O)_2+Na^+$]

(2,4-*t*$Bu_2C_6H_3$)(Mes*)PH 10. A stirred 1,4-dioxane (100 ml) suspension of lithium aluminium hydride (0.489 g, 12.9 mmol) and cerium trichloride (2.81 g, 11.5 mmol) was cooled in ice. To this powdered **3** (0.63 g, 1.1 mmol) was added in small batches. The mixture was heat to reflux and maintained at the temperature for 6 hours. Upon cooling an aliquot of the mother liquor was taken and investigated via $^{31}P\{^{1}H\}$ NMR spectroscopy. It was reveal that the major product was Mes*PH_2 (δ_P -129.9 (t, $^{1}J_{PH}$ = 210.1 Hz))[71] with significant amounts of Mes*P(=O)H_2 (δ_P -11.3 (t, $^{1}J_{PH}$ = 482.4 Hz))[72] also present. Some of the desired product **10** was also detected.

(2,4-*t*$Bu_2C_6H_3$)(Mes*)P^-. A hexane (20 ml) solution of **10** (0.22 g, 0.47 mmol) with TMEDA (0.3 ml, 2 mmol) was cooled in ice. A solution of *n*-butyllithium (0.2 ml of 2.5M solution in hexane, 0.5 mmol) was added dropwise. A red colour developed however an aliquot of the reaction mixture showed that the starting material (δ_P -67.1) was the sole phosphorus containing product displayed. The colour change was probably caused by an impurity present in miniscule proportions. The stirred solution was allowed to rise to room temperature and finally heated to reflux for 2 hours. Upon cooling the mother liquor was investigated via $^{31}P\{^{1}H\}$ NMR spectroscopy which revealed that no deprotonation had occurred.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)P$^-$. A THF (10ml) solution of **10** (0.15 g, 0.32 mmol) was cooled in ice. Either a solution of *s*-butyllithium (0.25 ml of 1.4M solution in cyclohexane, 0.35 mmol) or lithium diisopropylamide (0.2 ml of 2.0M solution in THF/*n*-heptanes/ethylbenzene, 0.4 mmol) was added dropwise. A red colour developed. This was allowed to rise to room temperature. An aliquot of the mother liquor indicated that no deprotonation had taken place as the starting material (δ_P -67.1) was the only peak in $^{31}P\{^1H\}$ NMR spectroscopy. The initial colour change may have been caused by the reaction of an impurity present in a tiny amount.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)P$^-$ A hexane (12ml) solution of (2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH **10** (0.13 g, 0.29 mmol) was cooled to -78 ^{o}C. A solution of *t*-butyllithium (0.2 ml of 1.9M solution in pentane, 0.38 mmol) was added dropwise. A colour change occurred. This was allowed to rise to room temperature slowly. An aliquot of the mother liquor showed a complex mixture of phosphorus containing products in $^{31}P\{^1H\}$ NMR spectroscopy, none of which were identifiable.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)HP•BH$_3$. The secondary phosphine (2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH **10** (0.488 g, 1.05 mmol) was dissolved in THF (30 ml) and cooled in ice. A solution of borane dimethyl sulfide complex (0.6 ml of 2.0M solution in diethyl ether, 1.2 mmol) was added dropwise. This was allowed to return to room temperature. An aliquot of the reaction mixture was taken and a $^{31}P\{^1H\}$ NMR spectroscopic experiment indicated that no dative bond had been formed.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)HP•BH$_3$. A toluene (30 ml) solution of **10** (0.53 g, 1.1 mmol) and borane dimethyl sulfide complex (0.6 ml of 2.0M solution in diethyl ether, 1.2 mmol) was stirred and heat to reflux and maintained at the temperature for 90 minutes. Upon cooling it was investigated via ^{31}P{^{1}H} NMR spectroscopy which revealed that the starting material (δ_P -67.1) was the only phosphorus containing compound present.

Mes*$_2$P(=O)Me 8. To a solution of **5** (1.30 g, 2.41 mmol) in THF (40 ml) cooled in ice, *n*-butyllithium (1.0 ml of 2.5M solution in hexanes, 2.50 mmol) was added dropwise. The mixture was stirred for 10 minutes, during which time the solution turned red-brown. Methyl iodide (1.25 ml, 20 mmol) was added slowly at 0 °C, resulting in the dark solution giving way to a pale yellow one as the solution was allowed to rise to room temperature. The volatiles were removed *in vacuo* and the creamy residue was taken up in dichloromethane and washed with water (3 × 10 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. The volatiles were removed *in vacuo* and the resulting solid was recrystallized from acetonitrile to give **8** as colourless crystals (0.69 g, 50%); mp 164-168 ºC; (Found: C, 80.32; H, 11.01; Calc. for $C_{37}H_{61}PO$: C, 80.38; H, 11.12); IR (KBr disk) υ_{max}/cm^{-1} 2961vs (υ_{CH}), 1587m, 1467m, 1188s ($\upsilon_{P=O}$), 1023s, 876s; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2963vs (υ_{CH}), 2907vs (υ_{CH}), 1591s, 1465s, 1448s, 1203s ($\upsilon_{P=O}$), 812s, 573s; δ_H (300.1 MHz; CDCl$_3$) 7.41 (1H, dd, $^4J_{PH}$ = 3.3, $^4J_{HH}$ = 2.3, Ar-H), 7.31 (1H, dd, $^4J_{PH}$ = 3.9, $^4J_{HH}$ = 2.2, Ar-H), 7.14 (1H, dd, $^4J_{PH}$ = 4.2, $^4J_{HH}$ = 2.2, Ar-H), 7.13 (1H, dd, $^4J_{PH}$ = 3.5, $^4J_{HH}$ = 2.2, Ar-H), 2.60 (3H, d, $^2J_{PH}$ = 11.4, P-CH$_3$), 1.56 (9H, s, o-*t*Bu), 1.45 (9H, s, o-*t*Bu), 1.24 (9H, s, p-*t*Bu), 1.23 (9H, s, p-*t*Bu), 0.67 (9H, s, o-*t*Bu), 0.59 (9H, s, o-*t*Bu); δ_C (75.5 MHz, CDCl$_3$) 160.0 (d, $^2J_{PC}$ = 6.7, o-C), 157.1 (d, $^2J_{PC}$ =

9.3, o-C), 156.1 (d, $^2J_{PC}$ = 5.8, o-C), 151.7 (d, $^2J_{PC}$ = 7.4, o-C), 149.0 (d, $^4J_{PC}$ = 4.1, p-C), 148.6 (d, $^4J_{PC}$ = 3.6, p-C), 132.7 (d, $^1J_{PC}$ = 97.0, ipso-C), 130.1 (d, $^1J_{PC}$ = 114.3, ipso-C), 125.3 (d, $^3J_{PC}$ = 11.5, m-C), 124.5 (d, $^3J_{PC}$ = 13.8, m-C), 123.2 (d, $^3J_{PC}$ = 11.7, m-C), 122.9 (d, $^3J_{PC}$ = 13.1, m-C), 41.1 (d, $^3J_{PC}$ = 3.3, o-$\underline{C}(CH_3)_3$), 41.0 (d, $^3J_{PC}$ = 3.8, o-$\underline{C}(CH_3)_3$), 40.8 (d, $^3J_{PC}$ = 2.8, o-$\underline{C}(CH_3)_3$), 39.5 (d, $^3J_{PC}$ = 2.0, o-$\underline{C}(CH_3)_3$), 33.6 (s, o-$C(\underline{C}H_3)_3$), 33.3 (s, 2 × p-$\underline{C}(CH_3)_3$), 33.2 (s, o-$C(\underline{C}H_3)_3$), 32.4 (s, o-$C(\underline{C}H_3)_3$), 32.4 (d, $^1J_{PC}$ = 69.5, P-CH_3), 31.7 (s, o-$C(\underline{C}H_3)_3$), 30.0 (s, 2 × p-$C(\underline{C}H_3)_3$); $\delta_{P\{^1H\}}$ (121.5 MHz, $CDCl_3$) 34.1 (s); δ_P (121.5 MHz, $CDCl_3$) 34.1 (q, $^2J_{HP}$ = 11.4); MS (ES+) *m/z* 553.4 ($M+H^+$), 575.4 ($M+Na^+$); MS (exact mass, ES+): 553.4533 ($M+H^+$), $C_{37}H_{62}PO$ requires 553.4538;

Mes*$_2$P(=O)Et 9. To a solution of **5** (0.72 g, 1.30 mmol) in THF (25 ml) cooled in ice, *n*-butyllithium (0.6 ml of 2.5M solution in hexanes, 1.50 mmol) was added dropwise. The mixture was stirred for 15 minutes, during which time the solution turned red-brown. Ethyl iodide (1.0 ml, 12.5 mmol) was added slowly. The stirred solution was allowed to warm up to room temperature and then slowly heated to 50 °C at which point the solution became pale yellow. The volatiles were removed *in vacuo*; the resulting creamy solid was dissolved in dichloromethane and washed with water (3 × 10 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. The volatiles were removed *in vacuo* to give crude **9** as a creamy yellow solid (0.71 g, 96%). This solid was recrystallized from acetonitrile to give analytically pure **9** as colourless crystals (0.05 g, 7%); mp 175-180 ºC; (Found: C, 80.46; H, 11.14; Calc. for $C_{38}H_{63}PO$: C, 80.51; H, 11.20); IR (KBr disk) υ_{max}/cm^{-1} 2963vs (υ_{CH}), 1597m, 1476m, 1390m, 1363m, 1184s ($\upsilon_{P=O}$), 1026m, 604s; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2963vs (υ_{CH}), 2907vs (υ_{CH}), 1598s, 1581s, 1469s, 1446s, 1185m ($\upsilon_{P=O}$), 821s, 573s, 267s; δ_H (300.1 MHz; $CDCl_3$) 7.49 (1H, dd, $^4J_{PH}$ = 2.7, $^4J_{HH}$ = 1.6, Ar-H), 7.28 (1H, dd, $^4J_{PH}$ = 3.6, $^4J_{HH}$ = 1.8, Ar-H), 7.23 (1H, dd, $^4J_{PH}$ = 3.8, $^4J_{HH}$ = 1.7, Ar-H), 7.08 (1H, dd, $^4J_{PH}$ = 2.7, $^4J_{HH}$ = 1.8, Ar-H), 2.65-2.95 (2H, m, $\mathrm{P{-}C}\underline{\mathit{H}}_2\mathrm{CH}_3$), 1.58 (9H, s, o-*t*Bu), 1.43 (9H, s, o-*t*Bu), δ1.40 (3H, t, $^3J_{PH}$ = 7.1, $\mathrm{PCH_2C}\underline{\mathit{H}}_3$), 1.23 (18H, s, 2 × p-*t*Bu), 0.69 (9H, s, o-*t*Bu) 0.60 (9H, s, o-*t*Bu); δ_C (75.5 MHz, $CDCl_3$) 161.4 (d, $^2J_{PC}$ = 7.4, o-C), 158.1 (d, $^2J_{PC}$ = 9.0, o-C), 157.8 (d, $^2J_{PC}$ = 5.7, o-C), 153.7 (d, $^2J_{PC}$ = 8.1, o-C), 150.2 (d, $^4J_{PC}$ = 3.4, p-C), 150.0 (d, $^4J_{PC}$ = 4.1, p-C), 133.2 (d, $^1J_{PC}$ = 109.2, ipso-C), 132.5 (d, $^1J_{PC}$ = 90.5, ipso-C), 127.2 (d, $^3J_{PC}$ = 11.2, m-C), 125.9 (d, $^3J_{PC}$ = 9.4, m-C), 125.8 (d, $^3J_{PC}$ = 7.3, m-C), 124.4 (d, $^3J_{PC}$ = 12.8, m-C), 42.6 (d, $^3J_{PC}$ = 3.3, o-$\underline{\mathit{C}}\mathrm{(CH_3)_3}$), 42.2 (d, $^3J_{PC}$ = 2.4, o-$\underline{\mathit{C}}\mathrm{(CH_3)_3}$), 42.1 (d, $^3J_{PC}$ = 3.3, o-$\underline{\mathit{C}}\mathrm{(CH_3)_3}$), 41.1 (d, $^3J_{PC}$ = 2.1, o-$\underline{\mathit{C}}\mathrm{(CH_3)_3}$), 35.0 (s, o-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 34.8 (s, o-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 34.7 (s, 2 × p-$\underline{\mathit{C}}\mathrm{(CH_3)_3}$), 33.7 (s, o-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 33.6 (s, o-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 33.3 (d, $^1J_{PC}$ = 63.7, $\mathrm{P}\underline{\mathit{C}}\mathrm{H_2CH_3}$), 31.4 (s, p-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 31.5 (s, p-$\mathrm{C(}\underline{\mathit{C}}\mathrm{H_3)_3}$), 13.0 (d. $^2J_{PC}$ = 4.2, $\mathrm{PCH_2}\underline{\mathit{C}}\mathrm{H_3}$); δ_P (121.5 MHz, $CDCl_3$) 47.5 (br s); MS (ES+) *m/z* 567.4 ($M+H^+$), 589.4 ($M+Na^+$); MS (exact mass, ES+) 567.4700 ($M+H^+$), $C_{38}H_{64}PO$ requires 567.4695.

Phosphindole 4. A THF (8 ml) solution of $Mes^*_2P(O)H$ **5** (0.14 g, 0.26 mmol) was cooled in ice. A solution of *n*-butyllithium (0.15 ml of 2.5M solution in hexanes, 0.37 mmol) was added dropwise. The mixture was stirred for 15 minutes, during which time a red-brown colour developed which indicated the successful production of **7**. A solution of iodine (0.5 g, 1.97 mmol) in THF (8 ml) was added dropwise. The stirred solution was allowed to rise to room temperature and then slowly heated to 50 °C. It was maintained at this temperature for an hour during which the purple colour of the solution persisted. The volatiles were removed *in vacuo*. The dark residue was dissolved in dichloromethane (10 ml) and the resulting solution was shaken with saturated aqueous solution of sodium thiosulfate (10 ml). The pale yellow organic layer was washed with water (3 × 20 ml), and dried over anhydrous magnesium sulfate. The volatiles were then removed *in vacuo* to give **4** as a colourless solid (0.10 g, 72%); δ_H (270.2 MHz; $CDCl_3$) 7.35 (2H, m, 2 x Ar-H), 7.11 (2H, m, 2 x Ar-H), 3.99 (1H, dd, $^2J_{PH}$ = 15.4, $^2J_{HH}$ = 7.5, $PC\underline{H}_A$), 2.64 (1H, triplet-like, $^2J_{PH}$ = 14.6, $PC\underline{H}_B$), 1.58 (9H, s, ^{t}Bu), 1.33 (3H, s, o-CCH_3), 1.28 (9H, s, ^{t}Bu), 1.27 (9H, s, ^{t}Bu), 0.83 (9H, s, ^{t}Bu), 0.77 (9H, s, ^{t}Bu); δ_P (109.4MHz, $CDCl_3$) 54.9(s); MS (ES+) *m/z* 559.4 (M+Na$^+$).

Mes*$_2$P(=O)R. A THF (5 ml) solution of Mes*$_2$P(O)H **5** (0.270 g, 0.50 mmol) was cooled in ice. A solution of *n*-butyllithium (0.2 ml of 2.5M solution in hexane, 0.5 mmol) was added dropwise. The mixture was stirred for 15 minutes, during which time the solution turned red-brown (an aliquot reveal the complete conversion to the phosphinite **7** (δ_P 106.4)). The electrophiles were then added neat, either (a) *tert*-butyl chloride (0.22 ml, 2 mmol) (b) trimethylsilyl chloride (0.26 ml, 2 mmol) (c) isopropyl iodide (0.2 ml, 2 mmol) or (d) benzyl chloride (0.25 ml, 2.2 mmol). The stirred solution was allowed to rise to room temperature. In all cases the red-brown phosphinite colour persisted for some time. Upon initiation of $^{31}P\{^1H\}$ NMR spectroscopic investigation was determined that a complex mixture of phosphorus containing products is the result. None of the peaks could be confidently be assigned except the phosphindole **4** (δ_P 54.9)[59] which was present in various proportions in all the mother liquors. Subsequent investigations where no electrophile was added also produced this phosphindole **4**.

(2,4-*t*Bu$_2$C$_6$H$_3$)PCl$_2$ 13. A solution of (2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH **10** (0.40 g, 0.85 mmol) in toluene (40 ml) was cooled in ice. A solution of phosgene (1.0 ml of 1.9M solution in toluene, 1.9 mmol) was added dropwise. The mixture was allowed to rise to ambient temperature slowly, at which point a sample of the reaction mixture was subjected to ^{31}P NMR spectroscopy, which indicated only starting material was present. Upon heating under reflux for 90 minutes a yellow colour developed. The volatiles were removed *in vacuo* to leave yellow oil, from which crystals of **13** formed upon standing. The crystals were examined by ^{31}P NMR spectroscopy (δ_P 166.9 in CDCl$_3$) and X-ray single crystal diffraction.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PCl 12. In a series of NMR spectroscopy tubes were placed portions of **10** (0.005-0.008 g, 0.011-0.017 mmol). Added to this was either chloroform (0.6 ml, 7.5 mmol) or tetrachloromethane (0.6 ml, 6.2 mmol) or 1,1,2,2-tetrachloroethane (0.6 ml, 5.7 mmol). The tubes were left in a well-lit environment and tested periodically via ^{31}P{^{1}H} NMR spectroscopy over the course of several weeks. In each case the starting material slowly decomposed to a forest of ^{31}P peaks, none of which were identifiable as the desired product.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PCl 12. To a toluene (30 ml) solution of (2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH **10** (0.21 g, 0.45 mmol) was added phosphorus trichloride (0.1 ml, 1.14 mmol). This was heated under reflux for 5 hours. It was then allowed to cool to room temperature. The volatiles were removed *in vacuo* to leave a solid. A ^{31}P{^{1}H} NMR spectroscopic investigation of this furnished the diagnostic starting material peak (δ_P -67.1) only.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PCl 12. A toluene (20 ml) solution of **10** (0.53 g, 1.1 mmol) and triethyl amine (1 ml, 7.2 mmol) was cooled in ice. A solution of phosgene (0.7 ml of 1.9M solution in toluene, 1.3 mmol) was added dropwise. This stirred solution was allow to rise slowly to room temperature during which time a colour change from clear/pale yellow to dark/brown occurred. An aliquot was taken and analysed via ^{31}P{^{1}H} NMR spectroscopy which showed a complex mixture of peaks none of which were identifiable.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PCl 12. A toluene (20 ml) solution of **10** (0.71 g, 1.5 mmol) was cooled in ice. Thionyl chloride (0.5 ml, 6.9 mmol) was added slowly. The reaction mixture was allowed to return to room temperature slowly and turned an inky black colour. An aliquot of the mother liquor was evaluated via ^{31}P{^{1}H} NMR spectroscopy. It was found to contain a range of ^{31}P containing species. The only one of which might be identified is at δ_P 167.1 which was assigned as 2,4-*t*Bu$_2$C$_6$H$_3$PCl$_2$ **13**.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)P(=S)H 14. Triethyl amine (3.0 ml, 21.5 mmol) was added to a stirred suspension of **10** (0.26 g, 0.56 mmol) and sulfur (0.03 g, 0.77 mmol) in toluene (20 ml) at room temperature. The sulfur dissolved over 10 minutes to leave a yellow solution, which was subsequently heated under reflux for 90 minutes. During this time the solution turned dark red. The volatiles were then removed *in vacuo*. The resulting dark red/brown solid was chromatographed on silica gel with 97:3 hexane:ethyl acetate as eluent. **14** was obtained as a pale yellow powder (0.125 g, 45%); see Figure 37 for NMR spectroscopy numbering scheme; mp 144-148 ºC; (Found: C, 76.89; H, 10.17. Calc. for C$_{32}$H$_{51}$PS: C, 77.10; H, 10.31); IR (KBr disk) υ_{max}/cm^{-1} 2961vs

(υ_{CH}), 2868vs (υ_{CH}), 1597s, 1475m, 1394s, 1362s, 1106m, 663s ($\upsilon_{P=S}$), 609m; Raman (powder in glass capillary) υ_{max}/cm^{-1} 2968vs (υ_{CH}), 2908vs (υ_{CH}), 1597s, 1467m, 1449m, 1202s, 926s, 828s, 685s, 664s ($\upsilon_{P=S}$), 564m; δ_H (300.1 MHz; CDCl$_3$) 8.95 (1H, d, $^1J_{PH}$ = 485.5, P-H), 7.66 (1H, dd, $^3J_{PH}$ = 18.5, $^3J_{HH}$ = 8.4, H24), 7.51 (1H, dd, $^4J_{PH}$ = 6.1, $^4J_{HH}$ = 1.9, H21), 7.49 (2H, d, $^4J_{PH}$ = 4.4, H3 & H5), 7.01 (1H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.9, H23), 1.57 (9H, s, 25-Me$_3$), 1.42 (18H, s, 7-Me$_3$ & 15-Me$_3$), 1.26 (9H, s, 11-Me$_3$), 1.22 (9H, s, 29-Me$_3$); δ_C (75.5 MHz, CDCl$_3$) 153.3 (s, C2 or C6), 153.2 (s, C2 or C6), 153.1 (d, $^2J_{PC}$ = 7.6, C20), 151.1 (s, C4 or C22), 151.0 (s, C4 or C22), 137.3 (d, $^2J_{PC}$ = 13.6, C24), 127.2 (d, $^1J_{PC}$ = 66.0, C1), 126.5 (d, $^1J_{PC}$ = 76.8, C19), 124.3 (s, C3 & C5 or C7), 124.2 (s, C3 & C5 or C7), 120.5 (d, $^3J_{PC}$ = 13.4, C23), 38.9 (s, C7 & C15), 37.4 (s, C25), 34.0 (s, C11), 33.9 (s, C29), 33.6 (s, 7-Me$_3$ & 15-Me$_3$), 32.2 (s, 25-Me$_3$), 31.0 (s, 29-Me$_3$), 30.1 (s, 11-Me$_3$); $\delta_{P\{1H\}}$ (121.5 MHz, CDCl$_3$) 17.3 (s); δ_P (121.5 MHz, CDCl$_3$) 17.3 (dd, $^1J_{HP}$ = 486.0, $^3J_{HP}$ = 17.6); MS (ES+) *m/z* 521.3 (M+Na$^+$); MS (exact mass, ES+): 521.3337 (M+Na$^+$), $C_{32}H_{51}PSNa$ requires 521.3347.

(2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)P(=Se)H. A toluene (10 ml) suspension of (2,4-*t*Bu$_2$C$_6$H$_3$)(Mes*)PH (0.3 g, 0.65 mmol) and grey selenium powder (0.06 g, 0.75 mmol) was made up. Triethyl amine (3 ml, 21.5 mmol) was added and the stirred suspension was heated under reflux for 5 hours. Upon cooling a sample of the solution revealed via $^{31}P\{^1H\}$ NMR spectroscopy that no reaction had occurred.

Mes*PMeH 11. A suspension of lithium aluminium hydride (1.00g, 26.7 mmol) in 1,4-dioxane (40 ml) was cooled in ice. Trimethylsilyl chloride (3.4 ml, 26.7 mmol) was then added slowly with stirring. Subsequently, powdered Mes*$_2$P(=O)CH$_3$ **8** (0.897g, 1.62 mmol) was added in small batches. The apparatus was fitted with a reflux condenser and the mixture was heated to 101 °C with stirring for 8-10 hours. The flask was cooled in ice and water (2 ml) was added slowly to hydrolyse the remaining hydride with the evolution of H_2 gas. The resulting suspension was filtered using glass sinter and the solid collected on the filter was washed through with dichloromethane (3× 20 ml). The volatiles were evaporated *in vacuo*. The yellow residue was then taken up with more dichloromethane and washed with water (3× 20 ml). The organic layer was separated, dried over anhydrous magnesium sulphate and the volatiles were removed *in vacuo*. The solid obtained was subjected to column chromatography on silica gel with hexane as eluent. Compound **11** emerged ahead of the co-product (2,4-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$)(Mes*)PH **10** ($\delta_P$ -67.1, d, $^1J_{PH}$ = 237.3 Hz). Fractions containing **11** were combined and the volatiles were removed to obtain **11** as a white solid (Yield range 0.22-0.35 g, 42-67%). δ_H (300.1 MHz; $CDCl_3$) 7.44 (2H, d, $^4J_{PH}$ = 2.1 Hz, Ar-H), 5.06 (1H, dq, $^1J_{PH}$ = 225.8, $^3J_{HH}$ = 6.9 Hz, PH), 1.63 (18H, s, 2 × o-^{t}Bu), 1.39 (9H, s, p-^{t}Bu), 1.14 (3H, dd, $^3J_{HH}$ = 6.9, $^2J_{PH}$ = 5.0 Hz, $PC\underline{H}_3$); δ_C (75.5 MHz, $CDCl_3$) 154.8 (d, $^2J_{PC}$ = 8.0 Hz, 2 × o-C), 149.5 (s, p-C), 135.4 (d, $^1J_{PC}$ = 30.1 Hz, ipso-C), 122.6 (d, $^3J_{PC}$ = 4.1 Hz, 2 × m-C), 38.9 (s, 2 × o-$\underline{C}(CH_3)_3$), 35.4 (s, p-$\underline{C}(CH_3)_3$), 34.1 (d, $^4J_{PC}$ = 7.1 Hz, 2 × o-$C(\underline{C}H_3)_3$), 31.8 (s, p-$C(\underline{C}H_3)_3$), 11.8 (d, $^1J_{PC}$ = 14.5 Hz, $P\underline{C}H_3$); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) -91.3 (s), δ_P (121.5 MHz, $CDCl_3$) -91.3 (d, $^1J_{HP}$ = 225.8 Hz)

6. Conclusions and unanswered questions

During the course of our synthetic endeavours, we investigated the reactivity of the extremely sterically encumbered phosphinic chloride Mes*$_2$P(=O)Cl **3** which was the ultimate starting material for all of the reactions detailed in this chapter. It was found that no reaction occurred when **3** was subject to reaction conditions which had previously been used to affect transformations, such as reactions with alkyllithiums and strong hydridic reduction agents (DIBAL and superhydride at room temperature etc). We conclude that **3** possesses extremely low reactivity at the phosphorus centre. Although, when more forceful reductive conditions are used, some synthetically significant transformations were possible. It was found that reduction with $LiAlH_4$/Me_3SiCl under forcing conditions eventually yielded the phosphine oxide Mes*$_2$P(=O)H **5** and secondary phosphine Mes*(2,4-*t*Bu$_2$C$_6$H$_3$)PH **10**. The deprotonation of **5** yielded the corresponding phosphinite Mes*$_2$P(=O)$^-$ **7** which was reacted with small electrophiles to afford the very crowded tertiary phosphine oxides **8** and **9**. Failure to quench the reactive phosphinite led to a cyclisation to produce the phosphindole **4**. At no time was the desired secondary phosphine Mes*$_2$PH **6** obtained.

In contrast, the phosphido anion Mes*(2,4-*t*Bu$_2$C$_6$H$_3$)P$^-$ was not detected when **10** was reacted with ^{n}BuLi even at elevated temperatures. Neither could the secondary chlorophosphine Mes*(2,4-*t*Bu$_2$C$_6$H$_3$)PCl be isolated or would the addition of $BH_3{\cdot}SMe_2$ to **10** form the corresponding borane adduct. It was therefore perhaps surprising when the elemental sulfur reacted cleanly with **10** to product the corresponding phosphine sulfide **14**; albeit at forcing conditions. This is an indication that despite the removal of one flanking t-butyl groups in the preparation of (2,4-*t*$Bu_2C_6H_3$)(Mes*)PH **10**, its phosphorus centre remains extremely sterically shielded.

The effects of having two Mes* groups attached geminally on a central phosphorus atom was the main thrust of this research. This arrangement leads to a huge amount of strain being placed on the molecular system and this is seen by the distortion into boat-conformation of all of the phenyl rings in the Mes* substituents of **5**, **8** and **9**. The computational studies (B3LYP and M06-2X level) show the extremely high strain energy (180 to 250 kJ mol^{-1}) that these compounds possess. Surprisingly, the strain calculated for secondary phosphine $Mes*_2PH$ **6** was almost identical to that for **3**. Our lack of success in isolating this compound hints at more complex factors governing its synthetic achievability. More detailed study of the steric and electronic factors preventing the isolation of **6** may be needed. This may also shed more light on sterically bulky compound in general.

Our work with regard to $Mes*_2P(=O)Cl$ **3** and the compounds deriving from it have been published in the chemical literature.[96]

Chapter 3 - A Study of Phosphorus Substituted Naphthalenes and Acenaphthenes

1. Introduction to PAHs

a. The structure of naphthalene and acenaphthene

Naphthalene and acenaphthene are polycyclic aromatic hydrocarbons (PAHs) which derive from coal tar.[97] The structure of naphthalene was first proposed by Emil Erlenmeyer in 1866.[98] It is the simplest PAH with a distinct odour which was historically used in moth balls. The unsubstituted naphthalene skeleton is planar with internal angles all close to the idealised 120° as can be seen in Figure 38.[99,100] These values can vary slightly with temperature.[101]

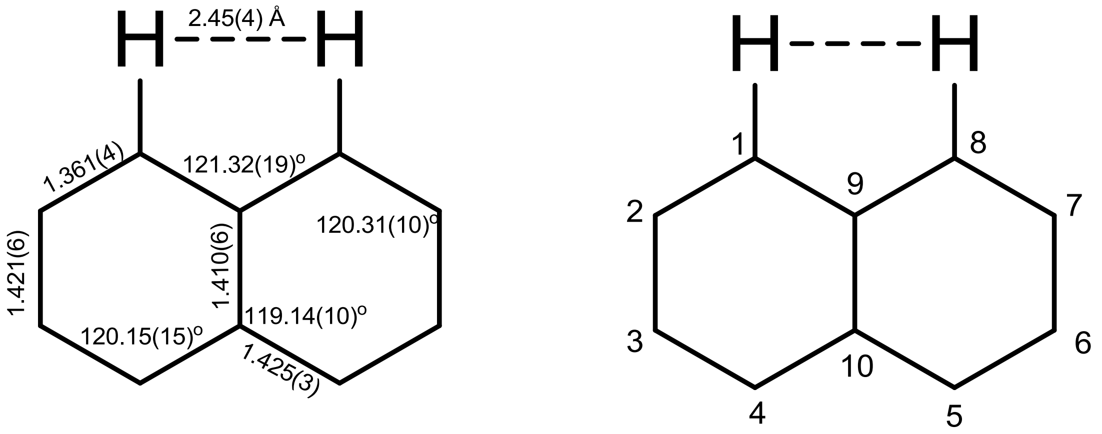


Figure 38 Internal bond lengths (Å), angles (°) and numbering scheme for unsubstituted naphthalene

In contrast, the addition of the ethylene linker in the 1,2-positions of the acenaphthene lessens the planarity of the ring slightly and there is a greater range of internal angles in the aromatic ring, see Figure 39.[102]

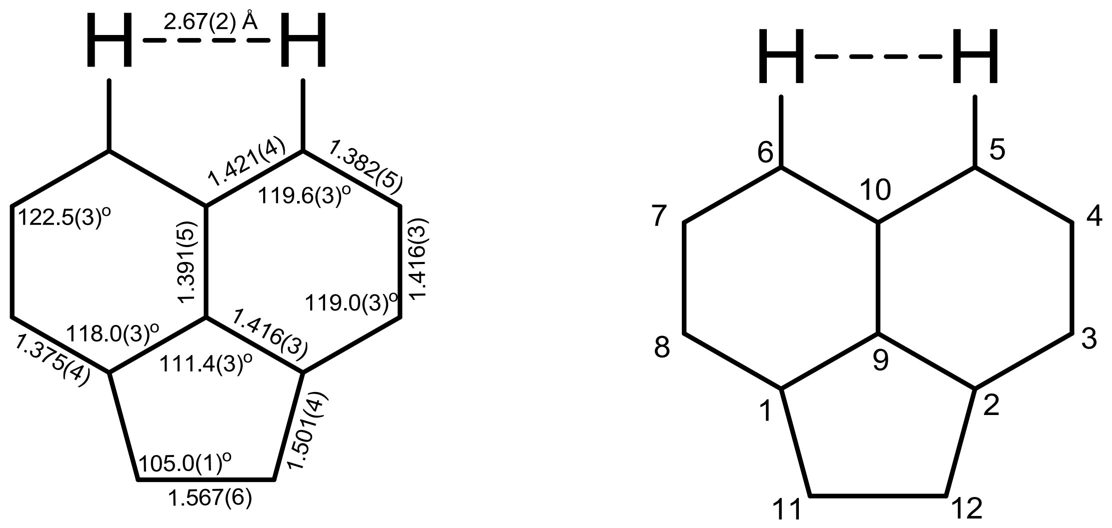


Figure 39 Internal bond lengths (Å), angles (°) and numbering scheme for unsubstituted acenaphthene. Additional angles not shown are C(1)-C(9)-C(10) = 124.2(1), C(9)-C(10)-C(5) = 116.6(2) & C(5)-C(10)-C(6) = 126.8(4)

These are both excellent structures as they provide a rigid backbone for further substitution. This is particularly pertinent with regard to discussion of the atoms placed in the *peri*-positions (positions 1,8 in naphthalene and 5,6 in acenaphthene).

b. *Peri*-substitution on naphthalene

By virtue of its skeletal structure, the hydrogen atoms stationed in the *peri*-positions in naphthalene are close together (2.45(4) Å)[101] and although this is greater than twice the van der Waals radii of hydrogen (2 × 1.06 Å);[103] it is significantly closer than comparable systems such as hydrogen atoms in the *ortho*-positions of a benzene ring (~3.1 Å). If one or both of these *peri*-positioned hydrogen atoms is/are replaced with an atom of a lower period, this may bring two nominally non-bonding atoms closer than the sum of their van der Waals radii. This will impose significant structural constraints on the system which can be relieved by distortion of the naphthalene ring system; the atoms in the *peri*-positions will as a result display bending in the plane of the ring and/or bending out of the mean plane of the ring, one above and one below. As a result there would be an increase in the *peri*-distance. Alternatively, the *peri*-substituted atoms could interact in some way that is sub-van der Waals in nature such as forming a formal bond. In general, the total steric strain inherent with the double *peri*-substitution of two non-hydrogen atoms is decentralized over the entire ring system with the deformation of both rings.[104] Table 7 shows the van der Waals radii for a number of common nuclei which might feasibly be attached to the *peri*-positions.[103]

Table 7 Selected van der Waals radii of common main group nuclei

Nucleus	$R_{vdW}{}^{a}$ (Å)
C	1.53
N	1.42
Si	1.93
P	1.86
Cl	1.75
Br	1.87
I	2.04

[a] R_{vdW} estimated by Pauling's approximation, R_{vdW} = covalent bond radius + 0.76

c. *Peri*-substitution on acenaphthene

The ethylene linker in the 1,2 position of acenaphthene can be considered as a bond between two *peri*-substituted alkyl groups on naphthalene (even though acenaphthene is itself a natural product derived directly from coal tar). The literature crystal data[102] has two independent molecules in the unit cell and this carbon-carbon single bond length C(11)-C(12) varies significantly between 1.552(10) and 1.576(8) Å; a weighted average (1.567(6) Å) is therefore reported.[102] Nevertheless, C(11)-C(12) is appreciably shorter than twice the van der Waals radius of carbon (~3.0 Å). This bond is also shorter than the 1,8 *peri*-distance in naphthalene. As a result, the hydrogen atoms which are on the 5,6-postions *para* to this are bent slightly away from each other and thus there is an increase in the *peri*-distance across the 5,6 divide to 2.67(2) Å. This is still considerably shorter than the unconstrained *ortho*-substituted benzene distance. This skeletal reorganisation where substituents bend away from each other in the plane of the mean aromatic rings is an important way of releasing the strain on a multiply substituted system, which was seen throughout this research endeavour.

d. The structural characteristics of bay region substituted phenanthrene and *ortho*-substituted benzene

It is advantageous to compare naphthalene and acenaphthene with the geometries of *ortho*-substituted benzene and bay-region disubstituted phenanthrene.[105] In an unconstrained benzene system the *peri*-distance of ~3.1 Å is large enough to comfortably accommodate many larger atoms *ortho* to each other, see Figure 40.[106] There are many examples in the literature which show alkyl groups or heteroatoms are substituted in the *ortho*-positions with no ring distortion. However, when atoms with very large van der Waals radii are present, bending in the plane of the aromatic ring has been shown to occur, such as in 1,2-diiodobenzene where the iodine-iodine through space distance is 4.0(1) Å (measured by electron diffraction).[107]

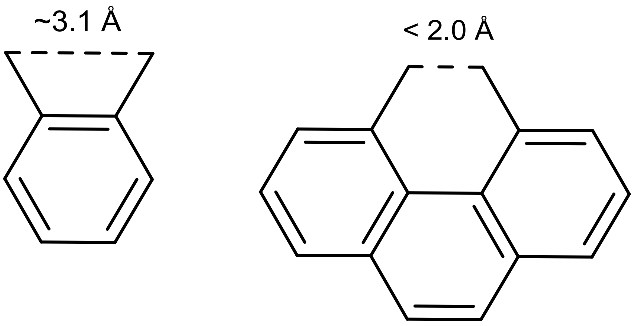


Figure 40 *Ortho*-distance in benzene and bay distance in phenanthrene

In the case of phenanthrene the very short "ideal" bay-region distance (< 2.0 Å)[108] means that the substitution of larger atoms on to one or both of these positions can not be achieved without a significant skeletal reorganisation, see Figure 40. In the case of 3,4,5,6-tetrafluoro-1,2,7,8-tetrakis(trifluoromethyl)phenanthrene, the *peri*-substituted fluorine atoms F(4)···F(7), are 2.390(2) Å apart and there is a dihedral angle of 27.6(4)° across C(4)-C(5)-C(6)-C(7) in Figure 41.[109] Much of the strain is alleviated by this loss of planarity.

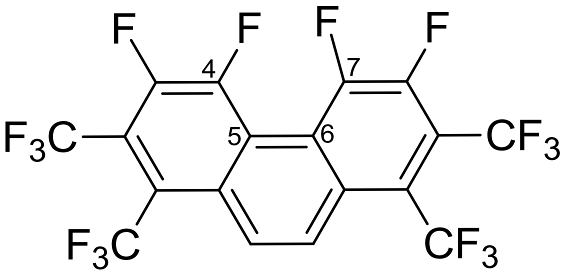


Figure 41 Structure of 3,4,7,8-tetrafluoro-1,2,9,10-tetrakis(trifluoromethyl)phenanthrene

In fact, single atom bridged species are the preferred method of achieving a relaxed polycyclic framework of phenanthrene[105]. This has been utilised in the production of the five membered sulfur and nitrogen hetrocycles such as phenanthro[4,5-bcd]thiophene[110] and 4H-benzo[def]carbazole.[111]

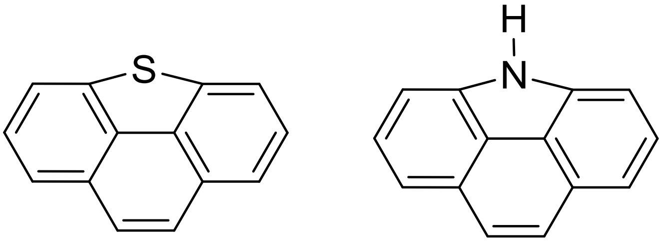


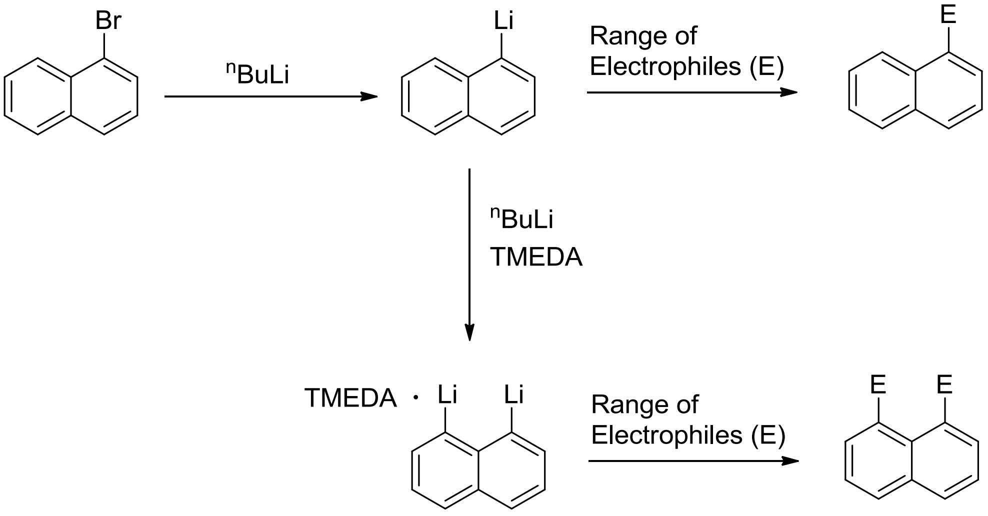
Figure 42 Selected examples of five-membered phenanthrene rings

e. Substitution on naphthalene rings

The most common starting material for both 1-monosubstituted and 1,8-disubstituted naphthalenes is 1-bromonapthalene. This can be synthesised easily via the bromination of naphthalene with elemental bromine, the product has been recovered in excellent yield (90 %).[112] 1-Bromonaphthalene is commercially available and quite cheap so for this synthetic study the purchased material was used. Addition of one equivalent of *n*-butyllithium, results in a facile lithium-halogen exchange, affording 1-lithionaphthalene in quantitative yield. This can be reacted with a wide selection of electrophiles, see Scheme 6. These include such diverse moieties as chlorophosphines[113] and borates,[114] which afford boronic acids used for Suzuki-Miyaura coupling reactions.[115,116]

Access to 1,8-doubly substituted products is gained via the reaction of 1-bromonapthalene with two equivalents of *n*-butyllithium and tetramethylethylenediamine (TMEDA)[117,118] to produce 1,8-dilithionaphthalene. This double metallation is achieved by first making 1-lithionaphthalene as above. To this initial mono-lithiated species TMEDA and a second equivalent of *n*BuLi are added. The subsequent deprotonative metallation proceeds regioselectively at the *peri*-

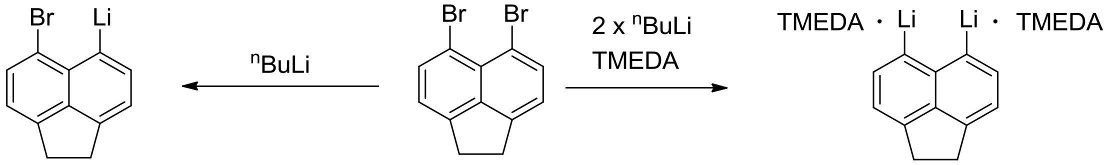
position, see Scheme 6. 1,8-Dilithionaphthalene can then be reacted with a library of electrophiles to give a large range of different products. The introduction to the *peri*-positions of sulfur,[119] silicon[120] and phosphorus[121] (to give just three examples) has been achieved without difficulty. This method is a vast improvement on some of the older literature procedures which suggest the production and isolation of 1,8-dibromonaphthalene first. This is made from a reaction of 8-bromo-1-naphthoic acid with lead tetraacetate (LTA) and irradiation with UV light.[122] The yield (40 %) of 1,8-dibromonaphthalene reported is low compared to the effectively quantitative yield that is achieved with double lithiation of 1-bromonapthalene.



Scheme 6 Mono and di-lithiation of 1-bromonapthalene

f. *Peri*-Substitution on acenaphthene rings

5,6-Dibromoacenaphthene is made by the addition of *N*-bromosuccinimide (NBS) to a DMF suspension of acenaphthene.[123] Although only moderate yields (20 – 30 %) are recovered, when this reaction is performed on a sufficiently large scale the quantity of pure product obtainable is satisfactory with view to its further use due to the trivial purification procedure used. A single lithium-halogen exchange on the 5,6-dibromoacenaphthene is achieved by the addition of one equivalent of *n*-butyllithium. The resultant (6-bromo-1,2-dihydroacenaphthylen-5-yl)lithium can be reacted with a multitudinous of electrophiles while leaving the bromine positioned *peri* to the exchange site still in place for potential further substitution.[124] This is an excellent way of putting two different groups across the *peri*-divide. A double metallation is accomplished via two equivalents of both *n*-butyllithium and TMEDA,[125,126] see Scheme 7. This has been used to attach sulfur, selenium and tellurium onto the acenaphthene backbone.[125]



Scheme 7 Mono and di-lithiation of 5,6-dibromoacenaphthene

g. Coordination chemistry of *peri*-substituted naphthalenes

Peri-substituted structures have been used to co-ordinate to an abundance of metal centres.[127] The most commonly used structure is the commercially available 1,8-bis(diphenylphosphino)naphthalene (dppn) which can be conceptualised as two triphenylphosphine groups (Ph_3P) coupled together; Ph_3P is one of the most widely utilised co-ordinating groups in the chemical canon. Dppn can act as a bi-dentate ligand towards the metal atoms,[118,128] the rigidity of its skeletal framework influences the environment around the metal centre, which may have potential application in catalysis. Many catalysed reactions are extremely sensitive to any subtle changes within the domain of reactivity so replacing two Ph_3P groups with a dppn group could profoundly change the activity of catalyst. Of course dppn is not the only the only ligand with *peri*-substituted structural motif. Metal complexes with naphthalene-1,8-dithiol,[129] (8-phenylthionaphth-1-yl)diphenylphosphine[130] and 1-(dimethylamino)-8-(diphenylphosphino)naphthalene[131] have been reported in literature. These ligands are shown in Figure 43.

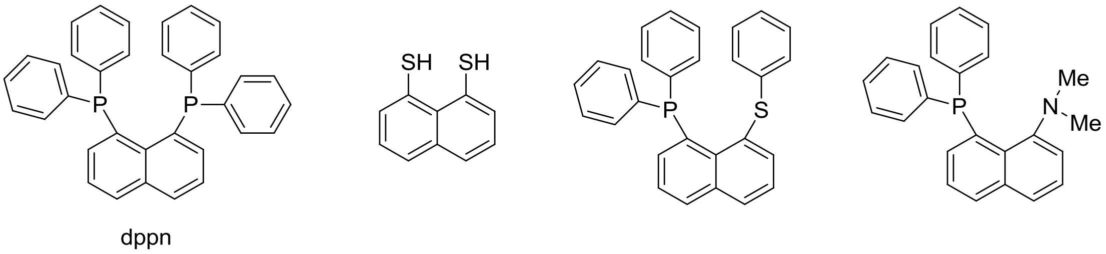


Figure 43 Selected bidentate ligands based on naphthalene backbone

h. Structure of *peri*-substituted naphthalenes and acenaphthenes

The use of naphthalene as a rigid backbone and the special geometrical features which *peri*-substitution affords has been reviewed recently.[105] Although its structural characteristics have been discerned for some time, the effects of forcing two non-hydrogen atoms into close proximity with each other has only latterly become a topic of exploration. At the heart of this current discourse is the very nature of a chemical bond itself (both physically and philosophically).[132] When two atoms are brought within sub van der Waals distances of each other, should there be automatic assumption that an attractive interaction is present between them?[133] Crystallographic techniques display the environment of a particular atomic centre and its proximity to other atomic centres. From this data chemical bonds are inferred, however detailed distribution of electrons in the structure can not be mapped easily except when higher resolution diffraction methods are used. Therefore theoretical calculations are used to give weight to the interpretation of crystal data. Any calculated model will have limitations due to computing power and assumptions built into the calculation to simplify them. As was previously alluded to in Chapter 2, such calculations can not always fully explain the experimental results found.

As was mentioned before, one of the means by which *peri*-substituted naphthalenes and acenaphthenes are analysed is the extent to which their skeletal structures distort to accommodate one or more large(er) atoms. One of the measures of this is known as the splay angle, which is calculated as the sum of the angles around the *peri*-region less 360°. In an unconstrained system this would be 0, if the splay angle is positive a repulsive interaction is occurring; if it is negative an attractive interaction is likely to be present.

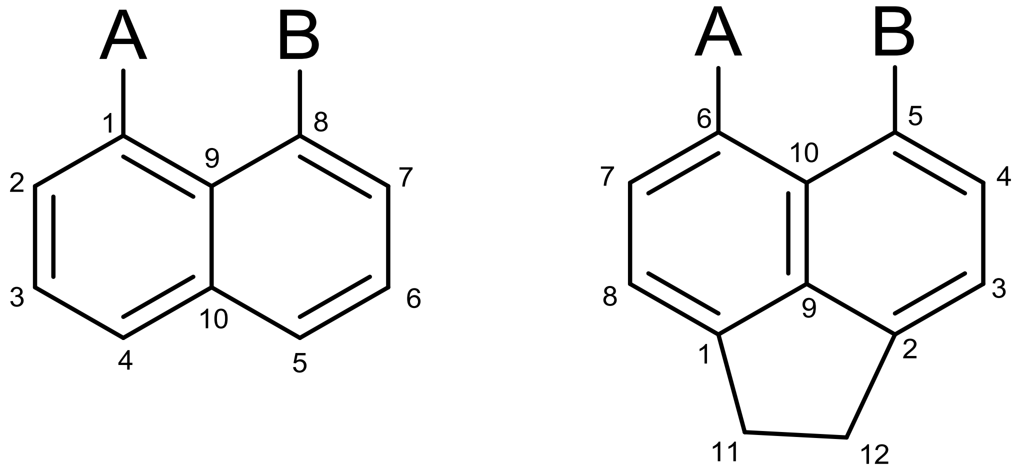


Figure 44 Generic structures of *peri*-substituted naphthalene and acenaphthene indicating numbering of the atoms.

The sum of the angles around the *peri*-region is calculated by adding the angles A-C(1)-C(9), C(1)-C(9)-C(8) & C(9)-C(8)-B for naphthalene and A-C(6)-C(10), C(6)-C(10)-C(5) & C(10)-C(5)-B for acenaphthene, as seen in the numbering scheme in Figure 44. Not all distortion occurs in the ring plane. Another method of increasing the *peri*-distance is for the atomic centres A and B to bend out of the mean ring plane, one above the plane and one below it. This increases the *peri*-distance without necessarily increasing the splay angle. Out-of-plane distortion leads to a twisting of the two rings which may lessen their planarity. This is quantified by the dihedral angles (sometimes known as the torsion angles) within the rings and between them. In a non-linear chain of atom (e.g. C(1)-C(9)-C(10)-C(5)), the dihedral angle is the angle between the bond vectors of the first two atoms and the second two (e.g. C(1)-C(9) and C(10)-C(5)). This deviation from planarity can also be envisaged as bond rotation around the C(9)-C(10) bond, see Figure 45.

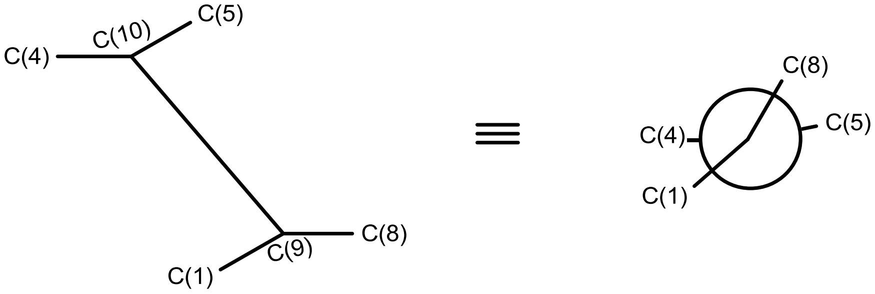


Figure 45 Sawhorse and Newman projections of the connecting ring atoms in naphthalene. The C(10)-C(9) bond is coming out of the plane in the Newman projection

For an unconstrained system such as unsubstituted naphthalene the C(1)-C(9)-C(10)-C(5) torsion angle would be essentially 180° as the rings are planar and the torsion angle of C(1)-C(9)-C(10)-C(4) would be 0°. The loss of planarity caused by the distorting effect of *peri*-substituted atoms may furthermore result in a degree of lost aromaticity as the orthogonal p-orbitals on the ring carbons may be bent out of place.

To illustrate the point with an example, some of the structural characteristics of 5,6-dibromoacenaphthene[102,134] are shown in Table 8.

Table 8 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean aromatic planes (Å) for 5,6-dibromoacenaphthene

Bond Length (Å)		**Dihedral angles (°)**	
Br(1)-C(5)	1.9061(16)	C(1)-C(9)-C(10)-C(6)	0.7(2)
Br(2)-C(6)	1.9052(17)	C(2)-C(9)-C(10)-C(5)	1.3(3)
Br(1)···Br(2) (*peri*-distance)	3.3077(7)	C(2)-C(9)-C(10)-C(6)	178.7(4)
C(11)-C(12)	1.549(4)	C(1)-C(9)-C(10)-C(5)	179. 3(4)
Bond Angles (°)		**Displacement from mean Ace plane (Å)[a]**	
C(1)-C(9)-C(2)	110.89(16)	Br(1)	0.057
C(5)-C(10)-C(6)	132.65(15)	Br(2)	0.041
Br(1)-C(5)-C(10)	124.20(14)		
C(10)-C(6)-Br(2)	123.94(13)		
Splay Angle (°)	20.79(15)		

[a] Distance from the mean plane fitted through atoms C(1) to C(10)

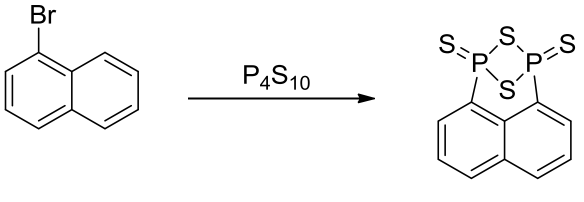
The bromine atoms clearly put a strain on the system which can be seen in the large positive splay angle observed. They both lie ~0.050 Å out of the bicyclical aromatic plane, which is not large deviation compared with values seen in our work reported below, but still considerable. The torsion angles are not large indicating that the aromatic ring system is largely planar.

With our knowledge of the skeletal features of both naphthalene and acenaphthene, we could embark on the main synthesis thrust of the project.

2. Production and Reactions of NapP$_2$S$_4$

a. Introduction

It was our aim to synthesis a range of compounds on the rigid naphthalene backbone with phosphorus present at one or both of the *peri*-positions. To do this the most favourable synthon to use is 1-bromonaphthalene. One of the ways of putting phosphorus atoms on to the *peri*-positions is via a somewhat bizarre and unpleasant reaction[135,136] where the 1-bromonaphthalene is heated to 240 °C with 0.1 equivalents of P_4S_{10} to produce naphthalenedithiadiphosphetane disulfide **15** (NapP$_2$S$_4$), see Scheme 8. Gaseous H_2S is one of the many by-products from this reaction and it must be neutralised in NaOH and bleach (sodium hypochlorite) solutions to prevent its release into the laboratory environment. However, the achievable yields (~25 %) for **15** can be considered satisfactory and thus this procedure provides a valuable means of attachment of phosphorus centres on to the *peri*-postions.[136]

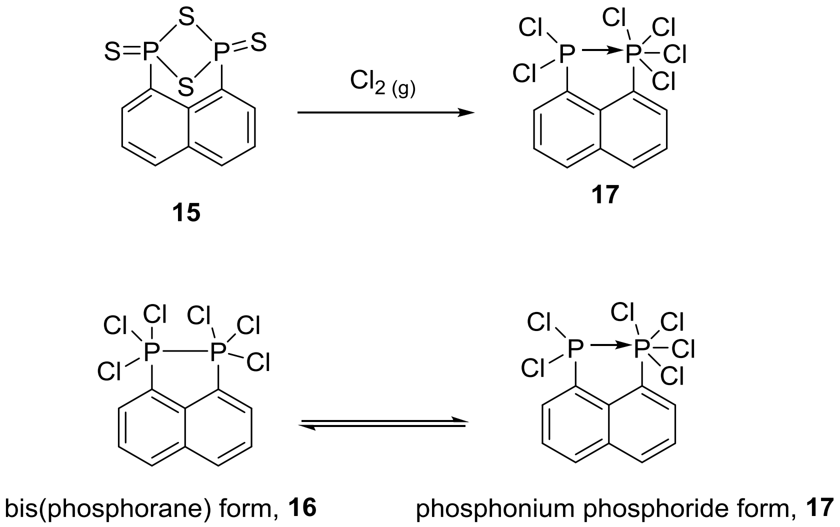


15

Scheme 8 Synthesis of NapP$_2$S$_4$ **15**

NapP$_2$S$_4$ **15** is a cyclic analogue of Lawesson's reagent (LR), which is widely used for thionation.[137] It has been shown that **15** can also convert a carbonyl (C=O) moiety to a thiocarbonyl (C=S) one.[138] It has been found that NpP$_2$S$_4$ **15** is generally not as reactive as LR, more forcing conditions being required in its reactions.

15 has been used as a synthon for further reactions. When reacted with chlorine gas,[139] $NapP_2Cl_6$ is produced which has been shown to be in an equilibrium between a symmetrical bisphosphorane **16** and an unsymmetrical phosphonium-phosphoride ylide **17** in solution, see Scheme 9.



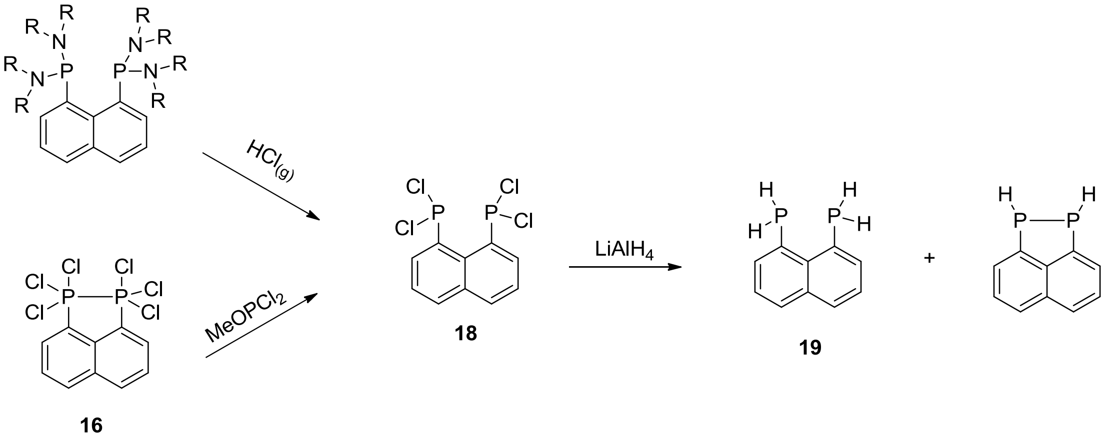
Scheme 9 Reaction of $NapP_2S_4$ **15** with chlorine gas

The $Nap(PCl_2)(PCl_4)$ form **17** was recovered as a yellow solid.[140] A chlorine migration instigates fluxionality on an NMR spectroscopic timescale and a peak for the bis(phosphorane) form **16** is also seen in the ^{31}P NMR spectrum.[141] It is noteworthy that the fluctuation of this molecule between two neutral phosphorus centres and the ylide form does not result in the breaking of the P-P bond. The P-P bond distance is much shorter than twice the Van Der Waals radius of phosphorus (~3.6 Å), so any cleavage of this bond would require a complete geometric reorganisation and most probably a distortion of the aryl backbone. Calculations and X-ray diffraction revealed that **17** has an unusually long P-P single bond (2.338(2) Å) for a formal bond between two phosphorus atoms; the splay angle is -6.0(2) and the *peri*-carbons are 2.512(7) Å apart.[140] The two phosphorus atoms in the **17** are positioned 0.020 and 0.050 Å above and below the mean aromatic plane; the bicyclical skeleton is essentially planar. In contrast, the phosphorus atoms in the 1,8-bis(dichlorophosphino)naphthalene (Nap(PCl_2)$_2$) **18** lie between 0.52 and 0.41 Å from the mean aromatic plane.[139] The P···P distance in **18** is 2.798(2) and 2.811(2) Å (two independent molecules) and the splay angles are 2.5(2) and 4.1(2)°; the central torsion angles of the naphthalene ring range between 4.1(2) and 6.7(4)°.[139] This is a real indication of the extent of repulsion between the two phosphorus moieties and is a stark contrast to **17**.

$NapP_2Cl_4$ **18** is a useful synthon. It can't be made directly from the reaction of PCl_3 with 1,8-dilithionaphthalene.[140] The most common method of synthesis is by adding an excess of gaseous HCl to $NapP_2(NR_2)_4$, see Scheme 10. The initially reported yield was very low (9%),[121] slight modifications of the procedure led to significant improvement in yields to 82%.[113] Another route to **18** is the treatment of $NapP_2Cl_6$ with $MeOPCl_2$ in refluxing toluene which furnishes the desired product in near quantitative yield.[139] This attest to the overall value of making $NapP_2S_4$ **15** (unpleasant reaction or not) and it subsequent further chemistry.

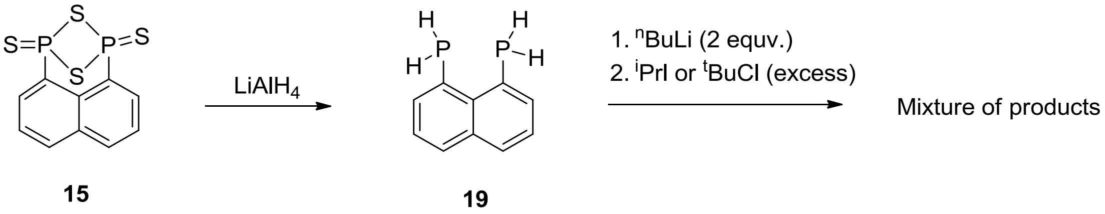
b. Reduction and further chemistry of $NapP_2S_4$

A reaction pathway that has not yet been explored in the literature is the reduction of **15** with a suitable hydridic reducing agent. The anticipated product 1,8-bis(phosphino)naphthalene **19** ($NapP_2H_4$) has been prepared before[113] by a different method, reduction of $NapP_2Cl_4$ **18** with $LiAlH_4$. Via this route the reaction proceeded smoothly and a good yield (77%) of **19** was obtained, although co-formation of a bridged by-product *trans*-1,2-dihydro-1,2-diphosphaacenaphthene was observed. This by-product is (at least formally) the result of dehydrogenative phosphorus-phosphorus coupling, see Scheme 10.[113]



Scheme 10 Preparation of $NapP_2Cl_4$ **18** and its reduction

In light of the previously published work it became our first goal to find a suitable reduction method for $NapP_2S_4$ **15**. We therefore subjected **15** to a standard reduction procedure with an excess of $LiAlH_4$ in THF at 0 °C. The resultant crude solid was analysed spectroscopically. The ^{31}P NMR spectrum obtained showed major peaks for **19** which were in good agreement with the published data[113] [$\delta_{P\{^1H\}}$ (109.4 MHz, $CDCl_3$) -105.6, δ_H (270.2 MHz; $CDCl_3$) 4.21 (d, $^1J_{PH}$ = 213.5) vs. δ_P -104.9, δ_H 4.58 ($^1J_{PH}$ = 207.7)]. There were also a number of unidentified by-products present. Due to the extreme sensitivity to oxygen and the pyrophoric nature of many primary phosphines[142] (including the monocyclic aromatic analogue 1,2-diphosphinobenzene $Ph(PH_2)_2$ **20**) it was decided to not purify the crude, but to use it for further reaction tainted with by-products. It has been shown[143] that **20** can undergo a double deprotonation with two equivalents *n*-BuLi. This dihydrophosphanide can be converted to the ortho-substituted bis-secondary phosphine $Ph(PHR)_2$ with the subsequent addition of an alkyl halide. We therefore decided to attempt to deprotonate the *peri*-positioned bis-primary phosphine **19** and introduce alkyl groups on to the phosphorus centres. After being stirred for 3 hours at -78 °C with the appropriate quantity of *n*BuLi, an excess of electrophile, either *iso*propyl iodide or *tert*-butyl chloride, was added. This was then allowed to rise to ambient temperature overnight. In both cases, ^{31}P NMR spectroscopic investigations of the reaction mixture reveal an abundance of peaks, none of which could be confidently assigned, see Scheme 11.

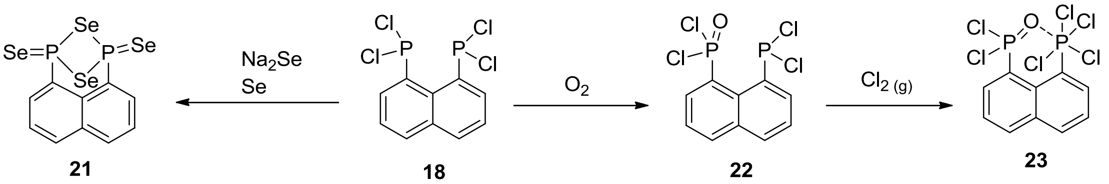


Scheme 11 Reduction of NapP$_2$S$_4$ **15** and its subsequent reactions

Despite these setbacks, NapP$_2$H$_4$ **19** may still be a good potential synthon, especially as it can be made in 2 steps from 1-bromonaphthalene in encouraging yields. However, the only further reaction of **19** published thus far is the protonation of one of the phosphorus centres with trifluoromethanesulfonic acid.[113] More thought may have to go into how **19** can be utilised as the starting material in order to make more *peri*-substituted naphthalene structures from it.

c. Further chemistry of NapP$_2$Cl$_4$

Similarly, there are very few further reactions of NapP$_2$Cl$_4$ **18** in the literature. One of them is the reaction of **18** with Na$_2$Se and powdered grey elemental Se to make a selenium analogue of **15**, see Scheme 12.[144] Although, this can be produced more directly from the reaction of $NapP_2S_4$ with first Ph_3P and subsequently a slight excess of elemental selenium.[144] This structure ($NapP_2Se_4$ **21**) has a similar motif to Woollins Reagent (WR) which is a selenation reagent used in a wide range of chemical applications.[145,146]



Scheme 12 Further reactions of $NapP_2Cl_4$ **18**

18 has also been oxidised with O_2 to give a structure $Nap(POCl_2)(PCl_2)$ **22** with a P^V and a P^{III} centre in the *peri*-positions.[147] Further chlorination of this structure results in a phosphoryl-phosphorane product **23** whose crystal structure shows hypercoordination of one of the phosphorus centres with the oxygen donating electron density to the phosphorus, see Scheme 12. Unlike the P-P bridged $Nap(PCl_2)(PCl_4)$ **17**, this compound **23** is quite strained with a splay angle of 9.3° and the phosphorus centres lying 0.50 and 0.48 Å above and below the mean bicyclical aromatic plane.[147]

It is a source of great surprise to us that **18** has so little further chemistry. There are innumerable examples of aryldichlorophorines reacting with alkyl/aryl lithiums in the literature,[25,148(to select just two)] however there is no precedent for reactions of dichlorophosphines attached to naphthalene backbones. It is hard to understand this seeming anomaly as aryl systems with much sterically bulkier groups such as mesityl ($MesPCl_2$)[149] and supermesityl (Mes^*PCl_2)[33] have been subject to exchange of phosphorus ligands with little difficultly. This may warrant further investigation.

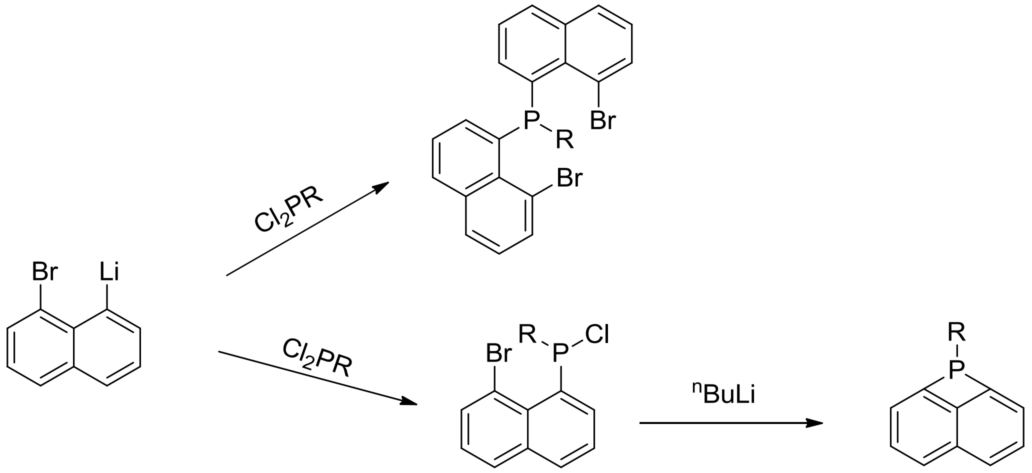
3. Protection of phosphorus-chlorine bonds

a. Introduction to protection strategies

As we mentioned previously, $NapP_2Cl_4$ **18** can’t be made directly from the reaction of PCl_3 and 1,8-dilithionaphthalene.[121] Instead a bis(dialkylamino)phosphine chloride was used to doubly add to the lithiated *peri*-positions of the naphthalene. These amino groups were then removed with HCl to reveal **18**.[113] The amino groups are acting as a protecting group which could be removed when the reaction is complete. This is the essence of protecting group chemistry, something that is placed on a moiety to give high chemoselectivity and to reduce the prevalence of side reactions. The ideal protecting group is one that can be placed at a specific site in quantitative yield via a reaction mechanism that causes no other alteration to the molecule. This protecting group must then remain in situ while the ensuing reaction is performed. It must finally be facile to remove the protecting group at the completion of the reaction to deprotect the reactive site in such a way that no other part of the molecule is affected.[150] Amines are the most common group to be used for the protection of phosphorus-chlorine bonds. They act as a placeholder for the chlorine which can be easily removed with HCl.

b. Our synthetic proposal

We aimed to produce a range of mono- and di-substituted acenaphthene moieties with only one alkyl or aryl group on the phosphorus centre. Without the use of a protecting group, alkyl/aryldichlorophosphines would have two reactive P-Cl bonds which would both be liable to react with lithiated naphthalene or acenaphthene species, see Scheme 13. The generic $RPCl_2$ species could react with two of the litiated skeletal backbones to produce a di(naphthalen-1-yl) tertiary phosphine (Nap_2PR)[151] instead of the desired secondary chlorophosphine, see Scheme 13. It has also been shown that $RPCl_2$ can reacts with both *peri*-positions[152,153] to attain a four membered phosphorus containing ring. Neither of these reactions is conducive to making the desired naphthalene or acenaphthene secondary chlorophosphine (NapP(Cl)R or AceP(Cl)R) in good yields with side reactions kept to a minimum.



Scheme 13 Reactions of dichlorophosphines with lithiated naphthalene

To that end, we investigated the possibility of using various amino groups to protect a range of alkyl and aryl dichlorophosphine leaving one P-Cl bond available for reaction. Conceptually, these mono-chlorinated compounds are built by starting from PCl_3. The order of reaction must then be determined, whether to exchange a chlorine atom for an amine or an alkyl/aryl group first. Further assembly can then occur with either an amine group[154] or an alkyl/aryl group[155] then substituted for a second chlorine atom. These $RP(Cl)NR'_2$ compounds could then be used in many diverse reactions.

c. The production of Et_2NPCl_2 and $^iPr_2NPCl_2$

Two useful synthons dichloro(diethylamino)phosphine (Et_2NPCl_2)[156] **24** and dichloro(diisopropylamino)phosphine ($^iPr_2NPCl_2$)[157] **25** were prepared from PCl_3 and two equivalents of the appropriate amine. The ammonium complex dialkylamine hydrochloride is filtered off as a by-product as the amine acts as both a reactant and a mild base in this reaction. These dichloro(dialkylamino)phosphines can be prepared in good yield (~75 %) after distillation on a large scale.

d. Synthesis of $PhP(Cl)N^iPr_2$ and $MesP(Cl)N^iPr_2$

The most straightforward route to chloro(diisopropylamino)phenylphosphine ($PhP(Cl)N^iPr_2$) **26** is by reacting commercially available phenyldichlorophosphine with two equivalents of diisopropylamine. This furnished the desired product as an oil in good yields after distillation under reduced pressure (~80%). Upon standing this clear liquid developed crystals which were deemed suitable for X-ray crystallographic analysis, see Figure 46 and Table 9. Although this is not a new product,[158] the crystal structure of **26** has not been reported up to now.

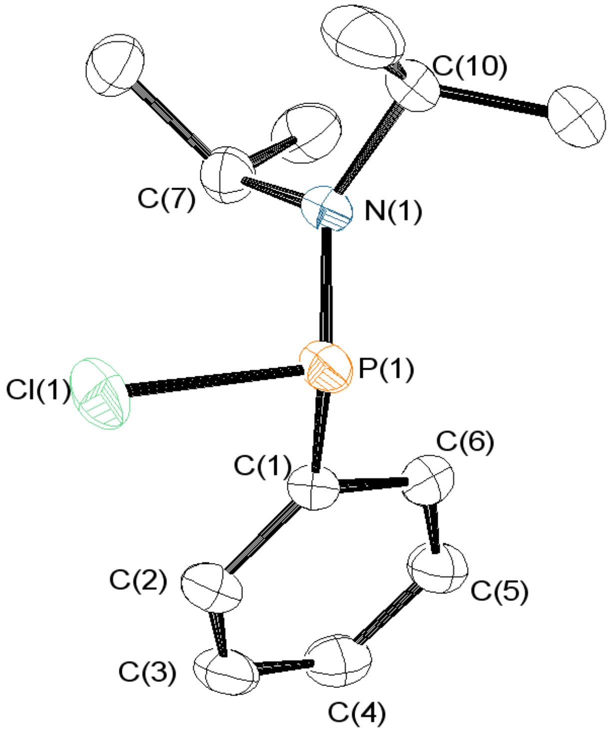


Figure 46 Molecular structure of **26**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

The reciprocal reaction with $PhPCl_2$ and Et_2NH was also performed with an excellent yield (~89 %). This is a liquid at room temperature and easily purified by distillation.[159] Further to this our attempts to crystallise at low temperature a sample of the compound suitable for X-ray crystallographic analysis were not successful. Nevertheless, the high yields achievable, even when reactions were conducted on a large scale, of both $PhP(Cl)N^iPr_2$ and $PhP(Cl)NEt_2$ **27** foster the conclusion that these are excellent synthons for subsequent reactions.[160]

Conversely to its unsubstituted phenyl counterpart, the synthesis of chloro(diisopropylamino)(2,4,6-trimethylphenyl)phosphine ($MesP(Cl)N^iPr_2$) **28** was best achieved via the reaction of mesityllithium with $^iPr_2NPCl_2$ **25**. This is also not a new product[161] however the crystal structure has not been reported hitherto. Crystals suitable for single crystal X-ray diffraction were grown via the slow evaporation of DCM under a flow of N_2, see Table 9 and Figure 47. Attempted recrystallisation in pentane as per literature did not yield pure product, however it was decided to use the impure solid for subsequent reactions anyway.

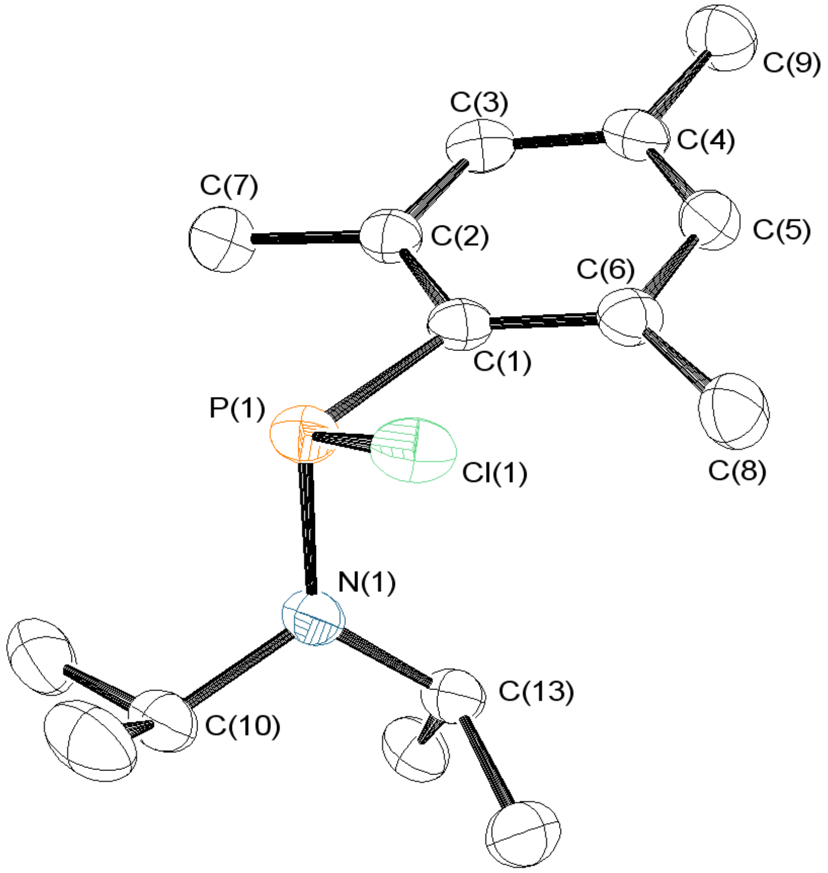


Figure 47 Molecular structure of **28**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

Further to this, we attempted to make $MesP(Cl)NEt_2$ **29** from the reaction of mesityllithium with the corresponding dichloro(diethylamino)phosphine. This afforded clear, yellowish oil which was distilled under reduced pressure to a clear liquid.[162] This recovered product proved not to be pure but was of sufficient quality for an NMR spectroscopic investigation.

e. X-Ray discussion of PhP(Cl)N^{i}Pr$_2$ and MesP(Cl)N^{i}Pr$_2$

The crystallographic attributes of these aryl(diisopropylamino)chlorophosphines were studied and compared in Table 9.

Table 9 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean aromatic plane (Å) for PhP(Cl)N^{i}Pr$_2$ **26** & MesP(Cl)N^{i}Pr$_2$ **28**

Bond length (Å)	**26**[a]	**28**
P(1)-C(1)	1.820(8), 1.824(7)	1.839(3)
P(1)-Cl(1)	2.140(3), 2.129(3)	2.2079(11)
P(1)-N(1)	1.638(6), 1.643(6)	1.651(2)
Bond Angle (°)		
Cl(1)-P(1)-N(1)	105.2(2), 105.1(3)	107.18(9)
Cl(1)-P(1)-C(1)	98.5(3), 99.6(3)	102.86(10)
N(1)-P(1)-C(1)	100.5(3), 101.9(4)	103.97(11)
C(1)-C(2)-C(7)	-	122.7(2)
C(1)-C(6)-C(8)	-	125.1(2)
Displacement from mean Ar plane (Å)[b]		
P(1)	0.003, 0.187	0.132
C(7)	-	0.029
C(8)	-	0.010
C(9)	-	0.051

[a] Two independent molecules
[b] Distance from the mean plane fitted through atoms C(1) to C(6)

Table 9 shows some selected parameters for PhP(Cl)N^{i}Pr$_2$ and MesP(Cl)N^{i}Pr$_2$.

The orientation of bonds around the central phosphorus atom of **26** shows clearly that the lone pair is having a distorting influence and causing all the bond angles to be sub-tetrahedral. The phosphorus centre itself deviates very little from the mean aromatic plane (an average of ~0.090 Å). The lack of *ortho*-substitution on this phenyl motif allows free rotation around the P(1)-C(1) bond as there are no steric clashes.

In comparison, **28** has more constrains placed upon it. The bond angles around the phosphorus atom are nearer to the idealised tetrahedral angle not because of a lessening of the lone pair influence but due to the *ortho*-substitution methyl groups on the aromatic ring. This steric competition is seen in both the in plane bending of the *ortho*-substituted CH_3 groups of 2.2(7) and 5.1(2)° away from the relax sp^2 hybridized angle and their bending out of the mean aromatic plane in the opposite direction from the phosphorus centre. It should be noted that the rotational barrier around the P(1)-C(1) bond is not so high as to cause a differentiation of the *meta*-substituted proton in ^{1}H NMR spectroscopy at room temperature as was witnessed in the spectra obtained from the $Mes^*_2P(=O)Cl$ **3** and compounds deriving from it. There is sufficient freedom of rotation on the NMR spectroscopy timescale for such protons to be magnetically equivalent.

f. Synthesis of $^tBuP(Cl)NR_2$

Following on from this work we decided to make a range of alkyl substituted $RP(Cl)NR'_2$ compounds. It was therefore desirable to make *tert*-butyl(chloro)diisopropylphosphinamine ($^tBuP(Cl)N^iPr_2$, **30**). Firstly, attempts were made to produce the synthon *tert*-butyldichlorophosphine from $^tBuLi/^tBuMgCl$ and PCl_3. These reactions provided disappointing results as both the Grignard Reaction and the alkyl lithium one did not produce the starting material cleanly as desired (see Experimental). It was therefore decided to purchase the commercially available $^tBuPCl_2$ and use that for further reactions. In a similar vein, we tried to make $^iPrPCl_2$ from PCl_3 and ^iPrMgI. It was found that the volatility of the desired product prevented its isolation from the solvent of the reaction mixture. $^iPrPCl_2$ was deemed too expensive to buy.

We discovered that when ${}^{t}BuPCl_2$ was reacted with two stoichiometric equivalents of $HN({}^{i}Pr)_2$ in a manner reminiscent of previous reactions that the dichloroalkylphosphine starting material was recovered exclusively. We therefore progressed to using a more forceful aminating agent in the guise of a 2.0M solution of lithium diisopropylamide (LDA). A large range of ${}^{31}P$ containing products were obtain, none of which could be identified. Consequently, we altered the focus of our work to the addition of a suitable ${}^{t}Bu$ nucleophile to $({}^{i}Pr)_2NPCl_2$. When a Grignard Reagent (from ${}^{t}BuCl$) was made and added to a solution of the dichloro(amino)phosphine it was found via ${}^{31}P$ NMR spectroscopy that the starting material reminded unaltered. Furthermore, it was found that the addition of a 1.9M solution of *t*-butyllithium to a cooled solution of $({}^{i}Pr)_2NPCl_2$ resulted in a large number of peaks being measured in the ${}^{31}P$ NMR spectroscopy once the mixture had equilibrated to ambient temperature.

Our lack of success was a cause of some surprise to us as ${}^{t}BuP(Cl)N({}^{i}Pr)_2$ **30** is a known product. It has been made via the reaction of $({}^{i}Pr)_2NPCl_2$ with ${}^{t}BuMgCl$[163] or ${}^{t}BuLi$ solution[164] and by reacting LDA solution with ${}^{t}BuPCl_2$.[165] We were somewhat perplexed by this outcome.

However, when we decided to change the amine group to diethylamine we had better reward. Two equivalents of $HNEt_2$ were reacted with ${}^{t}BuPCl_2$ to produce the expected product ${}^{t}BuP(Cl)N(Et)_2$ **31** as a clear oil in good yield (~83 %) after distillation.[166] Our endeavours to crystallise a sample of **31** in a sub-ambient temperature environment were not a success. When scaled up it was found that this reaction maintained the good yields observed. This would suggest that $^tBuP(Cl)N(Et)_2$ is an excellent synthon for subsequent reactions as the remaining phosphorus-chlorine bond has the potential for further chemistry.

g. Attempts to produce other RP(Cl)NR'$_2$ compounds

It was hoped that other alkyl substituted moieties could be produced in a similar way. To this end, a Grignard reagent of *iso*propyl iodide was made up and reacted with a $(^iPr)_2NPCl_2$. Disappointingly, this led to a complex mixture of phosphorus containing products, none of which were identifiable. The desired product $^iPrP(Cl)N(^iPr)_2$ **32** is a known compound,[167] however only one further reaction of it has been reported in the literature.[168] This is the production of a trichlorosilylphosphine $^iPrP[N(^iPr)_2]SiCl_3$ from the reaction of $^iPrP(Cl)N(^iPr)_2$ with $Cl_3Si\text{-}SiCl_3$. The difficulties faced in its production may be why it is not widely used as a synthon.

Another, potentially promising alkyl starting material used was benzyl chloride. When the Grignard Reagent $PhCH_2MgCl$ was added to Et_2NPCl_2 in ice and then allowed to equilibrate to room temperature, a ^{31}P NMR spectroscopic investigation showed a ratio of 1:1 starting material (δ_P 162.9) and another product (δ_P 145.6) was obtained. Attempts were made to separate two compound via distillation under reduced pressure but this proved unsuccessful. The desired product $PhCH_2P(Cl)NEt_2$ **33** is not a known compound so no purification procedures were forthcoming from the literature.

h. The nature of protecting groups

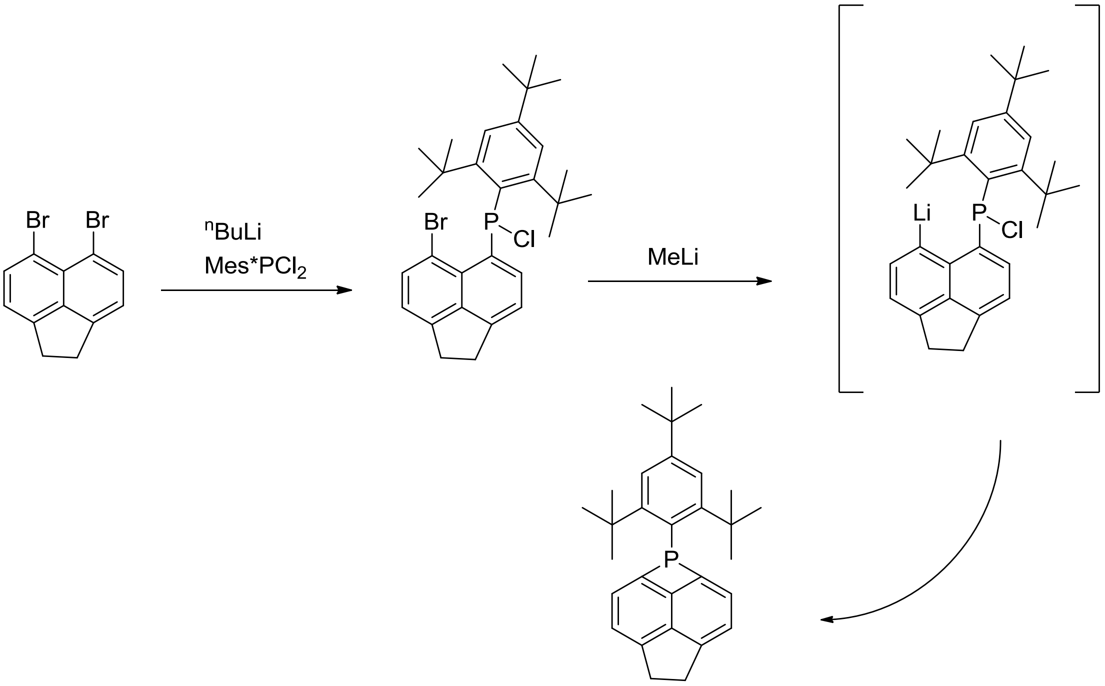
The use of protecting groups has provoked some controversy in the chemical community.[169] It has been suggested that because the use of protective motifs in this way requires at least two further steps in the reaction sequence (one for protection, one for deprotection) that there is an increase in the cost and complexity of target molecule synthesis. Although, we are inclined to agree that the use of protecting groups does bring an extra dimension of potential complication to the total synthesis of complex molecules, particular those of a biological nature, the use of amines to mask chlorophosphines is a vital component of our synthetic undertaking.

*4. Unexpected synthesis of Mes*P(NMe$_2$)$_2$*

a. The undesirable production of phosphete rings

A specific example of the effects of having two potentially reactive phosphorus-chlorine bonds on a single phosphorus centre is the reaction of the sterically hindered 2,4,6-tri-*tert*-butylphenyl (supermesityl, Mes*) moiety Mes*PCl$_2$ **1** with a mono-lithiated 5,6-dibromoacenaphthene. This resulted in monosubstitution occurring exclusively leading to the diarylchlorophosphine (6-bromo-1,2-dihydroacenaphthylen-5-yl)chloro(2,4,6-tri-tert-butylphenyl)phosphines [Ace(P(Cl)Mes*)Br].[153] A detailed study of the chemical literature reveals that Mes*PCl$_2$ is extremely unlikely to react with two mono-lithiated 5,6-dibromoacenaphthene backbones to make a triarylphosphine as the less sterically demanding diphenyl analogue Mes*PPh$_2$ had not been reported up to now. This is another indication of the sterically shielding nature of the Mes* motif. There are a limited number of literature examples of Mes*PCl$_2$ reacting with either 2 equivalents of alkyllithiums[170] to produce a compound with a Mes*PR$_2$ motif or with one alkyllithium[171] to leave one of the phosphorus-chlorine bonds intact (Mes*P(Cl)R)

The remaining brominated *peri*-position on Ace(P(Cl)Mes*)Br can be lithiated facilely with methyllithium. However, this results in a spontaneous cyclization reaction with the aryllithium reacting with the surviving phosphorus-chlorine bond, the consequence of which is the formation of a new four-membered phosphete ring, see Scheme 13 and Scheme 14.[153]



Scheme 14 The reactions of Mes*PCl$_2$ **1** with lithiated acenaphthenes

b. The protection of Mes*PCl$_2$ and the unexpected synthesis of Mes*P(NMe$_2$)$_2$

If the sterically demanding supermesityl moiety is to be used in our synthetic endeavours then a protection strategy for one of the phosphorus-chlorine bonds in Mes*PCl$_2$ must be devised to prevent the formation of this four-membered phosphorus ring. With regard to this, a sample of Mes*PCl$_2$ was reacted with two equivalents of HNEt$_2$ in a manner reminiscent of the reactions with less bulky RPCl$_2$ structures. A ^{31}P investigation of the resultant mixture showed that the starting material Mes*PCl$_2$ (δ_P 153.5, lit. value δ_P 152.5),[172] was by far the most abundant species present.

It was postulated that the ethyl groups place too much steric demand for this reaction to proceed. It was thus decided to refocus out efforts by using the smallest secondary amine possible, Me_2NH. When a Et_2O solution of Mes*PCl_2 was reacted with neat dimethyl amine, it was found that due to the low boiling point and volatility of the amine, it was too difficult to add the exact amount of Me_2NH to the reaction vessel. Thus the amount of Me_2NH added to the aryldichorophosphine was far in excess of the two equivalents that were stoichiometrically required. As a result the unexpected product Mes*P(NMe_2)$_2$ **34** was recovered, which was characterised by ^{31}P and ^{1}H NMR spectroscopy. It was also subjected to a single crystal X-ray diffraction, see Figure 48, Figure 49 and Table 10.

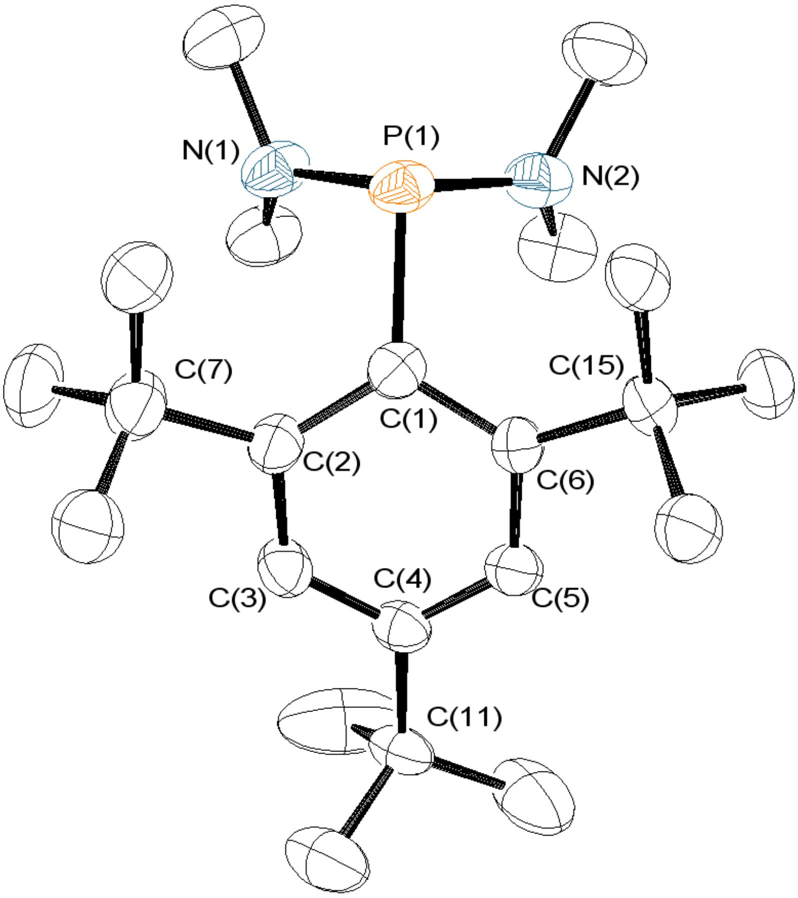


Figure 48 Molecular structure of **34**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

c. X-Ray discussion of Mes*P(N(CH$_3$)$_2$)$_2$

In order to properly analyse the structure features of our newly synthesised compound it was sagacious to compare it with other compound which display a Mes*PX$_2$ motif. These efforts are seen in Table 10.

Table 10 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean aromatic plane (Å) for Mes*P(NMe$_2$)$_2$ **34** and comparisons to similar structures

Bond Length (Å)	**34**	Mes*PCl$_2$[95]	Mes*PS$_2$[173]	Mes*P(SiMe$_3$)$_2$[174]
P(1)-X[a]	1.701(3), 1.702(3)	2.079(7), 2.076(7)	1.891(4), 1.892(3)	2.238(1), 2.255(1)
P(1)-C(1)	1.860(3)	1.772(13)	1.810(8)	1.884(3)
Bond Angle (°)				
X-P(1)-X	106.86(13)	101.5(3)	125.9(2)	111.03(6)
C(1)-P(1)-X	98.59(13), 100.34(13)	108.6(5), 105.1(5)	116.1(2), 118.0(3)	105.2(1), 127.0(1)
C(1)-C(2)-C(7)	125.8(3)	120.9(10)	127.9(6)	124.5(10)
C(1)-C(6)-C(15)	124.9(3)	124.9(10)	127.8(6)	125.6(10)
Dihedral angles (°)[b]				
C(1)-C(2)-C(3)-C(4)	7.1(4)	0.0(20)	1.5(8)	3.4(20)
C(1)-C(6)-C(5)-C(4)	6.3(4)	0.0(20)	0.1(8)	2.2(20)
C(2)-C(3)-C(4)-C(5)	10.4(4)	6.0(20)	0.2(8)	7.0(20)
C(3)-C(4)-C(5)-C(6)	10.4(4)	6.0(20)	0.6(9)	9.0(20)
C(5)-C(6)-C(1)-C(2)	23.8(4)	5.0(20)	1.5(8)	14.0(10)
C(6)-C(1)-C(2)-C(3)	24.2(4)	5.0(10)	0.8(8)	14.0(10)
Displacement from mean Ar plane (Å)[c]				
P(1)	1.001	0.686	0.071	0.903
C(7)	0.618	0.076	0.011	0.322
C(15)	0.609	0.235	0.026	0.306
C(11)	0.288	0.024	0.024	0.195
C(1)	0.154	0.043	0.006	0.091
C(4)	0.102	0.040	0.001	0.069

[a] X = N, Cl, S or Si
[b] Within the Aryl ring
[c] Distance from the mean plane fitted through atoms C(1) to C(6)

From Table 10 we can see that Mes*P(NMe_2)$_2$ **34** is quite strained. The phosphorus centre lies over 1.0 Å out of the mean aromatic plane. The lone pair on the phosphorus centre has a large impact on the geometry of the heteroatoms as all the bond angles on the phosphorus centre are sub-tetrahedral. The most drastic contrast is with the Mes*PS_2 structure as this is actually a P(V) compound with two phosphorus-sulfur double bonds. In the literature,[32] there is also a [Mes*PS]$_3$ structure where the phosphorus atoms are all P(III). This is a chair conformation 2,4,6-trisupermesityl-1,3,5,2,4,6-trithiatriphosphinane ring.

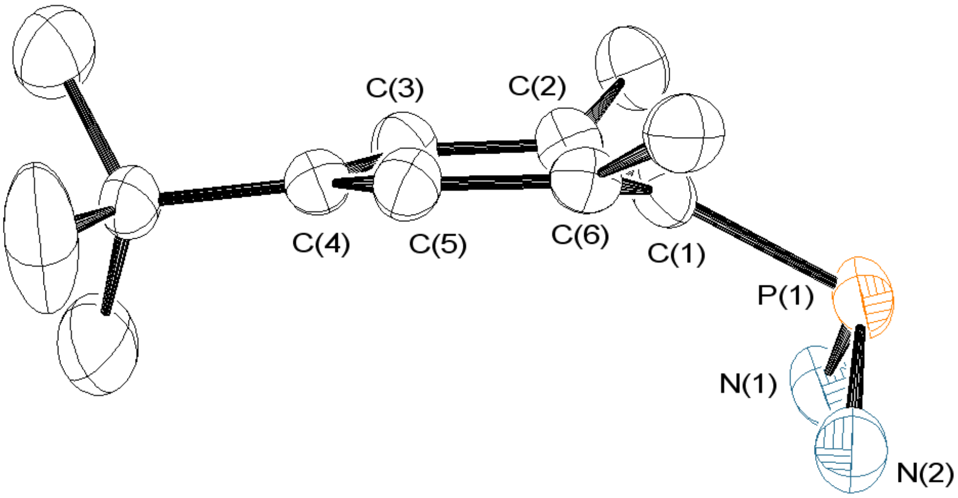


Figure 49 Another view of the molecular structure of **34** showing the level of out of plane bending which the phosphorus atom displays. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, amino alkyl groups and CH_3 groups from C(7) and C(15) excluded for clarity

The quaternary carbons of the *ortho*-^{t}Bu groups on **34** are bent a significant distance (~0.615 Å) out of the mean aromatic plane in the opposite direction from the phosphorus centre as can be seen from Figure 49. This is partly due to the buckling of the aromatic ring in to a boat conformation with the *ispo*- and *para*- aromatic carbons between ~0.10 and 0.15 Å out the same side of the mean aromatic plane as well as other geometry factors. This buckling is quantified by the large dihedral angles that are seen within the ring. Also significant is the angles that C(1)-C(2)-C(7) and its counterpart on the other side of the ring make of 124.9(3) and 125.8(3)° respectively. This in-plane deviation from the ideal sp^2 carbon geometry of 120° show that the phosphorus atom is interacting sterically with the $C(CH_3)_3$ groups, which are *ortho*-positioned on the aromatic ring.

The phosphorus-nitrogen bond lengths in **34** are significantly shorter than the corresponding P-X lengths in the comparison single bonded structures. This is due to Cl and Si belonging to a lower period. The double phosphorus-sulfur bonds in Mes^*PS_2 will obviously be shorter than P-S single bonds and thus not applicable. A better juxtaposition can be made with diethynyl(2,4,6-tri-tert-butylphenyl)phosphine ($Mes^*P(C{\equiv}CH)_2$) which has a phosphorus-carbon single bonds of 1.764(4) and 1.767(4) Å.[175] All of this contributes to making $Mes^*P(NMe_2)_2$ **34** an interesting structure to examine.

5. *Reactions of protected chlorophosphines with lithiated backbones*

a. The synthesis of single addition products

As mentioned previously, single[124] and double[126] lithiation of 5,6-dibromoacenaphthene can be achieved easily, see Scheme 7. These intermediate provide a platform from which a large range of new and exciting compounds can be synthesised. To this end, we investigated the reaction of the alkyl/aryl(chloro)(dialkylamino)phosphines which we previously produced with the lithiated aromatic skeletal rings, see Scheme 15.

Firstly, the reaction of $PhP(Cl)N^iPr_2$ **26** with mono-lithiated 5,6-dibromoacenaphthene at low temperature was explored. After the solid ionic by-products had been removed via filtration and the volatiles had been evaporated under reduced pressure, a yellow solid amorphous solid remained. After repeated recrystallisation with acetonitrile, a pure yellowy-orange powder product ($Ace[P(Ph)N(^iPr)_2]Br$) **35** was obtained in moderate yield (~32 %). This was fully characterised by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy, IR, Raman and ES MS; its purity was verified by microanalyses. Crystals of the product were obtained via the slow evaporation of a concentrated DCM solution. These were then successfully characterised by a single crystal X-ray diffraction, see Figure 50, Figure 54 and Table 11.

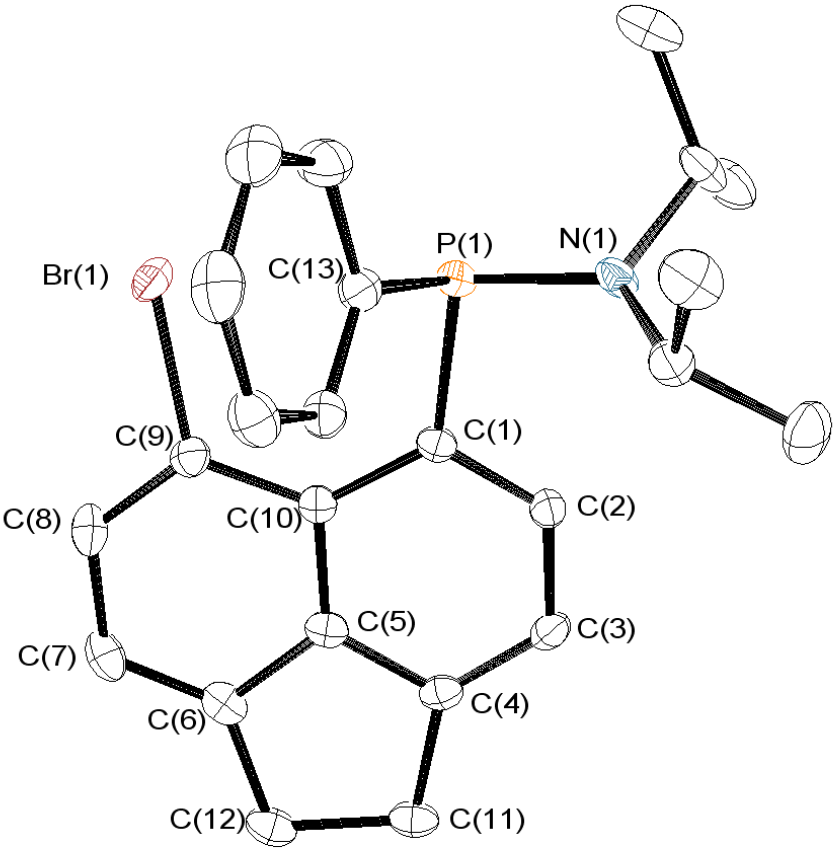
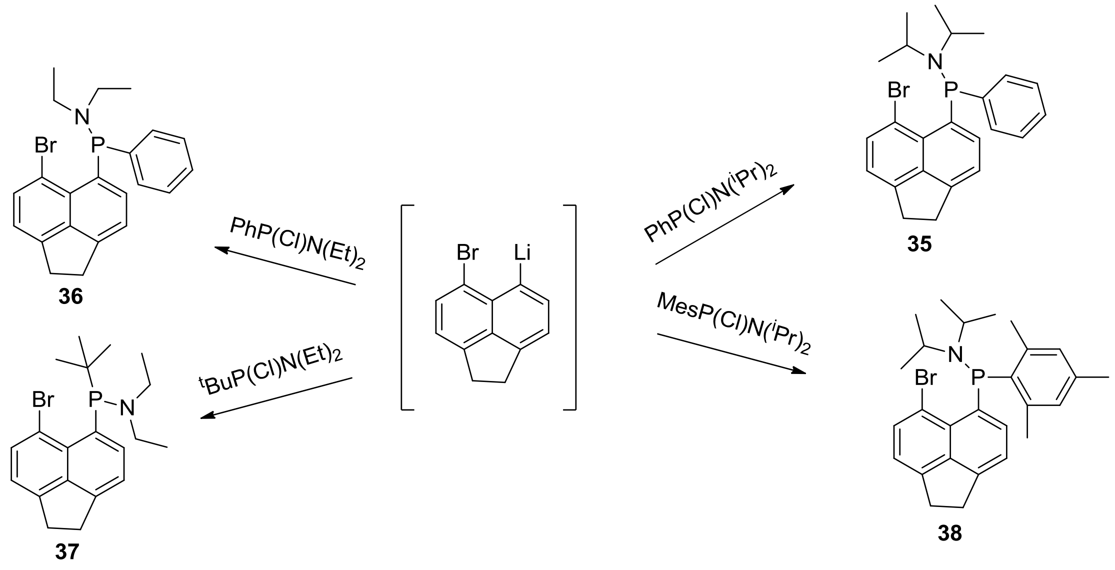


Figure 50 Molecular structure of **35**. Thermal ellipsoids are set at 50% probability, the hydrogen atoms are omitted for clarity.

A close analogue of this was produced when PhP(Cl)NEt$_2$ **27** was reacted with a mono-lithiated 5,6-dibromoacenaphthene ring. This reaction proceeded smoothly and the resultant red-brown solid (Ace[P(Ph)N(Et)$_2$]Br **36**) could be purified by washing with hot hexane to reveal a yellowy powder. The yield obtained (35 %) can be considered moderate to good. This powder was characterised fully by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy, IR, Raman and ES MS. Its purity could be verified by microanalyses and exact mass spectrometry to confirm that the correct product was in fact fabricated. Repeated attempt to grow crystals of this structure failed due to its lack of solubility of the product in many common solvents. When DCM was allowed to evaporate slowly from a concentrated sample of **36** the resultant material was a greasy amorphous solid. It came as some disappointment to us that our attempts to grow crystals suitable for X-ray crystallography did not succeed as it hampered our efforts to directly compare the solid state arrangement of this compound to **35.**



Scheme 15 The reaction of mono-lithiated acenaphthene with a range of electrophiles

Following on from this the mono-lithiated 5,6-dibromoacenaphthene was reacted with $^tBuP(Cl)N(Et)_2$ **31**. The procedure was executed as with other $RP(Cl)NR'_2$ compounds and the residue obtained when the volatiles were removed at the end of the reaction was a yellowish substance with a treacle-like consistency. When this was probed spectroscopically, it was discovered that there were two ^{31}P moieties present in an approximate 1:1 abundance; one was conformed to be the starting material (δ_P 161.2) and other was a peak from an unidentified compound (δ_P 68.9). This amorphous substance was allowed to stand and over time crystals developed within the residue. These crystals were deemed suitable for single crystal X-ray diffraction and the structure obtained was the desired product ($Ace[P(^tBu)N(Et)_2]Br$) **37**, see Figure 51, Figure 52, Figure 55 and Table 11.

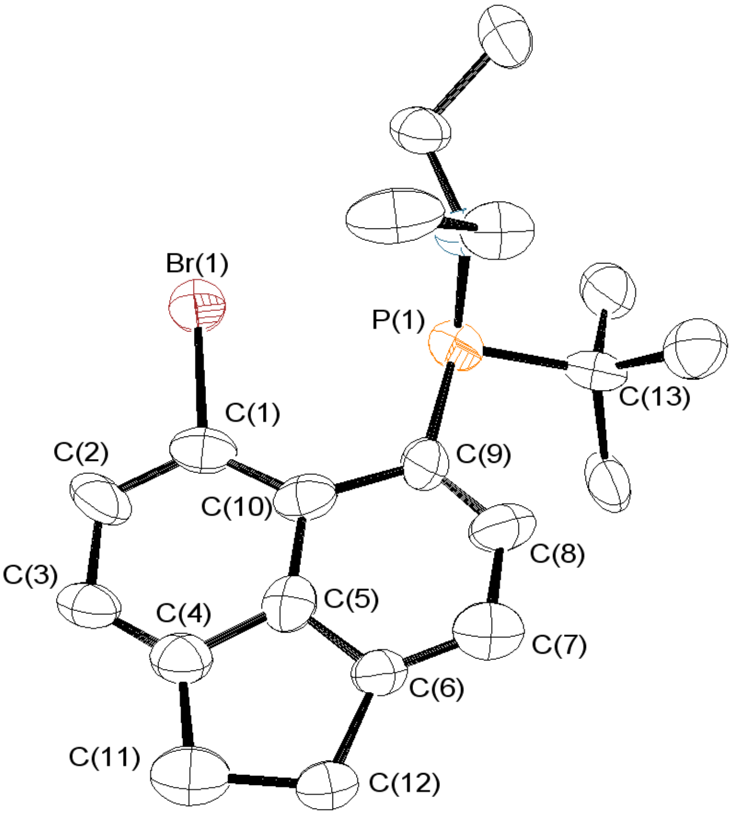


Figure 51 Molecular structure of **37**. Thermal ellipsoids are set at 50% probability, the hydrogen atoms are omitted for clarity.

Numerous attempts were made to purify this product via recrystallisation in a range of different solvent systems but at no time was a sample of satisfactory quality to perform a detailed NMR spectroscopic study obtained. A crude ^{31}P NMR spectrum is listed in the experimental section. It was the cause of some disappointment to us that we could not acquire a pure sample of **37**. Serious impediment was placed on our ability to further study its physical and chemical properties.

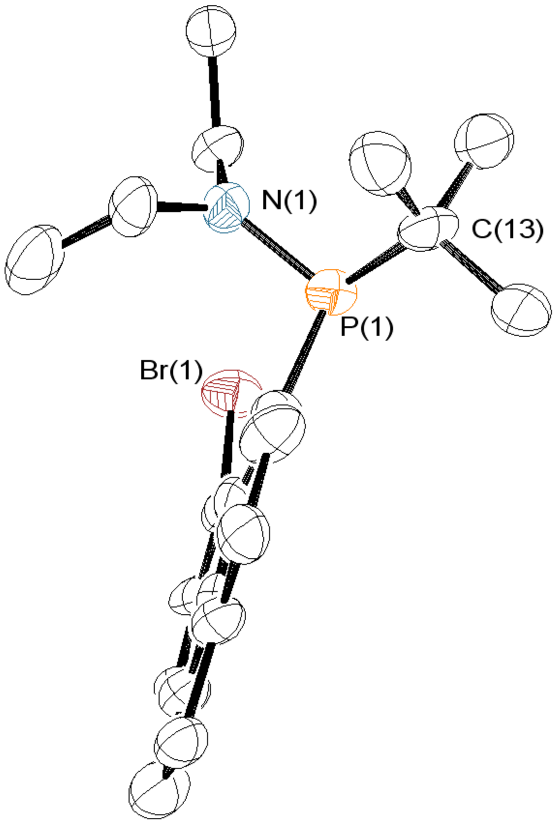


Figure 52 Molecular structure of **37** showing another angle. Thermal ellipsoids are set at 50% probability, the hydrogen atoms are omitted for clarity.

The impure substituted-aryl(chloro)(dialkylamino)phosphine MesP(Cl)N^{i}Pr$_2$ **28** was reacted with the mono-lithiated 5,6-dibromoacenaphthene in a similar way to previous reactions. On removal of the volatiles at the conclusion of the reaction a yellowish solid persisted which showed one major peak in ^{31}P NMR spectroscopy at δ_P 35.3; there were other peaks of varying intensities present also. We tried to obtain a pure sample via recrystallisation from a library of solvents, but alas this was not achieved. Crystallization via the slow evaporation of a concentrated sample in DCM of the residue did furnish some crystalline material which was deemed suitable for X-ray crystallographic analysis, see Figure 53, Figure 56, Figure 57 and Table 11. This demonstrated that the desired structure (Ace[P(Mes)N(^{i}Pr)$_2$]Br **38**) was indeed generated.

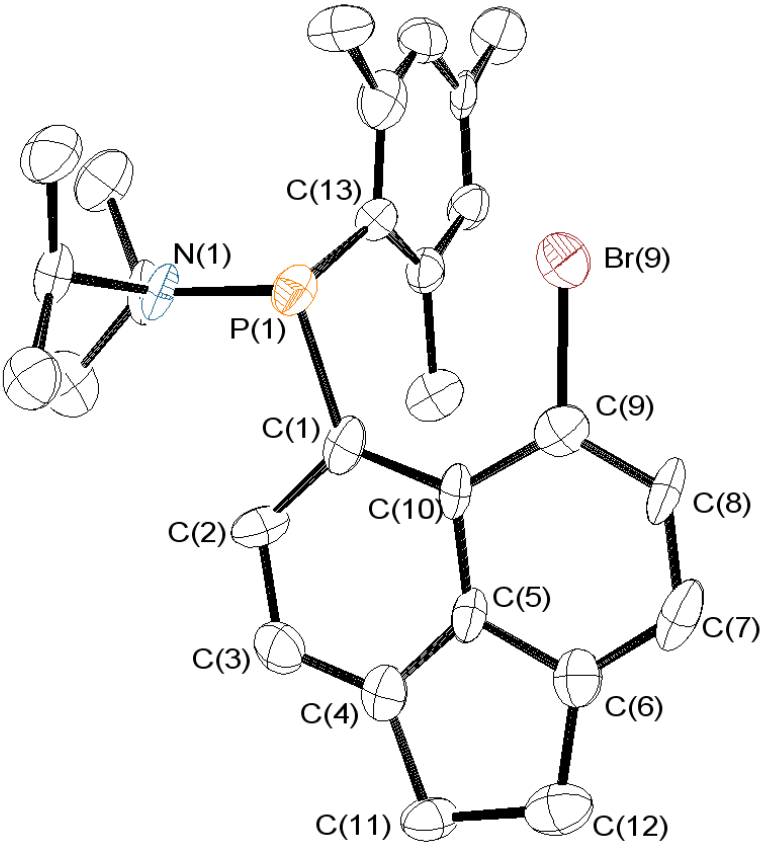


Figure 53 Molecular structure of **38** showing acenaphthene ring. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

In a similar vein, impure MesP(Cl)N(Et)$_2$ **29** was reacted with mono-lithiated 5,6-dibromoacenaphthene at low temperature as per standard procedure. On its return to room temperature, an aliquot of the reaction mixture revealed a proliferation of ^{31}P moieties; the most abundant was at δ_P 60.4 (s). Upon removal of the solvent and waste LiBr salts, an orange-yellow residue was found. Efforts were made to separate this mixture with the hope of obtaining a pure sample of Ace[P(Mes)N(Et)$_2$]Br **39**. A number of different crystallization scheme were utilised however no pure product was acquired. Concurrently, a concentrated sample of the residue in DCM was allowed to evaporate slowly, the material recovered from this was a greasy amorphous solid which was unsuitable for single crystal X-ray diffraction.

b. X-ray discussion of single addition products

Table 11 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean aromatic planes (Å) for Ace[P(Ph)N(^{i}Pr)$_2$]Br **35**, Ace[P(^{t}Bu)N(Et)$_2$]Br **37** & Ace[P(Mes)N(^{i}Pr)$_2$]Br **38**

Bond lengths (Å)	**35**	**37**[a]	**38**[b]
P(1)-C(1)/ P(1)-C(9)	1.855(3)	1.880(12), 1.874(13)	1.867(11), 1.885(12), 1.876(11)
P(1)-N(1)	1.700(2)	1.701(12), 1.698(12)	1.726(9), 1.707(9), 1.710(9),
P(1)-C(13)	1.851(3)	1.940(15), 1.868(14)	1.873(11), 1.877(12), 1.891(11)
Br(1)-C(9)/ Br(1)-C(1)/ Br(9)-C(9)	1.908(3)	1.917(10), 1.934(12)	1.911(11), 1.926(13), 1.923(10)
P(1)···Br(1)/Br(9)$_{(peri\text{-distance})}$	3.2671(10)	3.217(5), 3.225(4)	3.264(3), 3.247(3), 3.272(3)
Bond Angles (°)			
N(1)-P(1)-C(1)/ N(1)-P(1)-C(9)	103.34(11)	102.5(6), 104.3(6)	106.1(5), 105.4(5), 105.7(5)
C(1)-P(1)-C(13)/ C(9)-P(1)-C(13)	102.02(11)	105.2(6), 107.1(6)	106.5(5), 105.6(5), 105.8(5)
N(1)-P(1)-C(13)	101.27(10)	104.6(7), 105.1(7)	99.8(5), 102.4(5) 100.1(5),
C(13)-C(14)-C(19)	-	-	124.9(10), 125.6(10), 125.5(10)
C(13)-C(18)-C(21)	-	-	121.8(11), 122.0(11), 121.7(10)
C(4)-C(5)-C(6)	111.2(2)	111.2(10), 111.2(11)	109.9(10), 111.0(11), 110.0(10),
C(1)-C(10)-C(9)	131.0(3)	132.6(11), 131.9(9)	130.5(10), 132.2(11), 131.3(10)
P(1)-C(1)-C(10)/ P(1)-C(9)-C(10)	126.20(17)	119.8(10), 121.6(8)	127.2(9), 124.3(9), 125.2(8)
C(10)-C(9)-Br(1)/ C(10)-C(1)-Br(1)/ C(10)-C(9)-Br(9)	121.66(18)	122.4(10), 124.1(9)	121.7(8), 122.2(9), 122.7(8)
Splay Angle (°)	18.96(30)	17.6(11), 14.8(9)	19.4(10), 18.7(11), 19.2(10)

Dihedral angles (°)			
C(6)-C(5)-C(10)-C(9)	5.3(4)	7.9(17), 0.7(17)	1.8(14), 0.7(15), 1.3(14)
C(4)-C(5)-C(10)-C(1)	4.9(4)	1.1(17), 3.0(17)	2.4(14), 1.7(15), 2.6(14)
C(6)-C(5)-C(10)-C(1)	175.9(2)	175.9(10), 178.1(10)	179.2(9), 178.5(9). 177.3(9)
C(4)-C(5)-C(10)-C(9)	174.0(2)	179.6(11), 175.1(11)	176.7(8), 179.1(9), 178.9(8)
Displacement from mean Ace plane (Å)[c]			
P(1)	0.268	0.285, 0.376	0.071, 0.024, 0.043
Br(1)/ Br(9)	0.393	0.100, 0.277	0.207, 0.219, 0.227
Displacement from mean Ar plane (Å)[d]			
P(1)	0.169	-	0.258, 0.045, 0.200
C(19)	-	-	0.030, 0.041, 0.103
C(21)	-	-	0.150, 0.027, 0.023
C20)	-	-	0.135, 0.077, 0.138

[a] Two Independent Molecules
[b] Three Independent Molecules
[c] Distance from the mean plane fitted through atoms C(1) to C(10)
[d] Distance from the mean plane fitted through atoms C(13) to C(18)

Table 11 shows that Ace[P(Ph)N(^{i}Pr)$_2$]Br **35** has a large (3.2671(10) Å) *peri*-distance, which indicates a considerable repulsive interaction between the phosphorus centre and the bromine one. This is considerably larger than the unconstrained 5,6-acenaphthene distance of 2.67(2) Å. It also has a large splay angle (18.96(30)°) as the aromatic framework rearranges itself to lessen the steric repulsion felt. This also seen in the twisting of the bicyclical aromatic rings that is measured in the dihedral angles which vary from 4.9(4) to 6.0(2)° away from the relaxed acenaphthene values. The repulsion between the phosphorus and bromine centres results in them bending out either side of the mean acenaphthene plane to the tune of between 0.27 (P) and 0.39 (Br) Å, see Figure 54. The phosphorus atom is also displaced out of the mean aromatic plane of the phenyl group attached to it but to less of a degree (~0.17 Å). Angles around the phosphorus centre are all sub-tetrahedral, suggesting that the lone pair is having a distorting influence on the molecular geometry of the structure.

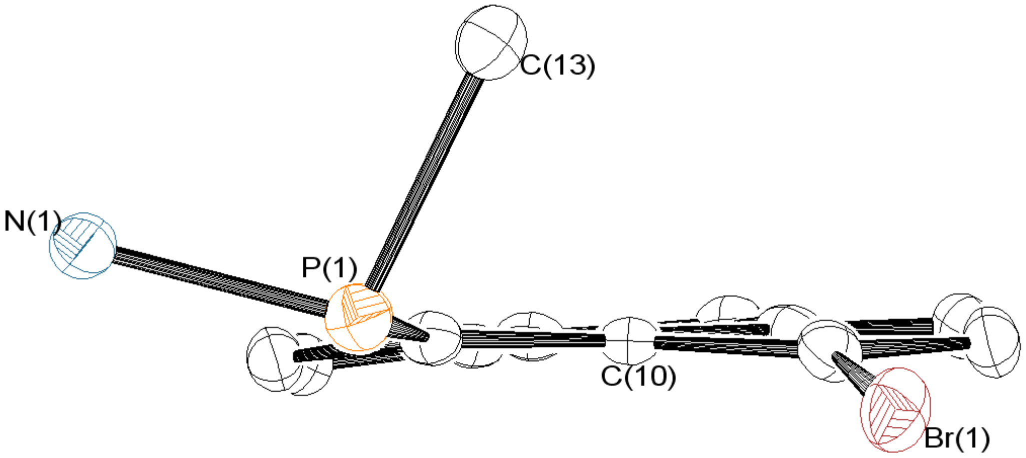


Figure 54 Molecular structure of **35** showing the extent of bending out of the mean aromatic plane. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, amino alkyl groups and phenyl group excluding C(13) are omitted for clarity.

In comparison, Ace[P(^{t}Bu)N(Et)$_2$]Br **37** has marginally shorter *peri*-distances of 3.217(5) and 3.225(4) Å, which are still significantly larger than the relaxed *peri*-distance of acenaphthene (2.67(2) Å). The out of plane bending observed shows an interesting differentiation between the *peri*-substituted heteroatoms as the phosphorus centre bending much further out of the mean aromatic plane (~0.28 and 0.37 Å) than the bromine is (~0.10 and 0.28 Å). The extent of displacement of the phosphorus atom from the mean aromatic plane in one of the independent molecules is similar to that seen in **35** but both are noticeably larger than the bending in **38**. The repulsive nature of this phosphorus-bromine interaction is further reinforced by the large positive splay angles observed (14.8(9) and 17.6(11)°) and the dihedral angles which show the deviation from planarity of the bicyclical aromatic system.

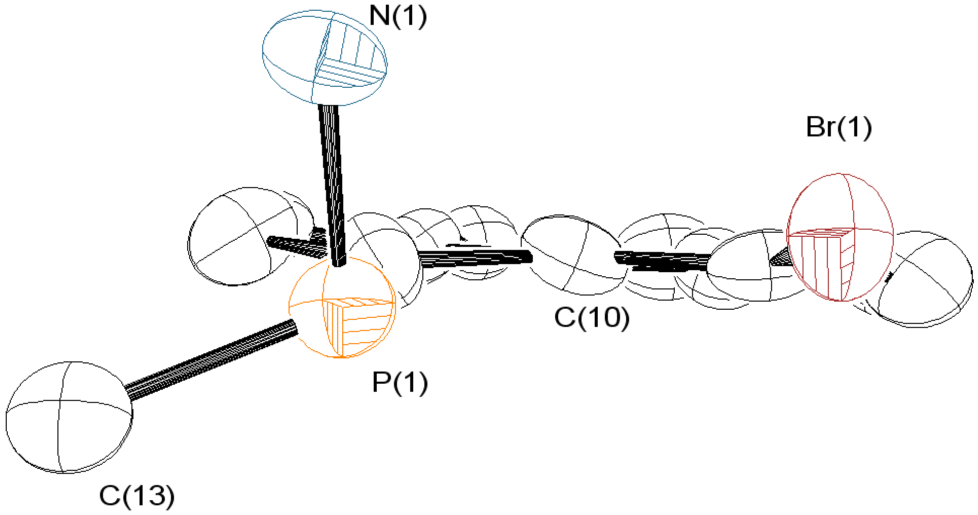


Figure 55 Molecular structure of **37** showing the bending of the phosphorus and bromine atoms out of the mean bicyclical plane. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, amine alkyl groups and the three CH_3 groups on C(13) are omitted for clarity.

Ace[P(Mes)N(^{i}Pr)$_2$]Br **38** displays the largest splay angles (18.70(11), 19.20(10) and 19.40(10)°) seen when compared to **35** or **37**. However there appears to be less contortion in the aromatic skeletal framework with torsion angles that deviate much less (from 0.7(15) to 3.3(9)°) from planarity than in **35** or **37**.

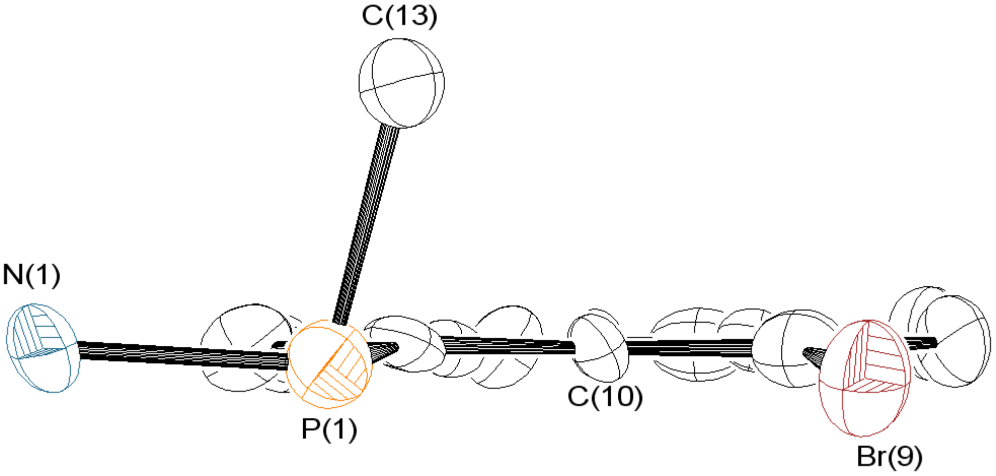


Figure 56 Molecular structure of **38** showing the bending of the phosphorus and bromine atoms out of the mean aromatic plane. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, amine alkyl groups and the entire Mes group (excluding C(13)) are omitted for clarity.

The bromine atom is relatively consistent by how much it bends out of this plane (~0.215 Å). The *peri*-distances observed (3.264(3), 3.247(3) and 3.272(3) Å) are very similar to **35**. This shows that there is a large repulsive interaction between the phosphorus and bromine centres. There is a large disparity in how much the phosphorus bends out of the mean aromatic plane formed from the mesityl group attached to it (~0.05 to 0.25 Å). This discrepancy is not easy to explain.

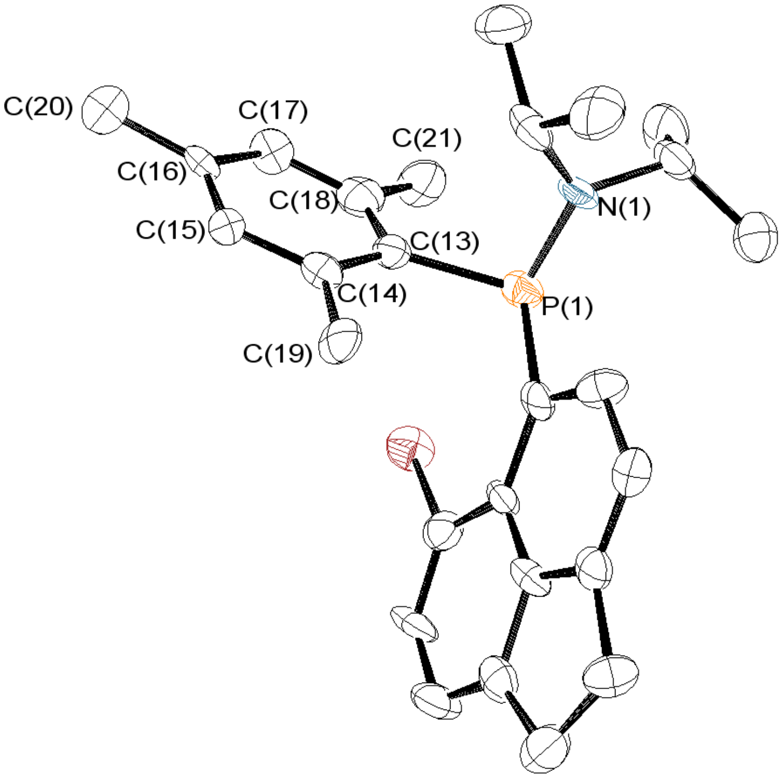


Figure 57 Molecular structure of **38** showing the connectivity around the phosphorus atom more clearly. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

The *ortho*-CH_3 groups on the mesityl ring do not undergo much out of plane distortion from the mean plane but they do demonstrate much in plane distortion with the methyl groups bending between 1.7(10) and 5.6(10)° away from the idealised sp^2 hybridized value, see Figure 57.

c. Synthesis of Ace[P(Ph)N(^{i}Pr)$_2$]$_2$

Taking these results on board, we transferred the focus of our synthetic endeavours to examining the reactions of alkyl/aryl(chloro)(dialkylamino)phosphines with di-lithiated 5,6-dibromoacenaphthene. We were hoping to add two of the same phosphine motifs onto the *peri*-positions to produce a range of compounds which (at least theoretically) may have an internal mirror plane.

To this end, two equivalents of PhP(Cl)N^{i}Pr$_2$ **26** were reacted with di-lithiated 5,6-dibromoacenaphthene in the presence of an excess of N,N,N′,N′-Tetramethylethane-1,2-diamine (TMEDA). Upon removal of the ionic by-products and the solvent, a redy-brown solid was obtained. After repeated recrystallisation in hexane and acetonitrile yellow microcrystalline material was isolated from this residue in a moderate (32 %) yield. These was fully characterised by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy, IR, Raman and ES MS; its purity was verified by microanalyses. Larger crystals were grown from slow evaporation of a concentrated DCM solution of the microcrystals. These were deemed suitable to be characterised by a single crystal X-ray diffraction, see Figure 58, Figure 59, Figure 60 and Table 12. The structure obtained was the desired product (Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40**).

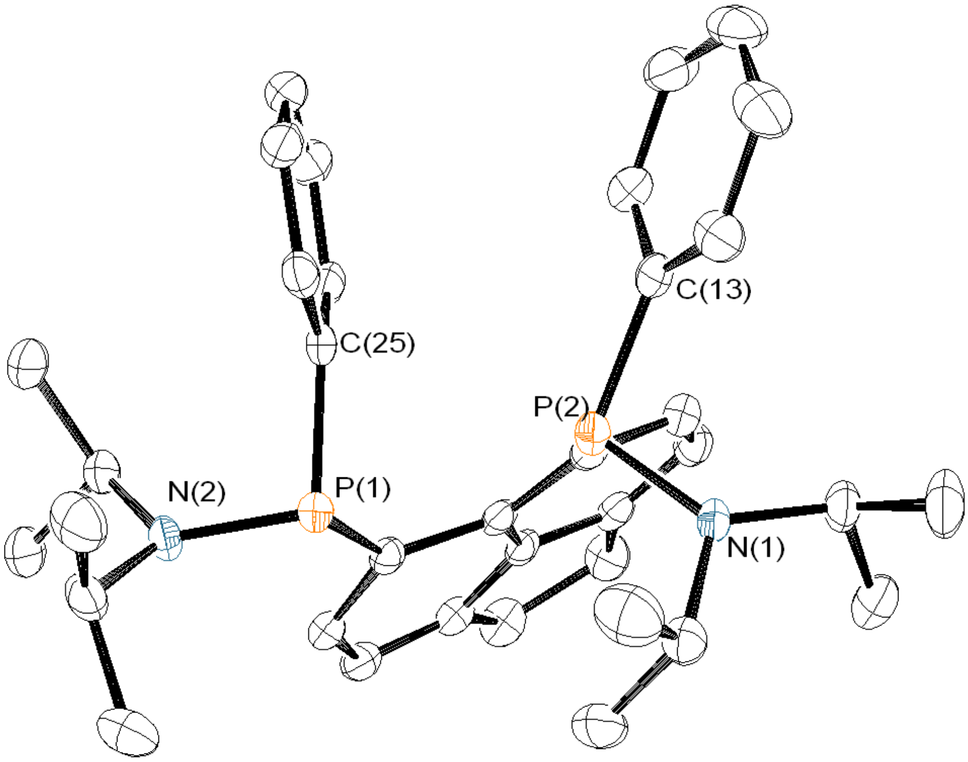


Figure 58 Molecular structure of **40** showing the connectivity around the phosphorus centre. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

With a phosphorus atom at each of *peri*-position, this is an interesting compound to study.

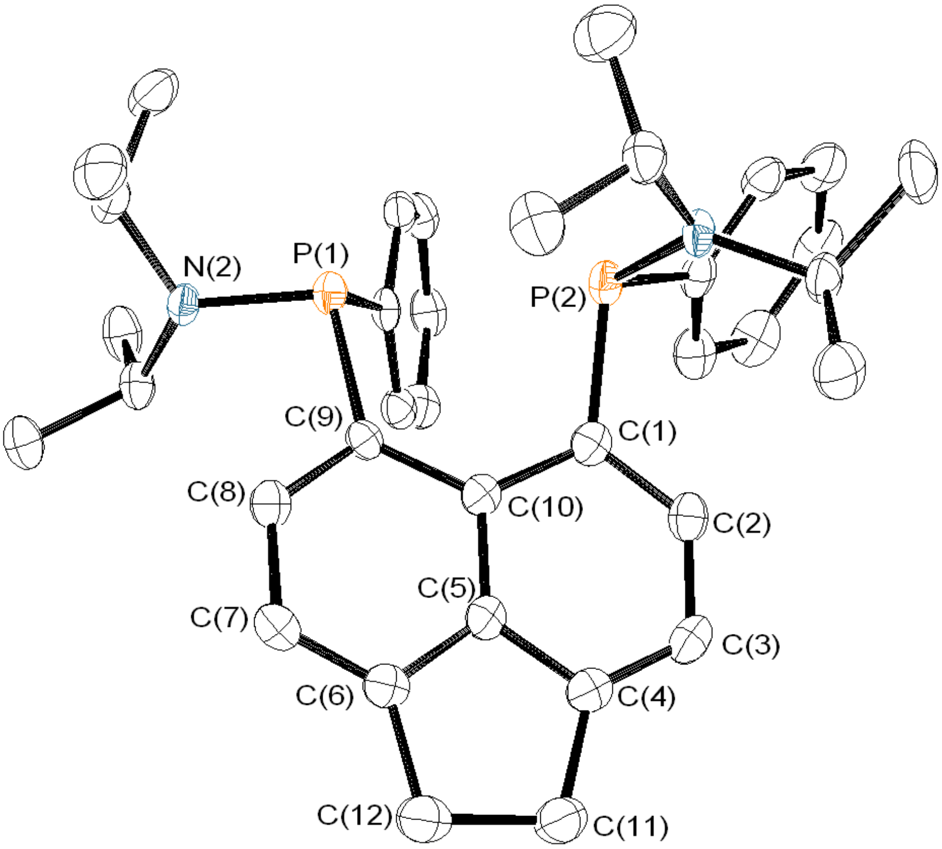


Figure 59 Molecular structure of **40** showing the acenaphthene ring carbons. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

d. X-ray discussion of double addition products

Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40** is unusual in that it is quite unlike any other crystals in the crystallographic database(s) or literature. The naphthalene system 1,8-bis(*tert*-butyl(phenyl)phosphino)naphthalene (Nap[P(^{t}Bu)Ph]$_2$) was therefore used for comparison purposes in Table 12.

Table 12 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean aromatic planes (Å) for Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40** and the comparison compound Nap[P(^{t}Bu)Ph]$_2$

Bond lengths (Å)	**40**	Nap[P(^{t}Bu)Ph]$_2$[176]
P(1)-C(9)	1.857(2)	1.8455(16)
P(2)-C(1)	1.850(3)	1.8466(15)
P(1)-N(2) or P(1)-$\underline{C}(CH_3)_3$	1.714(3)	1.8942(17)
P(2)-N(1) or P(2)-$\underline{C}(CH_3)_3$	1.6916(19)	1.9108(17)
P(1)-C(25)	1.846(2)	1.8340(16)
P(2)-C(13)	1.836(3)	1.8334(18)
P(1)···P(2)$_{(\textit{peri}\text{-distance})}$	3.1600(11)	3.0557(6)
Bond Angles (°)		
N(2)-P(1)-C(9) or $(CH_3)_3\underline{C}$-P(1)-C(9)	101.99(11)	101.41(7)
C(9)-P(1)-C(25)	102.00(10)	101.41(8)
N(2)-P(1)-C(25) or $(CH_3)_3\underline{C}$-P(1)-C(25)	100.92(10)	108.62(8)
N(1)-P(2)-C(1) or $(CH_3)_3\underline{C}$-P(2)-C(1)	107.01(9)	101.88(7)
C(1)-P(2)-C(13)	101.53(11)	101.97(7)
N(1)-P(2)-C(13) or $(CH_3)_3\underline{C}$-P(2)-C(13)	101.79(11)	106.38(8)
C(4)-C(5)-C(6)	111.2(2)	121.55(15)
C(1)-C(10)-C(9)	128.7(2)	123.48(13)
P(1)-C(9)-C(10)	125.5(2)	118.09(11)
C(10)-C(1)-P(2)	119.94(15)	118.37(12)
Splay Angle (°)	14.14(15)	- 0.06(13)
Dihedral angles (°)		
C(6)-C(5)-C(10)-C(9)	6.0(3)	10.3(2)
C(4)-C(5)-C(10)-C(1)	5.8(3)	10.7(2)
C(4)-C(5)-C(10)-C(9)	174.06(15)	168.8(1)
C(6)-C(5)-C(10)-C(1)	174.20(16)	170.1(1)
Displacement from mean Ace plane (Å)[a]		
P(1)	0.348	0.889
P(2)	0.551	0.912
Displacement from mean Ph plane (Å)		
P(1)[b]	0.315	0.143
P(2)[c]	0.117	0.200

[a] Distance from the mean plane fitted through atoms C(1) to C(10)
[b] Distance from the mean plane fitted through atoms C(25) to C(30)
[c] Distance from the mean plane fitted through atoms C(13) to C(18)

Table 12 shows some of the important structural data for Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40**. It demonstrates that **40** displays a phosphorus-phosphorus *peri*-distance of 3.1600(11) Å, which is much larger than the relaxed 5,6-acenaphthene distance of 2.67(2) Å. The splay angle is 14.14(15)° and there is significant twisting within the aromatic bicycle as indicated by the dihedral angles which are between 5.8(3) and 6.0(3)° away from the relaxed ideal. The phosphorus centres in **40** lie 0.34 and 0.55 Å away from the mean bicyclical aromatic plane, one either side of that plane.

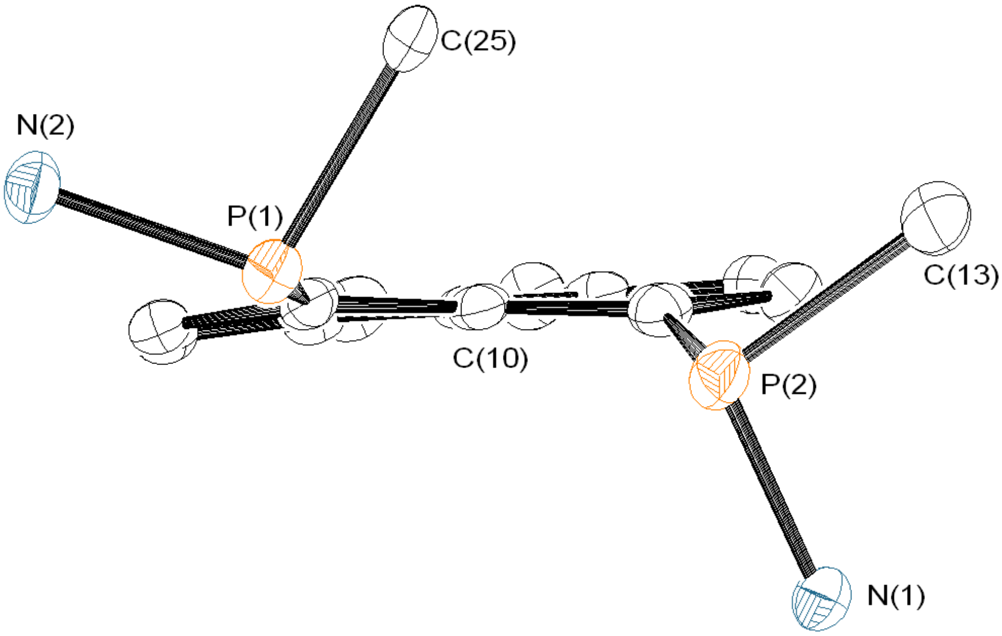


Figure 60 Molecular structure of **40** showing the extent of bending out of the mean aromatic plane. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, amino alkyl groups and phenyl groups excluding C(13) and C(25) are omitted for clarity.

All of this illustrates the large repulsion which is present between the two phosphorus centres. When this is compared to Ace[P(Ph)N(^{i}Pr)$_2$]Br **35**, it is seen that the effect of having a phosphorus atom on each of the *peri*-positions is a slight decrease in both the *peri*-distance and the splay angle, but the bending of the phosphorus centres out of the mean acenaphthene skeletal plane is more pronounced, with a corresponding increase in torsion angles. Each of the phosphorus atoms in **40** lie out of the mean aromatic plane of the phenyl group bonded to it. The bending of between ~0.11 and 0.31 Å observed can be considered significant as these phenyl groups have much greater degrees of freedom to rotate to a low energetic position compared with the acenaphthene backbone. All of the bonds around the central phosphorus atoms are sub-tetrahedral so the lone pairs on these atoms are having a distorting influence on the geometry observed.

In comparison, Nap[P(^{t}Bu)Ph]$_2$[176] has a small negative splay angles but a large out of plane distortion with both of the phosphorus centres lying around 0.90 Å from the mean bicyclical aromatic plane. This is also shown by the large amount of twisting seen in the acenaphthene ring with large torsion angles, which are between 9.9(1) and 11.2(1)° away from the relaxed ideal. The *peri*-distance of 3.0557(6) Å shows that there is a repulsive force between the two phosphorus atoms. The angles around the phosphorus atoms are much closer to the idealised tetrahedral angles. The ^{t}Bu groups on the phosphorus centres are more sterically demanding than the N(^{i}Pr)$_2$ groups and so the lone pairs are not as influential.

e. Synthesis of other double addition products

Owing to the successful synthesis of **40**, it was decided to examine the reactivity of di-lithiated 5,6-dibromoacenaphthene towards other alkyl/aryl(chloro)(dialkylamino)phosphines.

Two equivalents of the impure starting material MesP(Cl)NEt$_2$ **29** were added to a suspension of di-lithiated 5,6-dibromoacenaphthen in the presence of an excess of TMEDA. Upon remove of the insoluble salt and the solvent a brown residue remained. A ^{31}P NMR spectroscopic investigation of this revealed one major peak at δ_P 56.1, along with a number of unidentified peaks. Attempts were made to purify this via recrystallisation with a number of different solvent systems; however no pure product (Ace[P(Mes)NEt_2]$_2$ **41**) was ever isolated.

Furthermore, two equivalents of the impure aryl(chloro)(N,N-dialkyl)phosphinamine MesP(Cl)N^{i}Pr$_2$ **28** was reacted with di-lithiated 5,6-dibromoacenaphthene in the presence of an excess of TMEDA. At the completion of the reaction procedure, a red-brown solid persisted. Upon being analysed spectroscopically, it was discovered that this was a mixture of the phosphorus containing starting material (δ_P 126.7), a second unidentified peak (δ_P 27.2), along with a number of other, smaller peaks. We tried to isolate a pure sample of the desired product, Ace[P(Mes)N(^{i}Pr)$_2$]$_2$ **42** via recrystallisation but alas, none of the solvent combinations which were tested produced satisfactory results. Attempts to grow crystals by slow evaporation of a concentrated DCM solution of the product yielded a featureless amorphous solid.

Attempts were made to synthesis the di-*peri*-substituted Ace[P(^{t}Bu)N(Et)$_2$]$_2$ **43** from the di-lithiated 5,6-dibromoacenaphthene suspension with an excess of TMEDA and two equivalents of ^{t}BuP(Cl)N(Et)$_2$ **31**. On removal of the volatile and insoluble salts at the conclusion of the reaction, red-brown solid was obtained. A detailed ^{31}P NMR spectroscopic investigation of this residue revealed two major peaks, attributable to the alkyl(chloro)(dialkylamino)phosphine starting material (δ_P 161.2) and the single substitution products (δ_P 68.9), along with a number of unidentifiable peaks. This reaction was repeated a number of times but at no stage was the desired product **43** detected or isolated.

6. Further Chemistry of novel compounds Ace[P(Ph)N(^{i}Pr)$_2$]Br 35 and Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ 40

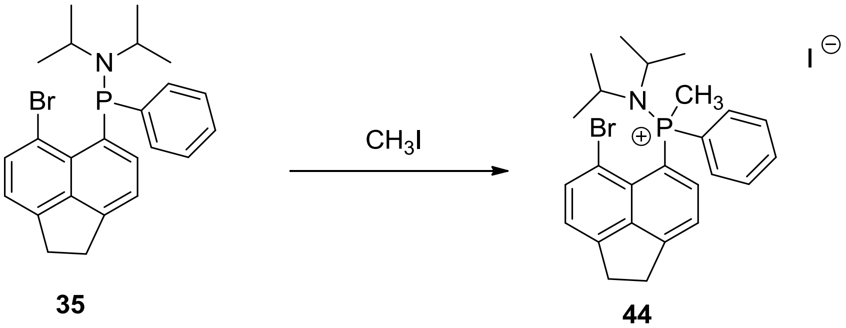
a. Introduction

Following on from our previous synthetic work, we decided to investigate the potential further chemistry of the recently made 5,6-disubstituted acenaphthene compounds Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40** and Ace[P(Ph)N(^{i}Pr)$_2$]Br **35**. Of particular interest was the degree of lability of the amino groups attached to the phosphorus centres. It has been documented before that amine groups are often used as protecting groups for phosphorus-chlorine bonds and that these placeholders are then removed facilely with an excess of HCl[121] or PCl_3[177] to regenerate the P-Cl bond. Of interest to us also would be the potential production of the bis-secondary phosphine Ace[P(Ph)H]$_2$ **48** from the reduction of **40** as it could be a useful synthon similar to our earlier work with $NapP_2H_4$ **19**, which we discussed previously.

b. Alkylation of Ace[P(Ph)N(^{i}Pr)$_2$]Br

The phosphorus centres have also retained their lone pairs which could be another potential route towards further reactivity. Their utilization would be a route to either a neutral P(V) compound or one or more positively charge phosphonium cations.

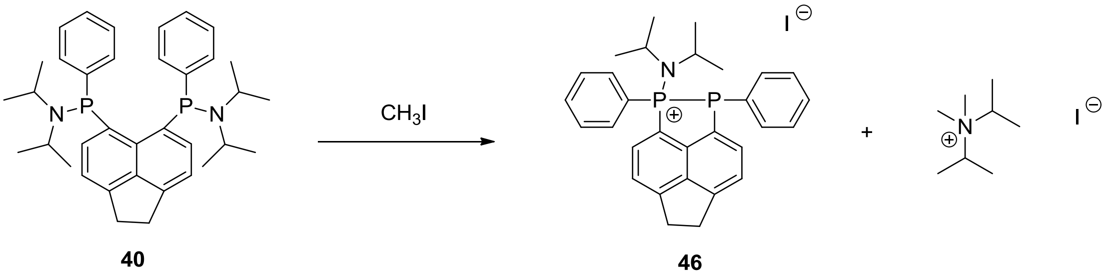
Upon reviewing the recent literature we found that the diphosphole structure Nap[PhP-PPh] has been reacted with two equivalents of methyltriflate to make a dicationic structure $(Nap[(CH_3)PhP\text{-}P(CH_3)Ph])^{2+}$ 2(OTf$^-$).[178] With this in mind we slowly added methyltriflate to a stirred toluene solution of **35** at -78 °C. Upon its return to room temperature, an aliquot of the reaction mixture was taken and analysed spectroscopically. This showed a proliferation of phosphorus containing compounds, none of which were identifiable. It was therefore deduced that a less forceful methylating reagent might be needed to achieve the desired mono-methylation. Consequently, an excess of methyliodide was added to a toluene solution of **35** (0.315 g) at -78 °C and this stirred mixture was then allowed to reach ambient temperature. The progress of this reaction was monitored via ^{31}P NMR spectroscopy which showed no change from the sole starting material peak (δ_P 35.4). However, over the course of a week, a white precipitate developed. This insoluble material was isolated by filtration and washed with fresh toluene. The filtrate was placed under reduced pressure and the solvent was removed. The residue was recrystallized in acetonitrile and it was confirmed to be exclusively starting material. Turning to the filtrand, a detailed spectroscopic study of this solid using ^{31}P, ^{1}H and ^{13}C NMR spectroscopy indicated that the desired product $\{Ace[P(Ph)N(^iPr)_2CH_3]Br\}^+ I^-$ **44** had been made but in incredible poor yield (~0.05 g), see Scheme 16. By the general standards of chemical synthesis this reaction was a failure as the amount of material produced was far below the expected value if this reaction was to be carried out stoichiometrically. Attempts were made to purify a sample by recrystallisation, however the ion nature of this compound made it insoluble in most standard laboratory solvents such as n-hexane, acetonitrile, THF and ether. No pure product was isolated.



Scheme 16 Methalation of $Ace[P(Ph)N(^iPr)_2]Br$ **35**

c. Alkylation of Ace[P(Ph)N(^{i}Pr)$_2$]$_2$

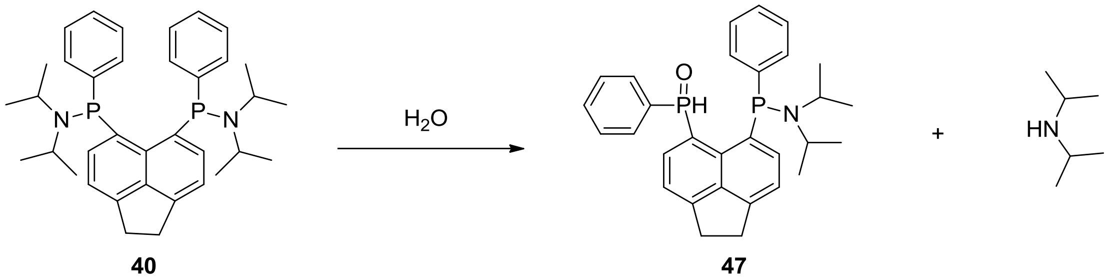
Following on from this, we decided to shift the focus of our synthetic work to **40**. A portion of **40** was dissolved in toluene and cooled to -78 °C; where upon an excess of methyliodide was added. After being allowed to rise to room temperature, this mixture was stirred for one week during which time the precipitation of a white solid occurred. This suspension was filtered and the solid was washed with fresh toluene. A comprehensive spectroscopic inquisition revealed that the recovered solid was not the desired bisphosphonium product [Ace{P(Ph)N(^{i}Pr)$_2$CH$_3$}$_2$]$^{2+}$ 2I$^-$ **45** but a one to one mixture of dimethyldiisopropylammonium iodide[179] [(CH$_3$)$_2$N(^{i}Pr)$_2$]$^+$ I$^-$ and a phosphine-phosphonium ring structure [Ace{P(Ph)N(^{i}Pr)$_2$}{P(Ph)}]$^+$ I$^-$ **46**, see Scheme 17. Attempts were made to isolate **46** as a pure crystalline material but it proved too difficult to separate it from its ionic co-product ^{i}Pr$_2$Me$_2$N$^+$I$^-$. Our efforts were encumbered by its lack of solubility in most common solvents.



Scheme 17 Methalation of Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40**

Evidently, one of the amino groups has been cleaved off a phosphorus centre to form the ammonium salt. This was a source of huge disappointment for us as the area of *peri*-positioned diphosphonium cations has been under-explored and might show interesting bonding motifs.

The filtrate which was recovered from this reaction was also examined and to our surprise a new product Ace(P(Ph)N(^{i}Pr)$_2$)(P(O)PhH) **47** had been formed. We postulated that this was the result of hydrolysis of the starting material **40**, see Scheme 18. We decided to repeat the reaction under even stricter water exclusion conditions, under an atmosphere of gaseous nitrogen and yet this phosphinamine-phosphine oxide **47** was recovered repeatedly, see Scheme 18. This is still the source of much bafflement to us. The solid was washed with mixture of hot 1,2-dichloroethane and hexane. Attempts were made to grow crystals suitable for single crystal X-ray diffraction via the slow evaporation of a concentrated DCM solution; however nothing deemed suit for crystallographic analysis was ever recovered. **47** has a large ($^1J_{HP}$ = 536.6) coupling constant between a phosphorus atom and the directly bonded hydrogen which is indicative of a P(V) compound. There are other examples in the literature of the peri-substitution of two phosphorus centres onto a naphthalene structures where one of the phosphorus centres is a P(V) centre and the other is a P(III) centre such as (8-(diphenylphosphino)naphthalen-1-yl)diphenylphosphine oxide[180] [Nap(PPh$_2$)(P(O)Ph$_2$)] and (8-(diphenylphosphino)naphthalen-1-yl)diphenylphosphine selenide[181] [Nap(PPh$_2$)(P(Se)Ph$_2$)]. Interesting [Nap(PPh$_2$)(P(Se)Ph$_2$)] has a P-P coupling constant of only 53 Hz while the coupling between the phosphorus centres in **47** is much larger ($^4J_{PP}$ = ~161 Hz). This shows the profound influence that the oxygen atom has on the phosphorus electronic configuration by drawing electron density away from the phosphorus atomic centre.

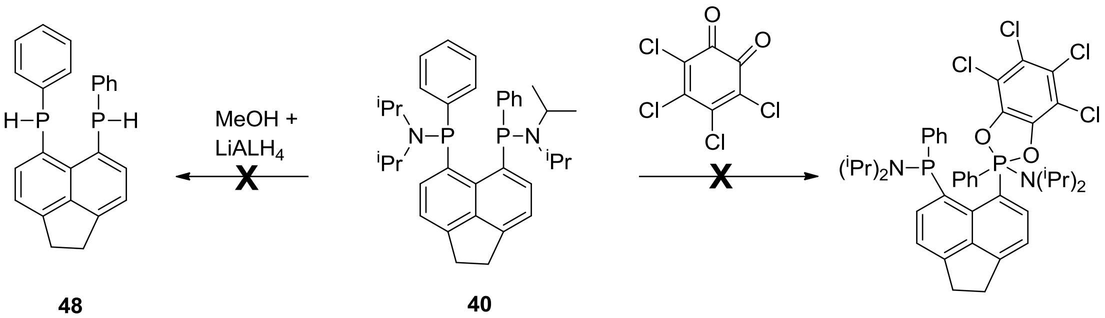


Scheme 18 Hydrolysis of Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40**

d. Reduction of Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ and its reaction with 1,2-dione

With our knowledge that the amino groups can be labile, we decided to test if diarylaminophosphines could be reduced to secondary phosphines directly. To this end we tried to reduce **40** to Ace[P(Ph)H]$_2$ **48** by boiling a 1,4-dioxane solution of it under reflux in the presence of an excess of lithium aluminium hydride and trimethylsilyl chloride for 5 hours. These were the same harsh conditions which were mentioned in Chapter 2 to reduce Mes*P(O)Cl **3** to (2,4-tBu$_2$C$_6$H$_3$)(Mes*)PH **10**. After being allow to cool to room temperature an aliquot of the reaction mixture was taken and examined using ^{31}P NMR spectroscopy. This revealed that only the starting material was present (δ_P 29.7). It perhaps should not have come as a huge surprise to us that this reaction did not proceed, as we wished as a cursory glance at the literature reveals that this kind of transformation is mentioned only once[182] and in a rather different set of circumstances. This suggests that the reduction of **40** must be achieved via a different route. We must find a way of substituting the amino group for something more amenable to be then removed with a reducing agent.

With this in mind, we looked at the potential for alcoholysis of the phosphine-amine bond. It is well established in the chemical literature[183,184] that alcohols can break amino bonds, especially in mildly acidic conditions. Dry methanol was added to **40** along with a single drop of triflic acid and this stirred suspension was heated under reflux for 4 hours. Over the course of this time, the mixture homogenised to a yellowish solution. An aliquot of the reaction mixture was examined spectroscopically and the results were encouraging with a major peak at δ_P 94.1 as well as some **47**, which manifests as two ^{31}P spectral shifts with a characteristic splitting pattern. This mixture was subjected to high vacuum to remove the MeOH. THF was added and then removed under reduced pressure. This process was repeated two more times to remove any trace of stray methanol from the solid residue. Finally, the solid was then dissolved in THF. This was added to an excess of powdered $LiAlH_4$ which had been cooled in ice. The stirred suspension was then heated under reflux for five hours. Upon cooling, an aliquot of the reaction mixture was removed and investigated by via ^{31}P NMR spectroscopy. This revealed a cacophony of different peaks, none of which were identifiable, see Scheme 19.



Scheme 19 The reduction of **40** and its reaction with 3,4,5,6-Tetrachloro-1,2-benzoquinone

It has also been shown that P(III) structures can be combined with cyclohexa-3,5-diene-1,2-dione ones to form new P(V) ring structures. The driving forces behind these transformations are the formation of new aromatic rings and the strong phosphorus-oxygen bonds[6] which are formed. 3,4,5,6-Tetrachloro-1,2-benzoquinone is used specifically because the chlorine centres draw electron density out of the ring to promote this impulse towards aromaticity. This has been combined with triphenylphosphine to make triphenylphosphine tetrachlorochatecholate[185] [$(Ph)_3PO_2C_6Cl_4$]. It was is this regard that a portion of **40** was dissolved in DCM and cooled to -78 °C and a DCM solution of one equivalents of 3,4,5,6-tetrachloro-1,2-benzoquinone was added. Upon its return to room temperature, a sample of the reaction mixture was taken and analysed by a ^{31}P NMR spectroscopic inquisition. It was revealed that a large number of phosphorus containing products had been produced. None of the peaks observed were attributable to any particular compound and certainly not **49**, see Scheme 19.

7. Experimental

General notes

All experiments were carried out in standard Schlenk glassware or in a glove box with strict exclusion of air and moisture, using either a nitrogen or argon atmosphere. Solvents were dried on an MBraun solvent purification system. The new compounds were fully characterized by $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, including measurement of $^1H\{^{31}P\}$, ^{31}P (^1H coupled), H–H DQF COSY, H–P HSQC and H–C HSQC experiments. Measurements were performed at 25 °C unless said otherwise; 85% H_3PO_4 was used as external standard in ^{31}P. ^1H and ^{13}C NMR spectroscopic shifts are relative to TMS, which was used as internal standard, or residual solvent peaks were used for calibration ($CHCl_3$ δ_H 7.26, δ_C 77.2 ppm). *J* values are given in Hz.

5,6-Dibromoacenaphthene. A stirred dimethylformamide (250 ml) suspension of 1,2-dihydroacenaphthylene (200 g, 1.297 mol) was cooled in ice and stirred vigorously. Separately, an *N*-bromosuccinimide (500 g, 2.81 mol) suspension in DMF (1000 ml) was place in a dropping funnel. The NBS suspension was added to the acenaphthene one over 5 hours with the low temperature maintained. This was stirred and allowed to rise to room temperature overnight. The yellow solid was filtered off and washed with 3 x 100 ml of ethanol. A suspension of the solid material was then heated under reflux in ethanol (500 ml) for 6 hours. The solid was filtered off and then suspended in fresh ethanol (500 ml) which was heated under reflux for a further 6 hours. The solid was recovered, fresh ethanol added and the suspension was heated under reflux for a third time. Finally, the insoluble material was isolated by filtration and washed with yet more ethanol (3 x 100 ml) to reveal a white/grey powder. This product was dried first by suction and then under high vacuum. Yield: 97.067 g, 24%. δ_H (270.2 MHz; $CDCl_3$) 7.77 (2H, d, $^3J_{HH}$ = 7.4, H4/7), 7.07 (2H, d, $^3J_{HH}$ = 7.4, H3/8), 3.28 (4H, s, H11 & H12)

$Cl_2PN(Et)_2$ 24. A mixture of phosphorus trichloride (40 ml, 458.5 mmol) and diethyl ether (500 ml) was stirred vigorously and cooled to 0 °C. Diethylamine (95 ml, 922.2 mmol) was added over 4 hours maintaining the low temperature. On completion of the addition, the mixture was stirred and allowed to rise to room temperature gradually overnight. The solid by-product $Et_2NH{\bullet}HCl$ was filtered off and washed through with fresh Et_2O (2 x 100 ml). The solvent was then removed *in vacuo* to give a clear liquid. This was distilled under reduced pressure to obtain **24** as a clear oil. Yield: 61.24 g, 76%. δ_H (400.1 MHz; $CDCl_3$) 3.27 (4H, dquart, $^3J_{PH}$ = 13.1, $^3J_{HH}$ = 7.2, 2 x $PNC\underline{H}_2CH_3$), 1.12 (6H, t, $^3J_{HH}$ = 7.2, 2 x $PNCH_2C\underline{H}_3$); δ_C (67.9 MHz, $CDCl_3$) 41.7 (d, $^2J_{PC}$ = 22.8 Hz, 2 x $PN\underline{C}H_2$), 14.2 (d, $^3J_{PC}$ = 4.2 Hz, 2 x $PNCH_2\underline{C}H_3$); $\delta_{P\{^1H\}}$ (197.9 MHz, $CDCl_3$) 162.3 (s);

$((CH_3)_2CH)_2NPCl_2$ 25. Same procedure as above with PCl_3 (30 ml, 343.8 mmol) and diisopropylamine (97.5 ml, 690 mmol) to obtain **25**. Yield: 52.89 g, 76% ; δ_H (300.1 MHz; $CDCl_3$) 3.86 (2H, m, 2 x $PNC\underline{H}$), 1.21 (12H, d, $^3J_{HH}$ = 6.8, 2 x $PNCH(C\underline{H}_3)_2$), δ_C (75.5 MHz, $CDCl_3$) 48.6 (d, $^2J_{PC}$ = 14.0, 2 x $PN\underline{C}H$), 23.8 (d, $^3J_{PC}$ = 8.3, 2 x $PNCH(\underline{C}H_3)_2$), $\delta_{P\{^1H\}}$ (121.5 MHz, $CDCl_3$) 169.4 (s);

$^tBuPCl_2$. A hexane (40 ml) solution of phosphorus trichloride (0.5 ml, 5.7 mmol) was cooled to -78 °C. A solution of *t*-butyllithium (3.0 ml of 1.9M solution in pentane, 5.7

mmol) was added dropwise. This was stirred for one hour at -78 °C and then allowed to rise to room temperature. A $^{31}P\{^{1}H\}$ NMR spectroscopic investigation showed that the starting material (δ_P 221.7) was the majority product. It also revealed that the desired product (δ_P 199.2)[186] and the result of double addition ($(^tBu)_2PCl$ (δ_P 145.7)[187] were also made.

^{t}BuPCl$_2$. An ethereal (40 ml) suspension of magnesium powder (0.54 g, 22.4 mmol) was cooled to 0 °C. The initiator 1,2-dibromoethane (0.1 ml, 1.2 mmol) was added dropwise and the suspension was then stirred for 10 minutes. 2-chloro-2-methylpropane (2.2 ml, 20 mmol) was added over 2 hours with the low temperature retained. On completion of the addition, the suspension was allowed to rise to room temperature and finally refluxed gently for 30 minutes. It was then cooled in ice again. Separately, a solution of phosphorus trichloride (1.8 ml, 20.28 mmol) in Et_2O was cooled to -78 °C. The Grignard reagent was added to this over 90 minutes. Upon completion of addition, the stirred mixture was allowed to rise to room. A sample of the reaction mixture was taken and subjected to a $^{31}P\{^{1}H\}$ NMR spectroscopic investigation. This showed the major product to be the starting material (δ_P 221.7) with some other ^{31}P peaks also presents.

^{i}PrPCl$_2$. The reaction was performed as above with 2-iodopropane (2 ml, 20 mmol). An aliquot of the reaction mixture reveal a number of ^{31}P compounds including the starting material (δ_P 220.9) and the desired product (δ_P 199.7)[186] along with other unidentified products. Attempts at isolation failed.

^{t}BuP(Cl)N(^{i}Pr)$_2$ 30. A suspension of magnesium powder (0.55 g, 22.6 mmol) in Et_2O (30 ml) was cooled in ice. The initiator 1,2-dibromoethane (0.1 ml, 1.2 mmol) was added and the mixture was stirred for 10 minutes. 2-chloro-2-methylpropane (2.2 ml, 20 mmol) was added over two hour maintaining the temperature at 0 °C. Upon completion of addition, the reaction mixture was allowed to slowly rise to room temperature and finally it was heated under reflux for one hour to drive the preparation of the Grignard reagent to completion. This solution was then cooled again in ice. Separately, an ethereal (80 ml) solution of 1,1-dichloro-N,N-diisopropylphosphinamine (3.1 g, 20 mmol) was cooled to -78 °C. The Grignard reagent was added to this dropwise. Upon completion of addition, the stirred mixture was allowed to equilibrate to room temperature slowly. A $^{31}P\{^1H\}$ NMR spectroscopic investigation showed that the starting material peak (δ_P 169.4) was the majority product.

^{i}PrP(Cl)N(^{i}Pr)$_2$ 32. Same procedure as above with 2-iodopropane (2 ml, 20 mmol). The result of a $^{31}P\{^1H\}$ NMR spectroscopic investigation of the mother liquor showed a complex mixture of phosphorus containing products, none of which were identifiable.

^{t}BuP(Cl)N(^{i}Pr)$_2$ 30. A hexane (35 ml) solution of 1,1-dichloro-N,N-diisopropylphosphinamine (0.8 ml, 5.1 mmol) was cooled to -78 °C. A solution of *t*-butyllithium (2.7 ml of 1.9M solution in pentane, 5.1 mmol) was added dropwise. It was allowed to remain at that temperature for one hour before slowly rising to room temperature. An aliquot was taken and analysed via $^{31}P\{^1H\}$ NMR spectroscopy which showed a cacophony of peaks none of which were identifiable.

^{t}BuP(Cl)N(Et)$_2$ 31. A solution of *tert*-butyldichlorophosphine (2.25 g, 14.15 mmol) in Et_2O (30 ml) was cool to 0°C and stirred vigorously. Diethylamine (3 ml, 28.7 mmol) was added over 2 hours maintaining the low temperature. On completion of addition, the mixture was stirred and allowed to rise to room temperature gradually overnight. The by-product $Et_2NH•HCl$ was filtered off and the retentate was washed through with additional Et_2O (2 x 10 ml). The solvent was then removed *in vacuo* to reveal a clear liquid. This was distilled under reduced pressure to obtain **31** as a liquid. Yield: 2.3 g, 83%; δ_H (300.1 MHz; $CDCl_3$) 3.06 (4H, m, 2 x $PNC\underline{H}_2$), 1.09 (9H, d, $^3J_{PH}$ = 14.6, $PC(C\underline{H}_3)_3$), 1.05 (6H, t, $^3J_{HH}$ = 7.1, 2 x $PNCH_2C\underline{H}_3$); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 160.4 (s);

^{t}BuP(Cl)N(^{i}Pr)$_2$ 30. Same procedure as above with *tert*-butyldichlorophosphine (1.78 g, 11.16 mmol) and diisopropylamine (3.2 ml, 22.64 mmol). An aliquot of the mother liquor indicated that no reaction had taken place as the starting material (δ_P 199.1) was the only peak in $^{31}P\{^1H\}$ NMR spectroscopy.

^{t}BuP(Cl)N(^{i}Pr)$_2$ 30. An ethereal (30 ml) solution of *tert*-butyldichlorophosphine (1.55 g, 9.74 mmol) was cooled in ice. A solution of lithium diisopropylamide (5.0 ml of 2.0M solution in THF/*n*-heptanes/ethylbenzene, 10 mmol) was added over one hour. This was stirred and allowed to warm to room temperature. An aliquot of the mother liquor was evaluated via $^{31}P\{^1H\}$ NMR spectroscopy. It was found to contain a range of ^{31}P containing species, none of which were identifiable.

$PhCH_2P(Cl)NEt_2$ 33. A stirred suspension of magnesium turnings (1.0 g, 41.15 mmol) in diethyl ether (75 ml) was cooled in ice. The initiator 1,2-dibromoethane (0.2 ml, 2.3 mmol) was added dropwise and this was stirred for 10 minutes. Benzyl chloride (4.7 ml, 40.8 mmol) was added over an hour with the low temperature maintained. It was then allowed to rise to room temperature and subsequently heated under reflux gently over 1 hour. It was then cooled in ice. Independently, an ethereal (180 ml) solution of 1,1-dichloro-N,N-diethylphosphinamine (6 ml, 40.3 mmol) was cooled to -78 °C. The Grignard reagent was added to this over 1 hour. Upon completion of addition, the stirred mixture was allowed to equilibrate to room temperature slowly. An aliquot was taken and analysed via $^{31}P\{^1H\}$ NMR spectroscopy which showed a 1:1 mixture of starting material (δ_P 162.9) and the presumed product **33** (δ_P 145.6). The volatiles were then removed *in vacuo* to reveal a yellowish liquid. Attempted were made to separate this crude liquor via distilled under reduced pressure. A pure sample of the product was not obtained.

$PhP(Cl)N(Et)_2$ 27. A solution of dichloro(phenyl)phosphine (14 ml, 103.2 mmol) in diethyl ether (250 ml) was cooled in ice with vigorous stirring. Diethylamine (21.6 ml, 206.7 mmol) was added dropwise for 2 hours with the temperature maintained at 0 °C. When the addition was complete the stirred suspension was allowed to reach room temperature overnight. The solid $Et_2NH•HCl$ was filtered off and the insoluble salt was washed with fresh Et_2O (2 x 75 ml). The volatiles were then removed *in vacuo* to give a slightly yellowish liquid. This was distilled under reduced pressure to obtain **27** as a clear liquid. Yield: 19.9 g, 89%; δ_H (300.1 MHz; $CDCl_3$) 7.80 (2H, m, *o*-ArH), 7.48 (3H, m, *m*-ArH and *p*-ArH), 3.18 (4H, m, 2 x $PNC\underline{H}_2$), 1.16 (6H, t, $^3J_{HH}$ = 7.2, 2 x $PNCH_2C\underline{H}_3$); δ_C (75.5 MHz, $CDCl_3$) 140.0 (d, $^1J_{PC}$ = 29.2 Hz, ipso-C), 131.1 (d, $^2J_{PC}$ = 20.3 Hz, *o*-C), 130.1 (s, *p*-C), 128.8 (d, $^3J_{PC}$ = 4.1 Hz, *m*-C), 44.3 (d, $^2J_{PC}$ = 12.8 Hz, 2 x PN$\underline{C}$H$_2$), 14.6 (d, $^3J_{PC}$ = 6.0 Hz, 2 x PNCH$_2\underline{C}$H$_3$); $\delta_{P\{1H\}}$ (121.5 MHz, CDCl$_3$) 142.2 (s);

PhP(Cl)N(^{i}Pr)$_2$ 26. Same procedure as above with dichloro(phenyl)phosphine (21 ml, 154.9 mmol) and diisopropylamine (44 ml, 311.34 mmol) to produce **26**. Yield: 31.02 g, 82%; δ_H (300.1 MHz; CDCl$_3$) 7.79 (2H, m, *o*-ArH), 7.46 (3H, m, *m*-ArH and *p*-ArH), 3.53 (2H, m, 2 x PNC$\underline{H}$), 1.34 (12H, d, $^3J_{HH}$ = 6.9, 2 x PNCHC$\underline{H}_3$); δ_C (75.5 MHz, CDCl$_3$) 140.0 (d, $^1J_{PC}$ = 28.1 Hz, ipso-C), 131.1 (d, $^2J_{PC}$ = 20.4 Hz, *o*-C), 129.7 (d, $^4J_{PC}$ = 1.2 Hz, *p*-C), 128.8 (d, $^3J_{PC}$ = 3.8 Hz, *m*-C), 48.6 (d, $^2J_{PC}$ = 13.9 Hz, 2 x PN$\underline{C}$H), 23.9 (d, $^3J_{PC}$ = 8.3 Hz, 2 x PNCH$\underline{C}$H$_3$); $\delta_{P\{1H\}}$ (121.5 MHz, CDCl$_3$) 132.8 (s);

Mes*P(N(CH$_3$)$_2$)$_2$ 34. A THF (30 ml) solution of 2-bromo-1,3,5-tri-*tert*-butylbenzene (2.33 g, 7.15 mmol) was cooled to -78 °C. A hexane solution of n-butyllithium (2.9 ml of 2.5M solution, 7.25 mmol) was added over 30 minutes and stirred for a further 30 minutes. Phosphorus trichloride (1 ml, 11.5 mmol) was added dropwise. On completion of this addition, the solution was allowed to rise to room temperature and finally heated under reflux for 20 minutes. Upon cooling to room temperature, an aliquot was subjected to ^{31}P NMR spectroscopy which confirmed the complete conversion to dichloro(2,4,6-tri-tert-butylphenyl)phosphine (δ_P 153.1). The insoluble salts were filtered off and then washed with fresh THF (2 x 10 ml). The solvent and excess PCl$_3$ were removed *in vacuo* to yield an off-white solid which was crude Mes*PCl$_2$. This was used without further purification.

A portion of the solid (0.398 g) was taken up in Et$_2$O (15 ml) and cooled in ice. Approximately 1 ml of dimethylamine (0.67 g, 14.8 mmol) was added via cannula. It was stirred for a further hour at 0 °C before being allowed to return to room temperature. The insoluble salts were filtered off and the retentate was washed through with additional Et_2O (2 x 10 ml). The filtrate was placed under reduced pressure and the volatiles were removed to leave a solid material, some of which was suitable for X-ray crystallographic analysis (**34**). No further purification was performed. δ_H (270.2 MHz; $CDCl_3$) 7.08 (2H, d, $^4J_{PH}$ = 3.31, ArH), 2.36 (12H, d, $^3J_{PH}$ = 9.92, 2 x $PN(C\underline{H}_3)_2$), 1.26 (9H, s, *p*-*t*Bu), 1.24 (18H, s, *o*-*t*Bu); $\delta_{P\{1H\}}$ (109.4 MHz, $CDCl_3$) 110.1 (s);

Mes*P(NEt$_2$)$_2$. A solution of impure Mes*PCl_2 (0.75 g) in Et_2O (30 ml) was cooled in ice. Diethylamine (0.45 ml, 4.3 mmol) was added over 2 hours maintaining the low temperature. On completion of addition, the mixture was stirred and allowed to rise to room temperature gradually overnight. The solid by-product $Et_2NH\bullet HCl$ was filtered off and washed through with fresh Et_2O (2 x 10 ml). The volatiles were removed under reduced pressure to yield a solid. When this was evaluated via $^{31}P\{^1H\}$ NMR spectroscopy it was found to contain mostly starting material (δ_P 153.5), along with some other unidentified ^{31}P containing products.

MesP(Cl)N(^{i}Pr)$_2$ 28. An ether (40 ml) solution of 2-bromo-1,3,5-trimethylbenzene (3 ml, 19.6 mmol) was cooled to -78 °C. A hexane solution of n-butyllithium (8 ml of 2.5M solution, 20 mmol) was added over 20 minutes with constant stirring. The mixture was maintained at -78 °C for one hour. Separately, an ethereal solution (80 ml) of 1,1-dichloro-N,N-diisopropylphosphinamine (4.04 g, 20 mmol) was cooled to -78 °C. The lithiated mesitylene solution was added dropwise via cannula to this. Upon the completion of addition the reaction mixture was allowed to rise to room temperature slowly. The insoluble material was filtered off and washed with fresh Et_2O (2 x 20 ml). The solvent was then removed *in vacuo* to afford a white solid. “Yield” 1.82 g, 65%. Crystals were grown by slow evaporation of concentrated solution in dichloromethane to product an X-ray quality sample of **28**. Attempts were made to purify a sample in pentane, however these were not successful. δ_P (109.4 MHz, $CDCl_3$) 128.7 (s);

MesP(Cl)N(Et)$_2$ 29. Procedure the same as above with bromomesitylene (3.1 ml, 20.24 mmol) and 1,1-dichloro-N,N-diethylphosphinamine (3.51 g, 20.17 mmol). A yellowish oil was obtained. This was distilled under reduced pressure to yield a clear liquid that was mostly **29**. Not pure. δ_H (270.2 MHz; $CDCl_3$) 6.87 (2H, s, ArH), 3.15 (4H, m, 2 x $PNC\underline{H}_2CH_3$), 2.35 (6H, s, 2 x *o*-CH_3), 2.22 (3H, s, *p*-CH_3), 1.13 (6H, t, $^3J_{HH}$ = 7.16, 2 x $PNCH_2C\underline{H}_3$); δ_P (109.4 MHz, $CDCl_3$) 154.6 (s)

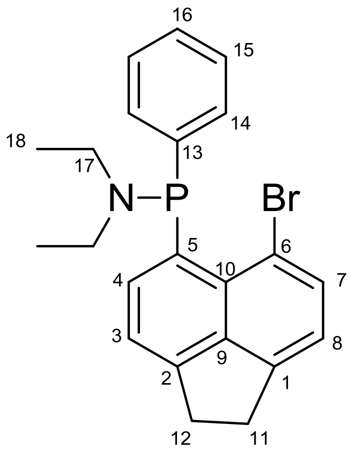


Figure 61 NMR spectroscopy numbering scheme for **36**

Ace[P(Ph)N(Et)$_2$]Br 36. A stirred suspension of 5,6-dibromoacenaphthene (3.1 g, 10 mmol) in diethyl ether (80 ml) was cooled to -78 °C. A hexane solution of n-butyllithium (4 ml of 2.5M solution, 10 mmol) was added over 20 minutes. This was then allowed to rise to 0 °C and maintain at this temperature for one hour before being cooled again to -78 °C. Separately, fresh Et_2O (15 ml) was added to chlorodiethylamino(phenyl)phosphine **27** (2.2 g, 10.2 mmol) and this solution was added to the monolithiated acenaphthene suspension over one hour with the temperature kept at -78 °C. It was allowed to stir and return to ambient temperature overnight. The solid by-product LiCl was filtered off and the insoluble salt was washed with fresh Et_2O (2 x 20 ml). The solvent was then removed *in vacuo* to give a redy-brown solid. Repeated washing in hot hexane furnished the desired product **36** as a pale yellow solid. Yield: 1.46 g, 35%; m.p. 183-186 °C; (Found: C, 64.14; H, 5.63; N, 3.30. Calc. for $C_{22}H_{24}PNBr$: C, 64.09; H, 5.62; N, 3.40) IR (KBr disk): υ_{max}/cm^{-1} 3046vs (υ_{CH}), 2963vs (υ_{CH}), 2927vs (υ_{CH}), 2855vs (υ_{CH}), 1599s, 1433s, 1373s, 1179s, 1019s, 919s, 697s; Raman (powder in glass capillary): 3076vs (υ_{CH}), 3047vs (υ_{CH}), 2929vs (υ_{CH}), 1563s, 1445s, 1318s, 1000s, 815m, 709m, 580s; δ_H (300.1 MHz; $CDCl_3$) 7.80 (1H, dd, $^3J_{HH}$ = 7.28 $^3J_{PH}$ = 4.43, H4), 7.63 (1H, d, $^3J_{HH}$ = 7.37, H7), 7.37

(1H, d, $^3J_{HH}$ = 7.28, H3), 7.29-7.26 (5H, Range, H14, H15 & H16), 7.10 (1H, d, $^3J_{HH}$ = 7.36, H8), 3.41 (2H, broadened s, H11 or H12), 3.38 (2H, broadened s, H11 or H12), 3.18 (4H, m, H17), 0.98 (6H, t, $^3J_{HH}$ = 7.0, H18); δ_C (75.5 MHz, $CDCl_3$) 148.0 (br s, C5), 146.8 (d, $^3J_{PC}$ = 1.6 Hz, C6), 143.2 (d, $^1J_{PC}$ = 7.8 Hz, C13), 142.2 (s, C2), 134.8 (s, C1), 134.5 (d, $^2J_{PC}$ = 5.4 Hz, C4), 134.3 (s, C7), 133.6 (d, $^2J_{PC}$ = 13.4 Hz, C10), 132.4 (d, $^2J_{PC}$ = 19.7 Hz, C14), 128.4 (s, C16), 128.3 (d, $^3J_{PC}$ = 4.4 Hz, C15), 120.8 (s, C8), 120.3 (s, C3), 116.3 (d, $^3J_{PC}$ = 1.9 Hz, C9), 45.3 (d, $^2J_{PC}$ = 17.6 Hz, C17), 30.5 (s, C11 or C12), 30.4 (s, C11 or C12), 15.0 (d, $^3J_{PC}$ = 2.4 Hz, H18); δ_P (121.5 MHz, $CDCl_3$) 58.6 (s); MS (ES+) *m/z* 412 (M+H$^+$); MS (exact mass, ES+) 412.0830 (M+H$^+$), $C_{22}H_{24}PN^{79}Br$ requires 412.0830;

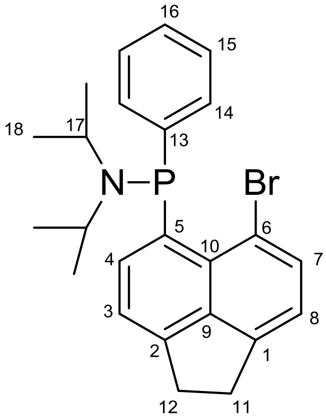


Figure 62 NMR spectroscopy numbering scheme for **35**

Ace[P(Ph)N(^{i}Pr)$_2$]Br 35. A stirred suspension of 5,6-dibromoacenaphthene (3.1 g, 10 mmol) in diethyl ether (100 ml) was cooled to -78 °C. A hexane solution of n-butyllithium (4 ml of 2.5M solution, 10 mmol) was added over 30 minutes. This was then allowed to rise to 0 °C and maintain at this temperature for one hour before being cooled to -78 °C again. A solution of **26** (2.43 g, 10 mmol) in Et_2O (15 ml) was then added to the (6-bromo-1,2-dihydroacenaphthylen-5-yl)lithium suspension over one hour with the temperature maintained at -78 °C. The coolant was removed and the suspension was allowed to rise to room temperature overnight with constant stirring. The solid by-product LiCl was filtered off and the insoluble salt was washed with fresh Et_2O (2 x 20 ml). The solvent was then removed *in vacuo* leave a yellowy solid. This was recrystallized in acetonitrile to give the desired product **35** as yellow/orange crystals. Yield: 1.45g 33%; mp 185-187 ºC; (Found: C, 65.55; H, 6.13; N, 3.22; Calc. for $C_{24}H_{27}PNBr$: C, 65.46; H, 6.18; N, 3.18); IR (KBr disk) υ_{max}/cm^{-1} 3045vs (υ_{CH}), 2967vs (υ_{CH}), 1652m, 1598s, 1359s, 1253m, 1175s, 1017s, 961m, 845s, 738s 695s, 512m; Raman (powder in glass capillary): 3046s (υ_{CH}), 2929vs (υ_{CH}), 1563s, 1442m, 1332s, 1001m, 816m, 579s; δ_H (300.1 MHz; $CDCl_3$) 8.16 (1H, dd, $^3J_{HH}$ = 7.25 $^3J_{PH}$ = 4.77, H4), 7.56 (1H, d, $^3J_{HH}$ = 7.36, H7), 7.43 (1H, d, $^3J_{HH}$ = 7.28, H3), 7.31-7.18 (5H, Range, H14, H15 & H16), 7.07 (d, $^3J_{HH}$ = 7.34, H8), 3.47-3.31 (6H, Range, H11, H12 & H17), 1.36 (6H, d, $^3J_{HH}$ = 6.64, H18), 1.03 (6H, br s, H18); δ_C (75.5 MHz, $CDCl_3$) 147.5 (d, $^1J_{PC}$ = 1.1 Hz, C5), 146.7 (d, $^3J_{PC}$ = 16.6 Hz, C6), 143.1, (d, $^1J_{PC}$ = 7.7 Hz, C13), 142.3 (broadened s, C1 & C2), 134.5 (d, $^2J_{PC}$ = 6.9 Hz, C4), ~134.4 (C_q overshadowed by other peaks, C10) 134.2 (s, C7), 133.5 (d, $^2J_{PC}$ = 20.6 Hz, C14), 128.3 (s, C16), 128.2 (d, $^3J_{PC}$ = 2.7 Hz, C15), 120.7 (s, C8), 119.9 (s, C3), 116.5 (d, $^3J_{PC}$ = 2.5 Hz, C9), 48.0 (d, $^2J_{PC}$ = 5.1, C17), 30.4 (s, C11 & C12), 24.6 (d, $^3J_{PC}$ = 5.4 Hz, C18), 24.1 (d, $^3J_{PC}$ = 5.3 Hz, C18); δ_P (121.5 MHz, $CDCl_3$) 35.3 (s); MS (ES+) *m/z* 378.24 ($M+O+H^+$-Br), 400.23 ($M+O+Na^+$-Br), 440.15 ($M+H^+$), 456.17 ($M+O+H^+$), 462.15 ($M+Na^+$), 478.15 ($M+O+Na^+$), 494.15 ($M+O+K^+$), 935.33 ($(M+O)_2+Na^+$)

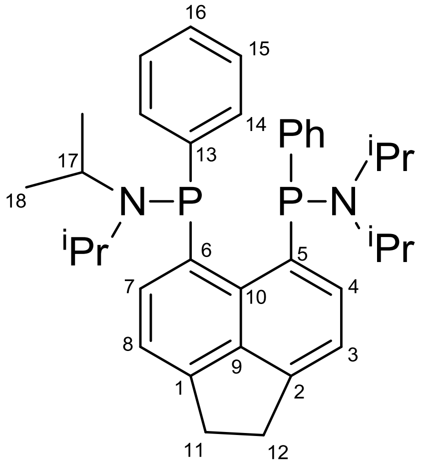


Figure 63 NMR spectroscopy numbering scheme for **40**

Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ 40. To an ethereal (120 ml) suspension of 5,6-dibromoacenaphthene (7.61 g, 24.38 mmol) was added N,N,N′,N′-Tetramethylethane-1,2-diamine (8 ml, 53.7 mmol) with constant stirring. This mixture was cooled to -78 °C and a hexane solution of n-butyllithium (20 ml of 2.5M solution, 50 mmol) was added over 20 minutes. The flask was allowed to rise to 0 °C and stirred at that temperature for 2 hours. During this time the appearance of the reaction mixture changed from a suspension of a light grey solid to a blood red solution. It was then cooled to -78 °C again. An Et_2O (40 ml) solution of **26** (11.45 g, 48.78 mmol) was added to the stabilized dilithiated acenaphthene over 1 hour. This was allowed to stir and rise to room temperature overnight. The solid by-product LiCl was filtered off and the retentate was washed with fresh Et_2O (2 x 20 ml). The volatiles were removed *in vacuo* to reveal a redy-brown solid. Repeated recrystallisation in first boiling hexane and then acetonitrile rendered light yellow microcryatals of **40** in moderate yield (4.6 g, 33%); mp 156-162ºC; (Found: C, 75.98; H, 8.07; N, 4.97; Calc. for $C_{36}H_{46}P_2N_2$: C, 76.03; H, 8.15; N, 4.93); IR (KBr disk) υ_{max}/cm^{-1} 3052vs (υ_{CH}), 2967vs (υ_{CH}), 2815vs (υ_{CH}), 1501m, 1586m, 1432m, 1382m, 1175m, 1014s, 958m, 845s, 739s; Raman (powder in glass capillary): 3054vs (υ_{CH}), 2966vs (υ_{CH}), 2925vs (υ_{CH}), 1588s, 1446s, 1323s, 1030s, 1001s, 821m, 711m, 585m; δ_H (300.1 MHz; CDCl$_3$) 7.72 (1H, d of pseudo-t, $^3J_{HH}$ = 7.15 $^3J_{PH}$ = 1.98, H4 & H7), 7.17 (2H, d, $^3J_{HH}$ = 7.15, H3 & H8), 6.92-6.80 (6H, Range, H14, H16), 6.70-6.65 (4H, Range, H15) 3.32 (4H, s, H11 & H12), 3.16 (4H, m, H17), 0.98 (12H, br s, H18), 0.88 (12H, d, $^3J_{HH}$ = 5.4, H18); δ_C (75.5 MHz, CDCl$_3$) 148.0 (s, C1 & C2), 142.1 (br s, C13), 140.6 (s, C9), 137.4 (s, C10), 135.6 (pseudo-t, $^1J_{PC}$ = 22.5 Hz, C5 & C6), 135.2 (s, C4 & C7), 132.9 (pseudo-t, $^3J_{PC}$ = 9.9 Hz, C15), 127.6 (s, C14), 126.8 (s, C16), 119.1 (s, C3 & C8), 47.8 (d, $^2J_{PC}$ = 8.6, C17), 30.6 (s, C11 & C12), 24.2 (broadened s, C18); δ_P (121.5 MHz, CDCl$_3$) 29.7 (s); MS (ES+) *m/z* 385.06 (M+O+H$^+$-2[N(^{i}Pr)$_2$]), 468.14 (M-N(^{i}Pr)$_2$), 601.29 (M+2O+H$^+$)

Ace[P(Mes)N(^{i}Pr)$_2$]Br 38. A stirred suspension of 5,6-dibromoacenaphthene (0.75 g, 2.42 mmol) in diethyl ether (20 ml) was cooled to -78 °C. A hexane solution of n-butyllithium (1 ml of 2.5M solution, 2.5 mmol) was added over 30 minutes. This was then allowed to rise to 0°C and maintain at this temperature for one hour before being cooled to -78 °C. Separately an ether (15 ml) solution of **28** (0.70 g, 2.45 mmol) was cooled to -78 °C. This was added to the lithiated solution over one hour. Upon the completion of this addition, the stirred mixture was allowed to equilibrate to room temperature. The insoluble salts were filtered off and washed with fresh Et$_2$O (2 x 10 ml). The solvent was then removed *in vacuo* to yield a solid. Crystals were grown by slow evaporation of concentrated solution in dichloromethane. No further purification done. Crystal structure of **38** obtained. δ_P (109.4 MHz, CDCl$_3$) 35.3 (s);

Ace[P(Mes)N(Et)$_2$]Br 39. Procedure the same as above with 5,6-dibromoacenaphthene (1.93 g, 6.21 mmol) and **29** (1.6 g, 6.21 mmol) to produce **39**. Not pure. δ_P (109.4 MHz, $CDCl_3$) 60.4 (s);

Ace[P(Mes)N(Et)$_2$]$_2$ 41. To a stirred suspension of 5,6-dibromoacenaphthene (1.57 g, 5.1 mmol) in diethyl ether (50 ml) was added TMEDA (1.7 ml, 11.4 mmol) and this was cooled to -78 °C. A hexane solution of n-butyllithium (4 ml of 2.5M solution, 10 mmol) was added over 30 minutes. Upon the completion of addition the mixture was allowed to rise to 0°C and maintain at this temperature for two hours before being cooled again to -78 °C. Separately an ether (30 ml) solution of **29** (2.58 g, 10 mmol) was cooled to -78 °C. This was added to the dilithiated solution over one hour. Upon the completion of addition, the stirred mixture was allowed to rise to room temperature slowly. The insoluble materials were filtered off and the retentate was washed through with additional Et_2O (2 x 20 ml). The volatiles were then removed *in vacuo*. No further purification done. Not pure. δ_P (109.4 MHz, $CDCl_3$) 56.1 (s);

Ace[P(Mes)N(^{i}Pr)$_2$]$_2$ 42. Procedure the same as above with 5,6-dibromoacenaphthene (0.4 g, 1.29 mmol), TMEDA (0.5 ml, 3.36 mmol) and **28** (0.74 g, 2.59 mmol). An aliquot of the reaction mixture revealed a mixture of starting material (δ_P 126.7) and the presumed product (δ_P 27.2).

Ace[P(^{t}Bu)N(Et)$_2$]Br 37. An ethereal (40 ml) suspension of 5,6-dibromoacenaphthene (1.65 g, 5.32 mmol) was cooled to -78 °C. A hexane solution of n-butyllithium (2.2 ml of 2.5M solution, 5.5 mmol) was added over 20 minutes. The suspension was then allowed to rise to 0°C and maintain at this temperature for one hour before being cooled down to -78 °C again. Independently, **31** (1.03 g, 5.26 mmol) was diluted in 10 ml of fresh Et_2O. This was then added to the monolithiated suspension over 1 hour, maintaining the low temperature. On completion of addition, the reaction mixture was allowed to rise to room temperature overnight. The insoluble salts were filtered off and wash through with fresh Et_2O (2 x 10 ml). The solvent was removed under reduced pressure. A syrupy residue remained. A ^{31}P NMR spectroscopic investigation of this revealed the starting material (δ_P 161.2) and the presumed product (δ_P 68.9) were present is a 1:1 ratio. Eventually, some crystals precipitated from the mixture and X-ray crystallography showed them to be the desired product **37**. Repeated attempts at purification yielded no better results.

Ace[P(^{t}Bu)N(Et)$_2$]$_2$ 43. To suspension of 5,6-dibromoacenaphthene (3.19 g, 10.3 mmol) in Et_2O was added TMEDA (3.5 ml, 23.5 mmol) and this was cooled to -78 °C. A hexane solution of n-butyllithium (8.3 ml of 2.5M solution, 20.75 mmol) was added over 30 minutes. On completion of this addition the stirred suspension was allowed to rise to 0°C. It was retained at this temperature for 2 hours before being cooled to -78 °C. Alongside, **31** (5.02 g, 20.6 mmol) was taken up in 15 ml of Et_2O. This was added to the dilithiated suspension over 90 minutes. This mixture was permitted to equilibrate to the ambient temperature. The insoluble material was filtered off and this retentate was washed with fresh Et_2O (2 x 20 ml). The volatiles were then removed *in vacuo*. A ^{31}P NMR spectroscopic investigation revealed a range of peaks. Some are attributable to the starting material (δ_P 161.2) and single substitution products (δ_P 68.9), others were no possible to attribute. Repetition proved no more successful.

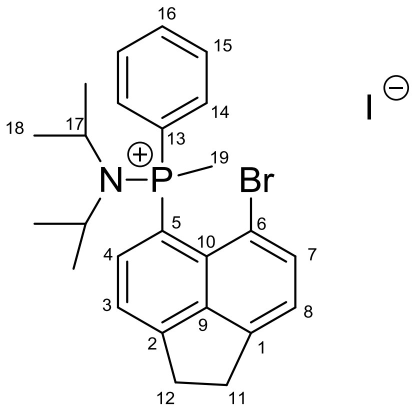


Figure 64 NMR spectroscopy numbering scheme for **44**

[Ace{P(Ph)CH$_3$N(^{i}Pr)$_2$}Br]$^+$ I$^-$ 44. A toluene (15 ml) solution of **35** (0.315 g, 0.715 mmol) was cooled to -78 °C. Iodomethane (1 ml, 16.06 mmol) was added with constant stirring. This solution was allowed to equilibrate to room temperature and was stirred for approximately a week. During this time a white precipitate promulgated while the mother liquor itself show starting material (δ_P 35.4) only via ^{31}P NMR spectroscopy. The precipitate was filtered off and washed with fresh toluene (2 x 10 ml). It was then dried first under suction and then under reduced pressure. Approximately 0.05 g of solid **44** recovered, see Figure 64 for NMR spectroscopy numbering scheme; δ_H (300.1 MHz; CDCl$_3$) 8.20 (1H, dd, $^3J_{HH}$ = 7.21 $^3J_{PH}$ = 18.62, H4), 7.85-7.73 (2H, range, H15), 7.76 (1H, d, $^3J_{HH}$ = 7.56, H7), 7.68 (1H, tt, $^3J_{HH}$ = 7.35, $^4J_{HH}$ = 1.72, H16), 7.58 (2H, m, H14), 7.58 (1H, $^3J_{HH}$ = 7.39, H3), 7.31 (d, $^3J_{HH}$ = 7.54, H8), 3.74-3.60 (2H, m, H17), 3.48 (2H, broadened d, $^3J_{HH}$ = 6.24, H12), 3.40 (2H, broadened d, $^3J_{HH}$ = 6.08, H11), 3.15 (3H, d, $^2J_{PH}$ = 12.29 Hz, H19), 1.42 (6H, d, $^3J_{HH}$ = 6.90 Hz, H18), 1.24 (6H, d, $^3J_{HH}$ = 6.60 Hz, H18); δ_C (75.5 MHz, CDCl$_3$) 158.3 (d, $^1J_{PC}$ = 3.0 Hz, C5), 149.4 (d. $^3J_{PC}$ = 2.0 Hz, C6), 143.1 (s, C2), 142.9 (s, C1), 142.3 (d, $^2J_{PC}$ = 11.0 Hz, C4), 138.3 (s, C7), 134.8 (d, $^4J_{PC}$ = 2.7 Hz, C16), 132.7 (d, $^3J_{PC}$ = 11.0 Hz, C15), 131.9 (d, $^2J_{PC}$ = 9.7 Hz, C10), 130.4 (d, $^2J_{PC}$ = 13.5 Hz, C14), 123.7 (s, C8), 120.2 (d, ${}^{3}J_{PC}$ = 14.0 Hz, C3), 113.1 (d, ${}^{3}J_{PC}$ = 2.7 Hz, C9), 113.0 (d, ${}^{1}J_{PC}$ = 95.7 Hz, C13), 51.4 (d, ${}^{2}J_{PC}$ = 4.0 Hz, C17), 31.2 (s, C12), 30.5 (s, C11), 24.4 (s, C18), 24.1 (br s, C18), 18.4 (d, ${}^{1}J_{PC}$ = 69.5 Hz, C19); δ_P (121.5 MHz, $CDCl_3$) 52.3 (s);

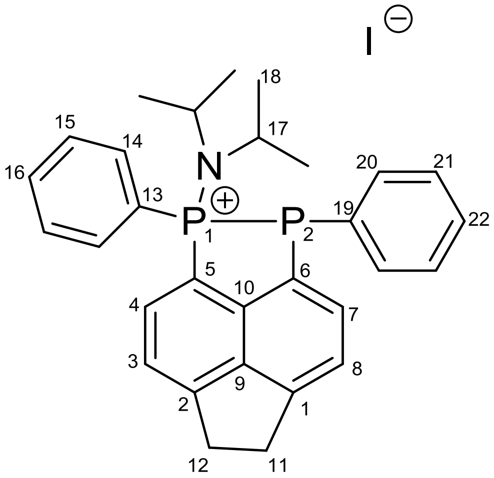


Figure 65 NMR spectroscopy numbering scheme for **46**

[Ace{P(Ph)N(^{i}Pr)$_2$}{P(Ph)}]$^+$ I$^-$ 46. A toluene (20 ml) solution of **40** (0.51 g, 0.897 mmol) was cooled to -78 °C. Iodomethane (1 ml, 16.06 mmol) was added. The solution was allowed to rise to room temperature and stirred constantly for a week. Throughout this time a white precipitate developed. The solid was separated by filtration and washed with fresh toluene (2 x 10 ml). It was dried by suction and then under reduced pressure. A ${}^{31}P\{{}^{1}H\}$ NMR spectroscopic investigation showed that the desired product diiodo 5,6-bis((diisopropylamino)(methyl)(phenyl)phosphonio)-1,2-dihydroacenaphthylene **45** was not the product recovered. However, two independent ionic compounds were made, 1-(diisopropylamino)-1,2-diphenyl-1,2,5,6-tetrahydroacenaphtho[5,6-cd][1,2]diphosphol-1-ium iodide **46** and N-isopropyl-N,N-dimethylpropan-2-aminium iodide were found. Approximately 0.15 g of solid **46** recovered, see Figure 65 for NMR spectroscopy numbering scheme; δ_H (300.1 MHz;

CDCl$_3$) 8.08 (1H, dd, $^{3}J_{HH}$ = 7.32, $^{3}J_{PH}$ = 9.71, H4), 7.83 (1H, pseudo-t, $^{3}J_{HH}$ = 7.03, H7), 7.75 (1H, dd, $^{3}J_{HH}$ = 7.20, $^{4}J_{PH}$ = 2.66, H3), 7.56 (1H, dd, $^{3}J_{HH}$ = 6.94, $^{4}J_{PH}$ = 1.64, H8), 7.31 (1H, dt, $^{3}J_{HH}$ = 7.09, $^{5}J_{PH}$ = 1.80, H16), 7.12 (2H, d of pseudo-t, $^{3}J_{HH}$ = 7.61, $^{3}J_{PH}$ = 4.10, H14), 7.01 (2H, m, H15), 6.93 (1H, dt, $^{3}J_{HH}$ = 7.46, $^{5}J_{PH}$ = 2.40, H22), 6.73 (2H, t-like, $^{3}J_{HH}$ = 7.36, H21), 6.37 (2H, d of pseudo-t, $^{3}J_{HH}$ = 8.19, $^{3}J_{PH}$ = 1.30, H20), 3.71 (2H, m, C17) 3.55 (2H, br s, H12), 3.53 (2H, br s, H11), 1.39 (6H, d, $^{3}J_{HH}$ = 6.72, H18), 1.01 (6H, d, $^{3}J_{HH}$ = 6.90, H18); δ_C (75.5 MHz, CDCl$_3$) 155.9 (d, $^{1}J_{PC}$ = 2.3 Hz, C5), 150.9 (br s, C6), 140.1 (d, $^{3}J_{PC}$ = 2.2, C9), 139.7 (br s, C2), 139.5 (s, C1), 135.4 (dd, $^{3}J_{PC}$ = 27.4, $^{4}J_{PC}$ = 11.0, C7), 135.0 (br s, C4), 134.8 (d, $^{4}J_{PC}$ = 3.2, C16), 134.0 (dd, $^{3}J_{PC}$ = 21.9, $^{4}J_{PC}$ = 5.7, C20), 133.2 (d, $^{4}J_{PC}$ = 11.0, C15), 131.5 (d, $^{5}J_{PC}$ = 4.6, C22), 130.1 (d, $^{3}J_{PC}$ = 13.9, C14), 129.5 (quart-like, $^{4}J_{PC}$ = 3.6, C21), 128.1 (dd, $^{1}J_{PC}$ = 25.6, $^{2}J_{PC}$ = 4.9, C19), 123.6 (d, $^{3}J_{PC}$ = 10.5 Hz, C3), 123.3 (d, $^{3}J_{PC}$ = 9.0 Hz, C8), 119.8 (d, $^{1}J_{PC}$ = 94.9 Hz, C13), 118.0 (d, $^{2}J_{PC}$ = 64.3, $^{2}J_{PC}$ = 4.1, C10), 51.4 (s, C17), 32.2 (s, C12), 31.6 (s, C11), 23.7 (d, $^{3}J_{PC}$ = 5.9, C18), 23.4 (d, $^{3}J_{PC}$ = 4.7, C18); δ_P (121.5 MHz, CDCl$_3$) 70.1 (d, $^{1}J_{PP}$ = 278.2, P1), -19.0 (d, $^{1}J_{PP}$ = 277.8, P2).

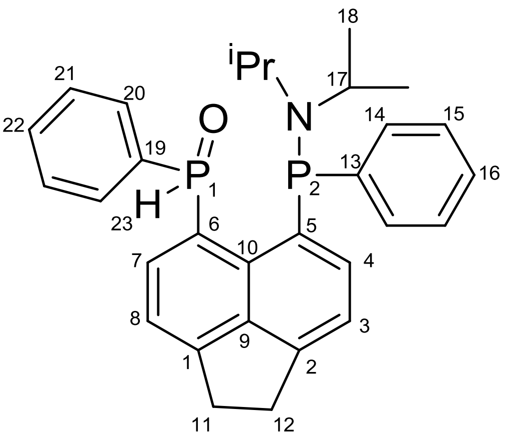


Figure 66 NMR spectroscopy numbering scheme for **47**

The filtrate from previous reaction was collected and the volatiles were removed *in vacuo*. The greyish solid residue was washed with a hot mixture of 1,2-dichloroethane and hexane to proffer an off-white powder **47** (~0.4 g), see Figure 66 for NMR spectroscopy numbering scheme; δ_H (300.1 MHz; $CDCl_3$) 9.60 (1H, d, $^1J_{PH}$ = 536.46, H23), 8.88 (1H, dd, $^3J_{HH}$ = 7.04, $^3J_{PH}$ = 15.03, H7), 7.73 (1H, m, $^3J_{HH}$ = 6.6, H4), 7.56 (1H, d, $^3J_{HH}$ = 6.7, H8), 7.32 (1H, d, $^3J_{HH}$ = 6.68, H3), 7.16-6.99 (6H, Range, H15, H16, H21 & H22), 6.94 (2H, m, C20) 6.73 (2H, m, $^3J_{HH}$ = 6.47, H14), 3.48 (2H, s, H11 & H12), 3.32 (2H, m, $^3J_{HH}$ = 5.81, H17), 1.25 (6H, d, $^3J_{HH}$ = 5.79, H18), 0.65 (6H, d, $^3J_{HH}$ = 5.71, H18); δ_C (75.5 MHz, $CDCl_3$) 153.6 (br s, C6), 150.4 (br s, C5), 140.6 (d, $^2J_{PC}$ = 7.8, C7), 139.4 (br s, C13), 137.7 (s, C4), 133.9 (d, $^4J_{PC}$ = 4.8, C2), 133.5 (d, $^4J_{PC}$ = 4.8, C1), 133.6 (d, $^1J_{PC}$ = 105.9, C19), 131.6 (d, $^3J_{PC}$ = 3.9, C21), 131.5 (s, C16), 131.1 (d, $^2J_{PC}$ = 14.6, C14), 128.7 (d, $^2J_{PC}$ = 12.4, C20), 127.7 (d, $^3J_{PC}$ = 4.1, C15), 127.2 (s, C22), 123.3 (s, C9), 122.1 (s, C10), 120.7 (s, C3), 119.6 (d, $^3J_{PC}$ =12.7, C8), 47.8 (d, $^2J_{PC}$ = 7.9, C17), 30.7 (s, C11 or C12), 30.6 (s, C11 or C12), 24.2 (m, C18); δ_P (121.5 MHz, $CDCl_3$) 31.0 (d, $^4J_{PP}$ = 161.4, P2), 22.0 (dd of pseudo-quart, $^4J_{PP}$ = 161.7, $^1J_{HP}$ = 536.6, $^3J_{HP}$ = 13.5, P1)

Ace[PhPH]$_2$ 48. A suspension of lithium aluminium hydride (0.27 g, 7.11 mmol) in 1,4-dioxane (30 ml) was cooled in ice. To this trimethylsilyl chloride (1 ml, 7.8 mmol) was added slowly with stirring. Powdered **40** (0.335 g, 0.59 mmol) was added in small batches. The flask was fitted with a reflux condenser and heated to 100 °C. The heating was continued for 5 hours at which stage the reaction mixture was allowed to return to ambient temperature. An aliquot of the suspension was taken and investigated via ^{31}P NMR spectroscopy which showed starting material as the sole signal (δ_P 29.7).

Ace[PhPH]$_2$ 48. To a stirred suspension of **40** (0.639 g, 1.12 mmol) in dry methanol was added a single drop of trifluoromethanesulfonic acid. This was heated under reflux for 4 hours and then allowed to cool to room temperature. An aliquot of the reaction mixture was taken and examined via ^{31}P NMR spectroscopy which showed the major peak at δ_P 94.1 along with starting material and **47**. The volatiles were removed *in vacuo* and the residue was taken up in THF (20 ml). This solvent was then removed under reduced pressure. This process was repeated twice more in order to completely remove any alcohol from the solid residue. Finally, a THF solution (30 ml) of the solid was cooled to 0 °C. A THF solution of lithium aluminium hydride (5 ml of 2.4M solution, 12 mmol) was added over 10 minutes with constant stirring. This mixture was allowed to rise to ambient temperature slowly. Upon investigating a sample of this mixture via ^{31}P NMR spectroscopy it was found that a proliferation of phosphorus containing product was obtain, none of which were identifiable.

Ace[P(Ph)N(^{i}Pr)$_2$]{$C_6Cl_4O_2$P(Ph)N(^{i}Pr)$_2$} 49. A DCM (15 ml) solution of **40** (0.32 g, 0.563 mmol) was cooled to -78 °C. Independently, 3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2-dione (0.14 g, 0.569 mmol) was dissolved in more DCM (5 ml). This was then added to the cooled solution over one hour. The reaction mixture was allowed to rise to room temperature overnight. An NMR spectroscopic investigation of this mixture revealed a proliferation of different ^{31}P peaks, all unidentifiable.

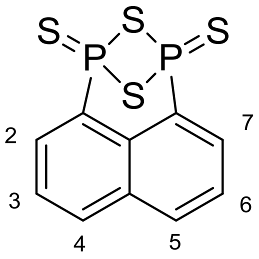


Figure 67 NMR spectroscopy numbering scheme for **15**

NapP$_2$S$_4$ 15. 1-Bromonaphthalene (103.11 g, 500.62 mmol) and P_4S_{10} (22.41 g, 50.52 mmol) were placed in a three-necked flask which was set up as illustrated, see Figure 68. The oil bath was preheated to 270 °C. The flask was lowered into the bath and the flow of nitrogen was stopped so that the stirred mixture heated as fast as possible. The increase in mixture temperature was monitored and at about 240 °C H_2S started to evolve and was neutralised in aqueous solutions of NaOH and bleach. The flask was left in oil bath for 4 minutes after first evolution of gas and then raised to allow it to cool down. Ethanol (75 ml) was added and the mixture was stirred for a further 30 minutes. The pale yellow solid was filtered of and washed with fresh Et_2O (2 x 50 ml) and toluene (3 x 40 ml). The product **15** was insoluble in most solvents. IR (KBr disk) υ_{max}/cm^{-1} 1484m, 902s, 760s, 741s, 671vs, 432s; δ_H (270.2 MHz; $CDCl_3$) 8.56 (2H, ddd, $^3J_{HH}$ = 7.16, $^4J_{HH}$ = 1.10, $^3J_{PH}$ = 21.76, H2/7), 8.31 (2H, dd, $^3J_{HH}$ = 8.26, $^4J_{HH}$ = 1.10, H4/5), 7.83 (2H, m, H3/6); δ_P (109.4 MHz, $CDCl_3$) 18.1 (s)

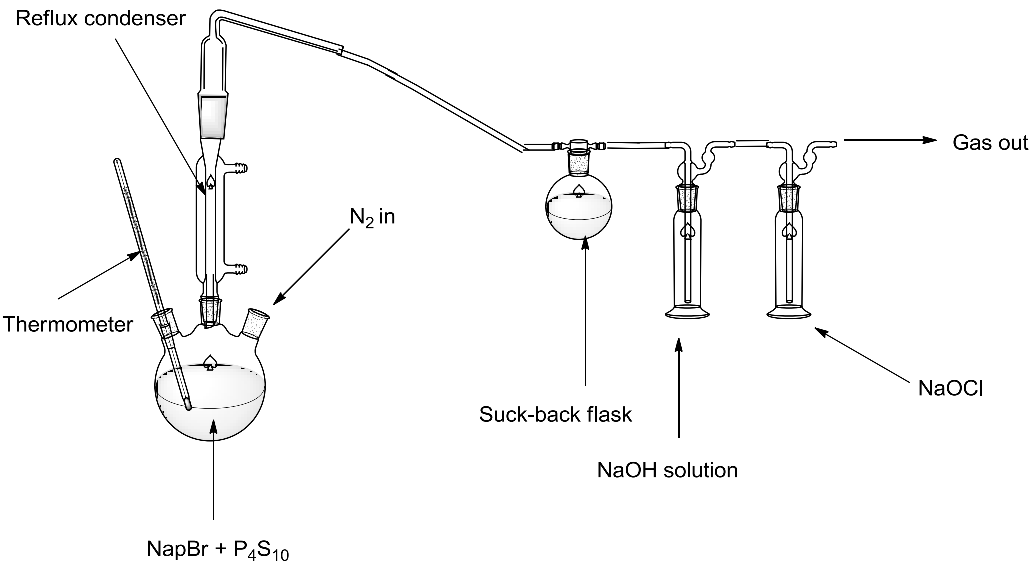


Figure 68 Set-up for synthesis of $NapP_2S_4$ **15**

$Nap(PH_2)_2$ 19. A stirred suspension of THF (65 ml) and $LiAlH_4$ (0.89 g, 23.45 mmol) was cooled in ice. **15** (0.79 g, 2.53 mmol) was added in small batches. The mixture was then allowed to rise to room temperature slowly. The suspension was concentrated down to a paste and then taken up in Et_2O (80 ml). Degassed water (12 ml) was added slowly to hydrolyse the excess hydride and the organic layer was separated off. The aqueous layer was washed with fresh Et_2O (2 x 20 ml) and the combined organic layers were past through anhydrous magnesium sulfate and then subjected to high vacuum to leave a solid residue of **19**. This was used without further purification. δ_H (270.2 MHz; $CDCl_3$) 4.21 (d, $^1J_{PH}$ = 213.5) $\delta_{P\{^1H\}}$ (109.4 MHz, $CDCl_3$) -105.6

Nap(PHR)$_2$. A stirred solution of 1,8-diphosphinonaphthalene (**19**) (0.384 g, ~2 mmol) and Et_2O (30 ml) was cooled to -78 °C. A hexane solution of n-butyllithium (1.6 ml of 2.5M solution, 4 mmol) was added over 20 minutes and the solution was maintained at -78 °C for 3 hours. An excess of the alkylhalide, either isopropyl iodide (0.5 ml, 5 mmol) or *tert*-butyl chloride (0.5 ml, 4.5 mmol), was added dropwise. This stirred solution was allowed to rise to room temperature slowly. An aliquot of the mother liquor was taken and investigated via $^{31}P\{^1H\}$ NMR spectroscopy. This revealed the presence of many ^{31}P containing compounds, none of which could be confidently assigned.

8. Conclusions and Unanswered Questions

The unique steric properties which naphthalene and acenaphthene exhibit make them interesting structures to study. It has been demonstrated that by altering the groups on the *peri*-positions, large changes in splay angle, *peri*-distance and distance from the mean bicyclical aromatic plane can be seen. Although this may seem to be of esoteric relevance, the study of non-bonding group which lie closer to each other than the sum of their van der Waals radii could provide new evidence for non-traditional bonding models. This is why they will be a topic of study for some time to come.

The rigid skeletal backbone has already been used as both monodentate[128] and bidentate[127] ligands in coordination chemistry.[127] It is well established that the ligands present can have a profound effect in metal catalysed reactions.

In our synthetic endeavour, we looked at using cheap commercially available starting materials to produce a range of di-*peri*-substituted naphthalene and acenaphthene in a few short steps. We found it necessary to use amine protecting groups to act as a placeholder for a phosphorus-chlorine bond so as to lessen the effect of unwanted side reactions. With this in mind we successfully isolated and crystallographically characterised $PhP(Cl)N^iPr_2$ **26**. Pure samples of $PhP(Cl)N(Et)_2$ **27** and $^tBuP(Cl)N(Et)_2$ **31** were also obtained but no crystalline specimens of these were collected. $MesP(Cl)N^iPr_2$ **28** was only made as an impure product although a previously unreported crystal structure of this compound was measured. Our attempts to make other alkyl/aryl(chloro)(dialkylamino)phosphines such as $^iPrP(Cl)N(^iPr)_2$ **32** and $PhCH_2P(Cl)NEt_2$ **33** proved to be unsuccessful. During this work the unexpected product Mes*P(NMe_2)$_2$ **34** was crystallised. This has a high degree of steric strain when compared to other Mes*PX_2

From the starting materials obtained, it was our aim to react these with either mono- or di-lithiated acenaphthene. Pure samples of Ace[P(Ph)N(^{i}Pr)$_2$]Br **35**, Ace[P(Ph)N(Et)$_2$]Br **36** and Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40** were isolated and fully characterised. Attempts to make Ace[P(^{t}Bu)N(Et)$_2$]Br **37** and Ace[P(Mes)N(^{i}Pr)$_2$]Br **38** were not as productive as we would have wished and pure samples of these were not isolated, however crystal structure were obtained and analysed.

We tried to make Ace[P(^{t}Bu)N(Et)$_2$]$_2$ **43**, Ace[P(Mes)N(^{i}Pr)$_2$]$_2$ **42** and Ace[P(Mes)N(Et)$_2$]$_2$ **41** but it proved insurmountable to obtain pure samples of these products.

We probed the further reactions of NapP_2S_4 **15**. We found that this could be reduced to the bis-primary phosphine NapP_2H_4 **19** with the suitable reducing agent. Attempts were made to double deprotonate this and to then alkylate it to a bis-secondary phosphine Nap(PHR)$_2$. This proved unsatisfactory as a proliferation of phosphorus containing product was obtained.

We wanted to investigate the further reaction of **35** and **40**, so we probed the lability of their amino groups with respect to reducing agents. We found that the phosphorus-anime bond is surprisingly resilient to such attack. The use of alcoholysis might offer a route to the bis-secondary phosphine by making a Ace[P(Ph)OR]$_2$ moiety first. We were particularly keen to avoid the chlorination of the phosphorus-amino bond with gaseous HCl because although this is a well researched synthetic route, we aimed to use the mildest conditions possible.

Also scrutinized was the susceptibility of the lone pairs on the phosphorus centres to react, which would be a formal change of oxidation state from P(III) to P(V). When the methylating agent methyl iodide was added to the mono-phosphorus **35**, a small amount of the desired product $\{Ace[P(Ph)N(^iPr)_2CH_3]Br\}^+ I^-$ **44** was recovered. The incredible low yield does not reflex well on the effectiveness of this transformation. More dishearteningly, when the corresponding reaction was performed with MeI and **40** an amino group was cleaved off and a phosphine-phosphonium complex, **46** was obtained, in poor yield. More strangely with this reaction was its propensity to produce the product of partial hydrolysis $Ace[P(Ph)N(^iPr)_2)(P(O)PhH]$ **47**.

There are several examples in the literature of 3,4,5,6-tetrachloro-1,2-benzoquinone been used to make benzodioxaphospholes,[188] however none are similar to our starting materials. We found that clean reactions did not occur when this was reacted with **40**.

In general, a lack of crystallisability has impeded the progress of this work. We believe that we have merely scratched the surface of what is possible from the reactions of alkyl/aryl(chloro)(dialkylamino)phosphines with mono- or di-lithiated naphthalene or acenaphthene backbones.

Chapter 4 – The unexpected synthesis of Dewar benzene motif

a. The influence of supermesityl group in our research work

The main thrust of our synthetic endeavours was to investigate how a molecular system responds to the presence of two bulky groups close to the phosphorus centre. Our utilization of 2,4,6-tri-*tert*-butylphenyl (Mes*) has been well documented in the production of a number of geminally bis(supermesityl) substituted phosphorus compounds such as **5**, **8** and **9**.[96] These bulky groups influenced the geometric features seen in their respective crystal structures, with large deviations from planarity observed in many of the substituted phenyl rings. It is with this in mind that we report formation of an unexpected species **50**; see Figure 69 and Figure 70. The bicyclo[2.2.0]hexa-2,5-diene ring present in **50** is colloquially known as Dewar benzene (DB).

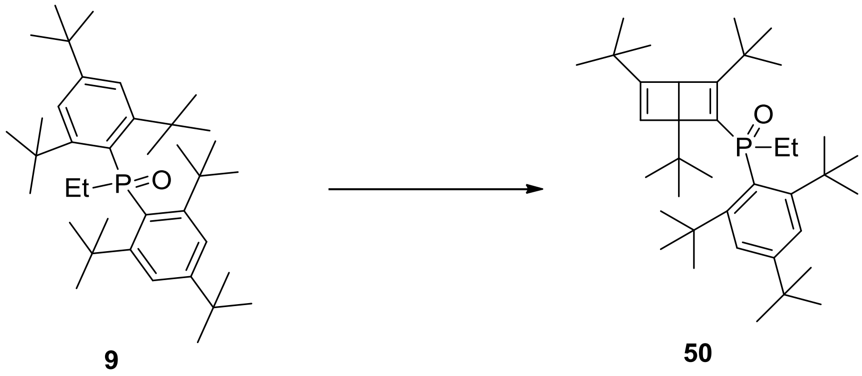


Figure 69 The rearrangement of one Mes* group in **9** to a Dewar benzene in **50**

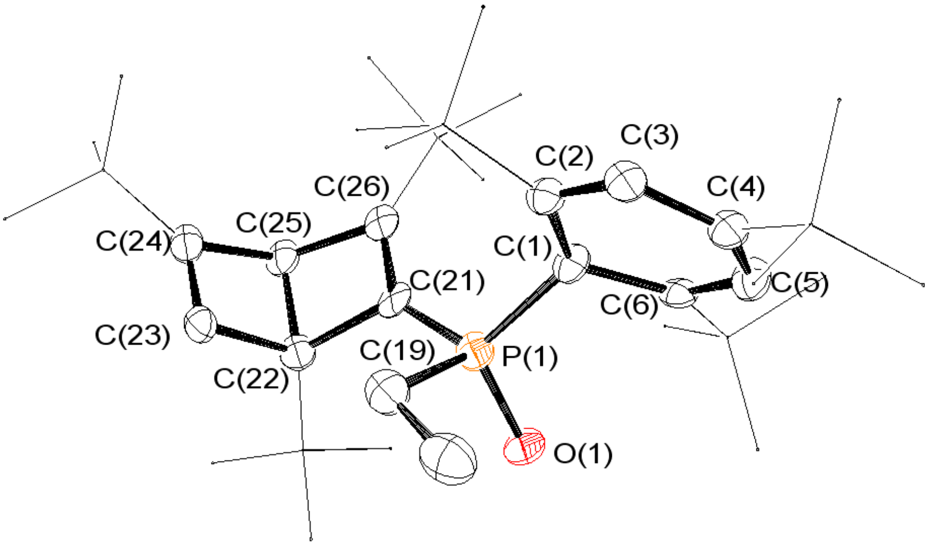


Figure 70 Molecular structure of **50**. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

b. The production of compound 50 containing a Dewar benzene motif

A hexane solution of the (extremely hindered) phosphine oxide Mes*$_2$P(O)Et **9** was placed in a flask with a rubber septum stopper pierced by a steel needle to permit air flow. The solvent was allowed to evaporate over the course of three weeks. This resulted in the formation of a large number of small crystals, which were covered in oil. A ^{31}P NMR spectrum of a sample of these crystals and oil showed that many phosphorus containing compounds were present. Some of these crystals were of sufficient quality for X-ray structural analysis, the results of which are seen in Table 13. The formation of **50** is likely to be the result of an intramolecular rearrangement within one of the supermesityl groups to produce two fused cyclobutene rings.

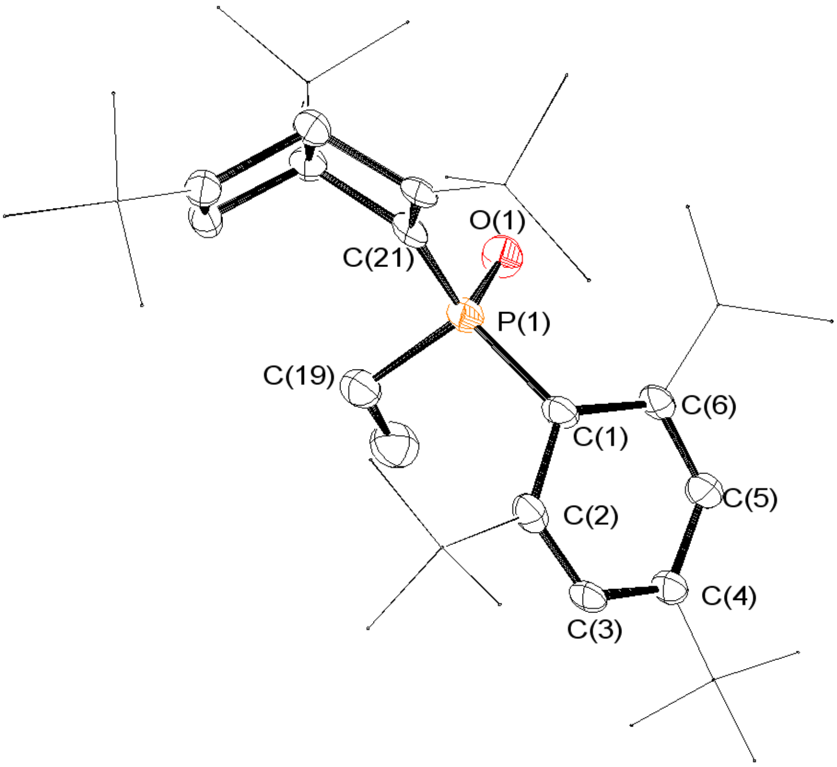


Figure 71 Molecular structure of **50** showing the angle between the two mean cyclobutene planes. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. *t*Bu groups are drawn as wireframe for clarity.

We were unable to obtain any other data pertaining to this unique structure bar its crystal structure, as a pure sample was never isolated. However, we think that the crystallographic data alone is of sufficient interest to warrant study.

c. X-ray discussion of 50

Table 13 Bond distances (Å), bond angles (°), torsion angles (°) and displacement from mean phenyl planes (Å) in compound **50**

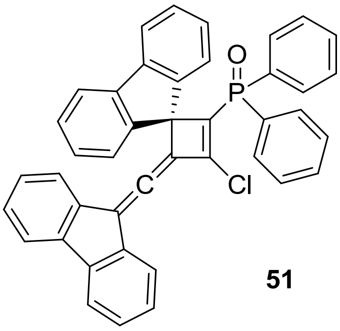
Bond lengths (Å)		**Dihedral angles (°)**	
P(1)-O(1)	1.499(4)	C(1)-C(2)-C(3)-C(4)	0.3(6)
P(1)-C(1)	1.856(5)	C(1)-C(6)-C(5)-C(4)	4.8(6)
P(1)-C(19)	1.837(5)	C(2)-C(3)-C(4)-C(5)	10.2(6)
P(1)-C(21)	1.804(4)	C(3)-C(4)-C(5)-C(6)	7.8(6)
C(21)-C(26)	1.360(5)	C(3)-C(2)-C(1)-C(6)	13.3(5)
C(22)-C(25)	1.566(5)	C(2)-C(1)-C(6)-C(5)	15.4(5)
C(23)-C(24)	1.325(6)	C(22)-C(21)-C(26)-C(25)	5.0(3)
		C(23)-C(22)-C(25)-C(24)	0.9(3)
Bond Angles (°)			
C(1)-P(1)-C(21)	118.38(18)	C(22)-C(21)-C(26)	92.1(3)
O(1)-P(1)-C(1)	111.2(2)	C(1)-C(2)-C(7)	129.5(4)
O(1)-P(1)-C(19)	105.44(19)	C(1)-C(6)-C(15)	128.4(3)
O(1)-P(1)-C(21)	110.79(16)	C(21)-C(22)-C(27)	121.5(4)
C(1)-P(1)-C(19)	104.25(19)	C(21)-C(26)-C(35)	140.1(5)
C(19)-P(1)-C(21)	105.5(3)	C(25)-C(22)-C(27)	119.2(3)
C(2)-C(1)-C(6)	117.7(4)		
Distance from mean phenyl plane[a] (Å)		**Distance from mean cyclobutene plane (Å)**	
P(1)	1.126	P(1)[b]	0.187
C(1)	0.098	C(21)[b]	0.034
C(4)	0.075	C(27)[b]	1.194
C(7)	0.317	C(27)[c]	1.168
C(15)	0.310	C(35)[b]	0.315
C(11)	0.294	C(31)[c]	0.108

[a] Distance from the mean phenyl plane fitted through atoms C(1) to C(6)

[b] Distance from the cyclobutene mean plane fitted through atoms C(21), C(22), C(25) & C(26)

[c] Distance from the cyclobutene mean plane fitted through atoms C(22), C(23), C(24) & C(25)

Table 13 shows a selection of the structural parameters seen in the crystal structure of **50**. The phosphorus-oxygen and phosphorus-carbon (both ethyl and Mes* group) bond lengths are broadly similar to the parent compound Mes*$_2$P(O)Et **9**. The P(1)-C(21) bond length of 1.804(4) Å is in line with one of the very few analogues compound **51**, which we could find of a P(V) centre bonded to a cyclobutene group (1.7958(12) Å),[189] see Figure 72.



51

Figure 72 Example of a P(V) centre bonded to a cyclobutene group[189]

The C(1)-P(1)-C(21) angle in **50** (118.38(18)°) is much more obtuse than the corresponding angle in **9** (109.54(10)°). As a result of this, the other angles around the phosphorus centre in **50** become more acute than their equivalents in **9**. Figure 73 shows the extent to which the flanking *ortho*-^{t}Bu groups undergo bending in the mean phenyl plane, 8.4(3) and 9.5(4)° away from the idealised sp^2 hybridized carbon angle of 120°. They are also displaced about 0.31 Å out of this same mean plane as documented in Table 13.

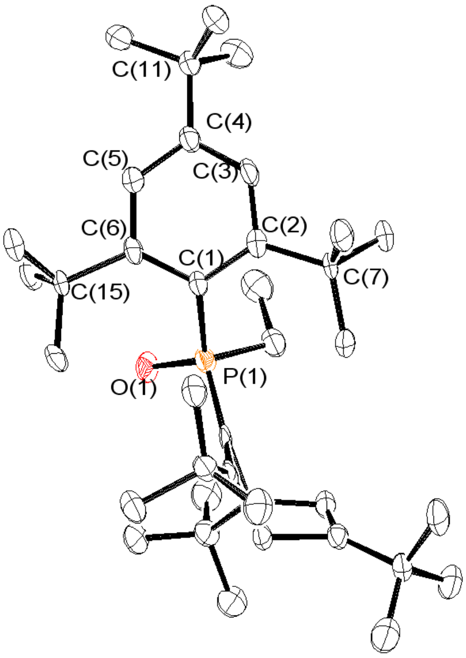


Figure 73 Molecular structure of **50** showing the in plane bending of the *ortho*-^{t}Bu groups. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

The phosphorus centre is displaced out the opposite side of the mean aromatic plane to the tune of 1.126 Å, as seen in Figure 74. The quaternary carbon of the *para*-^{t}Bu group is displaced 0.294 Å out the same side of the mean phenyl plane as the phosphorus atom.

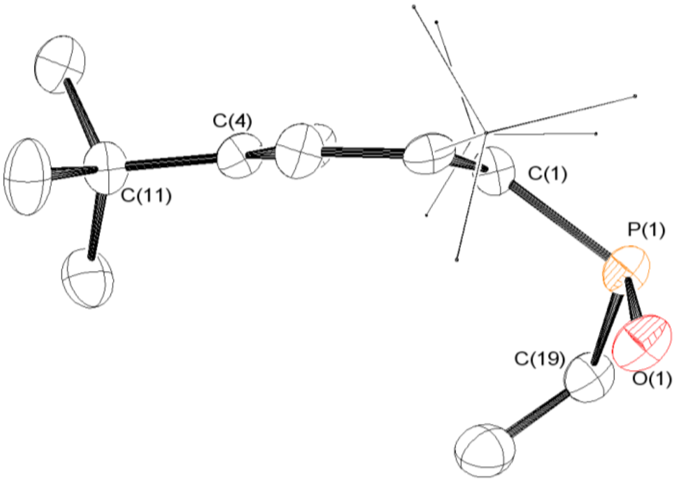


Figure 74 Molecular structure of **50** showing the out of plane displacement which the phosphorus centre displays. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and the substituted Dewar benzene ligand are omitted for clarity. *Ortho-t*Bu groups are drawn as wireframe for clarity.

The torsion angles seen within this aromatic ring are quite pronounced, with distortion of up to 15.4(5)° away from planarity, see Table 13. This indicates that the system is under an appreciable amount of strain with the ring adopting a boat-like structure with the *para*-C and *ipso*-C atoms displaced 0.075 and 0.098 Å out of the mean phenyl plane respectively, see Figure 74.

The phosphorus centre lies much closer (0.19 Å) to the mean plane of the cyclobutene group C(21)-C(22)-C(25)-C(26) than to the mean plane of the Mes* group (1.126 Å). C(22) is now a sp^{3} tetrahedral carbon centre so C(27) is displaced significantly (1.168 and 1.194 Å) from the mean cyclobutene planes, see Figure 75 and Table 13.

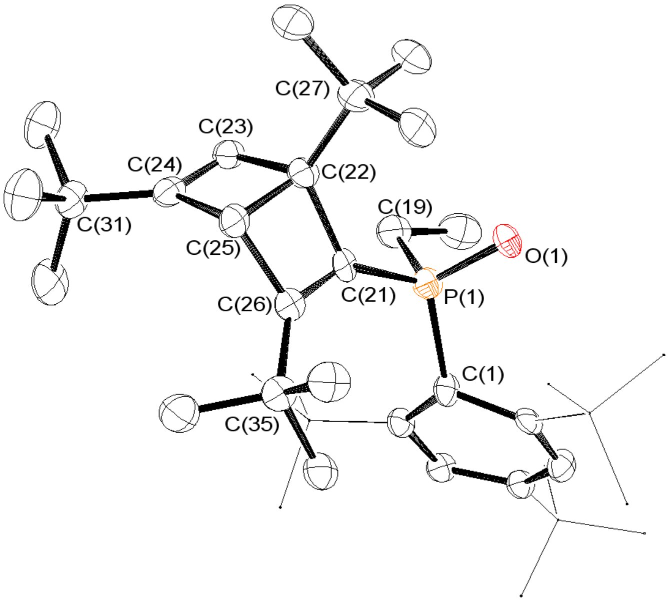
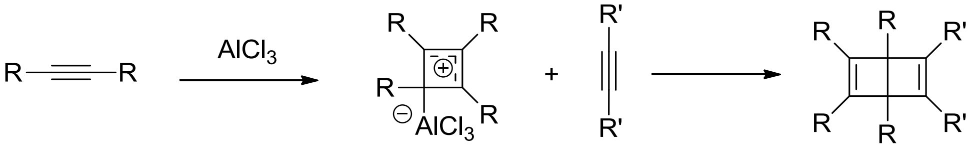


Figure 75 Molecular structure of **50** showing the connectivity around the Dewar benzene substituent. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. The Mes* *t*Bu groups are drawn as wireframe for clarity.

The *t*Bu group on C(35) is positioned much further away from the phosphorus centre (4.009(4) Å) than the *ortho*-substituted atomic centre C(7) and C(15) (3.597(5) and 3.399(6) Å respectively). In contrast C(27) lies only 3.716(5) Å away from the phosphorus centre. As a result the angles between the mean Mes* phenyl plane and the mean cyclobutene plane C(21)-C(22)-C(25)-C(26) is close to a right angle (85.31°). The angle between the mean planes of cyclobutene rings C(21)-C(22)-C(25)-C(26) and C(22)-C(23)-C(24)-C(25) is 117.5°, as seen in Figure 71 and Figure 75.

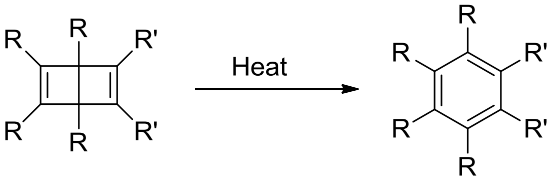
d. Other Dewar benzene structures in the literature

Bicyclo[2.2.0]hexa-2,5-diene (DB) is a benzene valence isomer[190] and the first examples of structures with this motif were isolated in the 1960s.[191,192] The synthesis of these is somewhat of a niche pursuit. It has been generally achieved via the trimerization of alkynes, often in the presence of $AlCl_3$,[193,194,195] see Scheme 20.

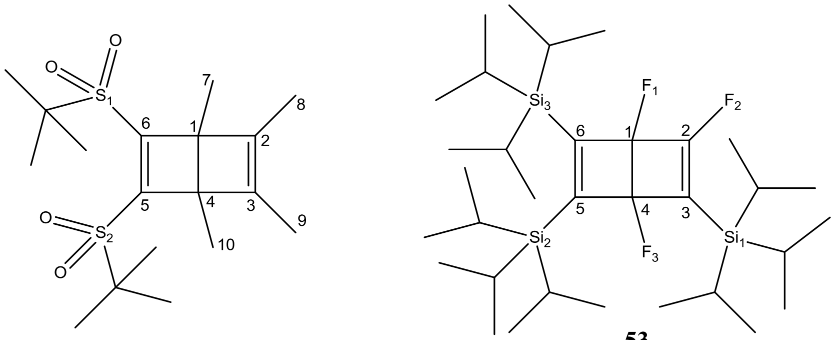


Scheme 20 Generic procedure for Dewar benzene generation

There have been a number of structural[196,197] and theoretical[198] studies into the precise configuration of the DB. As with **50**, the compounds studied show large deviations from the standard bond angles and distances. This structural motif has also been used as a ligand in coordination chemistry[199] and had been shown to undergo rearrangement to the corresponding benzene structure when subjected to heating >130 °C,[200] see Scheme 21.



Scheme 21 Rearrangement of Dewar benzene to substituted phenyl ring



52 **53**

Figure 76 Other Dewar benzene compound from the literature with heteroatoms directly attached

Figure 76 and Table 14 show two compounds from the literature,[201,202] which also display a DB motif with heteroatoms substituted onto the ring. The angle between the mean planes of cyclobutene rings C(1)-C(2)-C(3)-C(4) and C(1)-C(4)-C(5)-C(6) are 116.1° and 123.0° respectively for **52** and **53**.

Table 14 Bond distances (Å), bond angles (°) and displacement from mean planes (Å) in compounds **52**[201] and **53**[202]

Bond lengths (Å)	**52**	**Distance from mean cyclobutene plane[a] (Å)**	**52**
C(1)-C(4)	1.602(6)	S(1)	0.144
C(2)-C(3)	1.315(6)	S(2)	0.453
C(5)-C(6)	1.345(5)		
C(1)-C(7)	1.520(5)	**Bond Angles (°)**	
C(5)-S(2)	1.782(5)		
		C(1)-C(4)-C(10)	122.2(3)

Bond lengths (Å)	**53**	**Distance from mean cyclobutene plane (Å)**	**53**
C(1)-C(4)	1.534(4)	Si(1)[b]	0.085
C(2)-C(3)	1.341(4)	Si(2)[a]	0.137
C(5)-C(6)	1.380(4)	Si(3)[a]	0.012
C(1)-F(1)	1.385(3)	F(2)[b]	0.072
C(5)-Si(2)	1.905(3)		
Bond Angles (°)			
C(4)-C(1)-F(1)	121.0(3)		

[a] Distance from the cyclobutene mean plane fitted through atoms C(1), C(4), C(5) & C(6)
[b] Distance from the cyclobutene mean plane fitted through atoms C(1), C(2), C(3) & C(4)

The bond lengths and bond angles observed within the Dewar benzene rings of **52** and **53** are very similar to those seen in **50**. The cyclobutene rings within **52** and **53** are essentially planar with the dihedral angles between bond vectors all approximately zero.

e. Dewar benzene and Mes* groups

The elucidation of the crystal structure **50** was an unexpected result of the synthetic work carried out during the course of this research endeavour. Due to the lack of other information we can not determine the prevalence of this DB compound within the crude solid which was recovered from the synthesis of **9**. As **50** is a one off product with no definite driving force behind this intramolecular rearrangement, it is probable that the ^{t}Bu groups substituted on the phenyl ring convey enhanced stability to the DB arrangement to allow it to be isolated and preliminarily studied. An exact synthetic procedure is not reported here so further work may be needed to find a reproducible route to **50**.

Concluding Remarks and Future Work

1. Geminally Bis(supermesityl) Substituted Phosphorus Compounds

a. Radicals and Mes* group

At the start of this research venture, we were initially interested in the production of sterically hindered phosphinyl radicals. Although main group radicals are generally reactive and have extremely short life spans, by using bulky groups it was hoped that the persistence of phosphorus containing species could be increased to allow their isolation and potential use in spin labelling. A diverse range of phosphorus centred radicals have been studied and these have been collated recently.[49,203]

We were particularly interested in the advantages the use of Mes* might bestow upon reactive systems such as its encapsulating nature and the large electron rich aromatic framework which could increase stability. This work was foreshadowed by the generation of a diphosphanyl radical from the diphosphene Mes*P=PMes*.[9,52]

b. Attempted synthesis of Mes^*_2PH 6 and the Mes* substituted structures which were produced

It was for these reasons that the synthesis and isolation of the secondary phosphine Mes^*_2PH **6** and chlorophosphine Mes^*_2PCl **2** was such an important aim of ours. We postulated that **2** and **6** could provide the necessary synthons to be easily transformed into the desired phosphinyl radical Mes*$_2$P·. However, despite our persistent attempts we found that the starting material which we employed, Mes*$_2$P(=O)Cl **3** could not be reduced to **6** via the reductive methods employed. During the course of our research work we did however produce a range of extremely sterically hindered phosphine oxides (**5**, **8** & **9**), a phosphine sulfide (**14**) and a secondary phosphine (**10**) which we believe are valuable additions to the chemical canon.[96]

c. Potential for further reactions of Mes*-substituted structures

As always there are unanswered question and untried experiments lingering at the conclusion of this work. The sterically hindered secondary phosphine **10** has a lone pair close to the phosphorus centre which may prove to be receptive to interaction with a strong Lewis acid. Drawing electron density away from the phosphorus atom might in turn increase the acidity of the hydrogen directly bonded to the phosphorus. This was one of the ideas behind making a borane adduct of **10** which we hoped would relieve some of the steric strain around the phosphorus centre and allow deprotonation. Regrettably no borane adduct was formed when **10** was heated with a complex of BH_3, however a stronger Lewis Acid may be able to entice the lone pair to react as was seen in the synthesis of the sulfide **14**.

The phosphine oxide structures **5**, **8** and **9** have a strong phosphorus-oxygen double bond which has been shown to be incredibly resistant to reduction. However there are numerous literature examples of phosphine oxide ligands which datively bond through the oxygen to a metal centres.[204,205] This is a means of reactivity which we did not explore and may prove to be fertile territory in the large field of coordination chemistry. It would be of particular interest to see their interaction with harder metal ions such as Zn^{2+} and Cd^{2+} which have been shown to have an affinity for $Ph_3P{=}O$ ligands.[206,207] There is much potential for new ligands in zinc catalysed reactions and the phosphine oxides reported in this synthetic study may increase the library of catalytic structures.

The use of Mes* as a means of steric protection for main group species will continue into the future. Its unique encapsulating properties will make it a valuable ligand for phosphorus for many years to come.

2. *Peri-Substituted Naphthalene and Acenaphthene*

a. Interactions between *peri*-substituted phosphorus centres

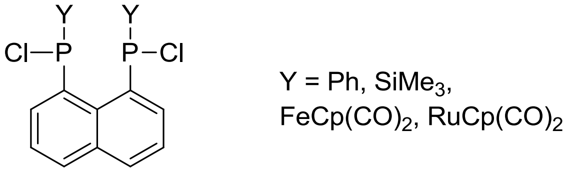
It has been well documented during the course of this work how groups attached to the *peri*-positions of naphthalene or acenaphthene can be brought together to sub-van der Waals radii distances. It was our aim to synthesis such structure with a phosphorus atom present at one or both of the *peri*-sites. The significant ring distortion seen in structures such as $Nap(PCl_2)_2$ **18** or $Ace[P(Ph)N(^iPr)_2]_2$ **40** is an indication of the strain that the substitution of large groups on the *peri*-positions places on the aromatic manifold. This synthetic work could be described as being part of a larger ongoing effect by people within the Kilian and Woollins research groups to explore the use of these backbones in target molecule synthesis.[105.125,127]

b. Synthetic Significance of novel *peri*-substituted compounds

The synthesis of mono-phosphorus *peri*-substituted acenaphthene structures (**35**, **37** and **38**) was only a qualified success and more work will need to be done on purification protocols to isolate some of these products and fully characterise them. Another aspect of these products not explored is the potential for further substitution of the remaining *peri*-position occupied by bromine. This may be route to the synthesis of mixed systems with other main group centres onto the other *peri*-position.[124,208]

Further to this, it has being discussed that aminophosphine motifs can be deprotected with HCl. This revelation of a P-Cl group is a means of reactivity which we did not explore in detail. The phosphorus-chlorine bond is labile to attack by a nucleophile with the chloride ion Cl^- acting as a leaving group. This could be an important way of attaching a range of new substituents to the phosphorus centre.

There has also been some preliminary theoretical work on the subject of four-centre-eight-electron bonds which could utilise *peri*-substituted P-Cl groups.[209] Figure 77 shows how *peri*-substitution brings the phosphorus centres close together with the other substituent Y acting as an electron donating group.



54

Figure 77 Generic structure of potential 4c-4e bonding motifs

It has been theorised that these four atomic centres (Cl-P···P-Cl) in **54** could orient themselves in such a way to allow the necessary orbital overlap. The choice of group Y may influence the formally non-bonding P···P distance and determine the degree of interaction observed. Exploration of 4c4e$^-$ bond motifs with *peri*-positioned chlorophosphines could provide a fascinating insight into the nature of these unusual bonding models. The exact nature of what is (and what isn't) a chemical bond has generated much discussion in the chemical literature.[210,211] Any further chemical or crystallographic data into sub-van der Waals interactions improve our knowledge of the nature of bonding.

With two P(III) centres on the *peri*-positions there is a potential for using them as bidentate ligands for a range of metals (particularly softer metals) as has been discussed before. Ace[P(Ph)N(^{i}Pr)$_2$]$_2$ **40** and analogues of it are potential candidates for such bidentate ligands.

This research endeavour has only scratched the surface of possibilities in regard to *peri*-substituted naphthalene and acenaphthene and their further application. There is a huge scope for further work with these skeletal backbones, which we are sure, will provide the basis for novel compounds for years to come.

X-Ray Crystallography Structural Refinement Data

Table 15, Table 16, Table 17 and Table 18 list details of the data collection and refinements for new structures reported. The X-ray data was collected and solved by Prof. Alex Slawin, Rebecca Randall, Lucy Wakefield and Kasun Athukorala Arachchige.

X-ray quality crystals of **4**, **5**, **8**, **9**, **10** and **14** were obtained by slow evaporation of concentrated solutions in dichloromethane. Crystals of **13** were obtained from toluene. Crystals of **50** were obtained from hexane. Data for compounds **4**, **5**, **8**, **9**, **10** and **50** were collected at 93(2) K using MoKα radiation (λ = 0.71075 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Mercury ccd detector with ω and φ scans. X-ray crystal data for compound **13** were collected at 173(2) K using CuK\α radiation (λ = 1.54178 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Saturn rotating anode detector with ω. X-ray crystal data for compound **14** were collected using the St Andrews Robotic Diffractometer (Rigaku Saturn70 ccd) at 125(2) K with graphite monochromated MoKα radiation (λ = 0.71075 Å). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. The positions of the hydrogen atoms were idealized except for structures **5**, **10** and **14**, which were refined isotropically subject to distance constraint. Refinements were done by full-matrix least squares based on F^2 using the program SHELXTL.[212]

X-ray quality crystals of **28**, **35**, **38** and **40** were obtained by slow evaporation of concentrated solutions in dichloromethane. Crystals of **26** and **37** were obtained from neat samples left standing over time. Crystals of **34** were obtained from Et_2O. Data for compounds **26**, **34**, **35** and **40** were collected at 93(2) K using MoKα radiation (λ = 0.71075 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Mercury ccd detector with ω and φ scans. X-ray crystal data for compound **28** were collected at 93(2) K using MoKα radiation = 0.71073 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Saturn rotating anode detector with ω and φ scans. X-ray crystal data for compounds **37** were collected at 273(2) K using MoKα radiation (λ = 0.71075 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Saturn724 ccd detector with ω and φ scans. X-ray crystal data for compounds **38** were collected at 125(2) K using MoKα radiation (λ = 0.71075 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Saturn70 ccd detector with ω scans. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. The positions of the hydrogen atoms were idealized. Refinements were done by full-matrix least squares based on F^2 using the program SHELXTL.[212]

Table 15 Details of the X-ray data collections and refinements for compounds **4**, **5**, **8** and **9**

Compound	**4**	**5**	**8**	**9**·CH_2Cl_2
Empirical formula	$C_{36}H_{57}OP$	$C_{36}H_{59}OP$	$C_{37}H_{61}OP$	$C_{38}H_{63}OP$ CH_2Cl_2
M_T	536.82	538.84	552.86	651.82
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$Pbca$	$P2_1$	$P2_1/c$
a/Å	9.005(3)	10.7468(19)	11.039(4)	20.653(4)
b/Å	11.305(4)	20.780(5)	10.854(5)	11.1027(18)
c/Å	32.513(11)	29.975(6)	14.610(6)	17.718(3)
α/°	90	90	90	90
β/°	90	90	100.892(10)	111.573(4)
γ/°	90	90	90	90
V/Å^3	3309.8(19)	6694(3)	1719.0(12)	3778.0(12)
Z	4	8	2	4
Total reflections	5739	6057	5639	6894
Independent reflections	2735	5365	5048	5803
R_{int}	0.3093	0.0470	0.0570	0.0322
R(obs)	0.1657	0.1060	0.0765	0.0468
wR(all data)	0.4747	0.2903	0.2115	0.1505
Flack parameter	-	-	0.57(17)	-

Table 16 Details of the X-ray data collections and refinements for compounds **10**, **13**, **14** and **50**

Compound	**10**	**13**	**14**	**50**
Empirical formula	$C_{32}H_{51}P$	$C_{14}H_{21}Cl_2P$	$C_{32}H_{51}PS$	$C_{38}H_{63}OP$
M_T	466.73	291.18	499.79	566.89
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/c$	*Pnma*	$P\bar{1}$	$P\bar{1}$
a/Å	17.188(6)	11.026(8)	9.398(5)	9.814(3)
b/Å	10.133(4)	9.837(8)	12.868(7)	14.486(4)
c/Å	17.471(5)	14.012(11)	14.381(7)	14.731(4)
α/°	90	90	108.860(7)	116.846(9)
β/°	92.519(10)	90	100.484(9)	90.330(7)
γ/°	90	90	105.905(8)	105.427(8)
V/Å^3	3039.7(17)	1520(2)	1511.2(13)	1781.7(8)
Z	4	4	2	2
Total reflections	5488	1450	5281	6223
Independent reflections	4124	919	3448	3297
R_{int}	0.0480	0.6117	0.1206	0.1069
R(obs)	0.0562	0.1763	0.1342	0.0871
wR(all data)	0.1730	0.4399	0.2935	0.2233
Flack parameter	-	-	-	-

Table 17 Details of the X-ray data collections and refinements for compounds **26**, **28** and **34**

Compound	**26**	**28**	**34**
Empirical formula	$C_{12}H_{19}ClNP$	$C_{15}H_{25}ClNP$	$C_{22}H_{41}N_2P$
M_T	243.72	285.78	364.55
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	9.709(5)	13.472(5)	10.273(3)
b/Å	10.296(6)	8.488(3)	19.844(6)
c/Å	13.740(8)	15.339(5)	11.826(4)
α/°	89.10(3)	90.00	90.00
β/°	84.03(2)	113.930(8)	98.420(8)
γ/°	86.03(3)	90.00	90.00
V/Å^3	1362.7(12)	1603.1(9)	2384.7(13)
Z	4	4	4
Total reflections	8686	2898	14250
Independent reflections	4844	2302	4326
R_{int}	0.0503	0.0469	0.0575
R(obs)	0.1173	0.0693	0.1004
wR(all data)	0.2536	0.1544	0.2293
Flack parameter	-	-	-

Table 18 Details of the X-ray data collections and refinements for compounds **35**, **37**, **38** and **40**

Compound	**35**	**37**	**38**	**40**
Empirical formula	$C_{24}H_{27}BrNP$	$C_{20}H_{27}BrNP$	$C_{27}H_{33}BrNP$	$C_{36}H_{46}N_2P_2$
M_T	440.36	392.32	482.44	568.72
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	7.604(3)	8.129(3)	25.998(6)	10.958(2)
b/Å	31.027(10)	9.046(3)	15.371(4)	12.119(3)
c/Å	9.332(3)	29.152(13)	18.467(4)	13.820(2)
α/°	90.00	84.16(4)	90.0000	67.00(3)
β/°	105.857(8)	86.67(4)	98.771(5)	72.95(3)
γ/°	90.00	64.08(3)	90.0000	78.83(3)
V/Å^3	2117.7(12)	1917.7(12)	7293(3)	1608.6(6)
Z	4	4	12	2
Total reflections	11257	15724	14728	10335
Independent reflections	3732	8125	9648	5686
R_{int}	0.0300	0.1086	0.1571	0.0386
R(obs)	0.0371	0.1239	0.1512	0.1032
wR(all data)	0.0842	0.3840	0.3464	0.1032
Flack parameter	-	-	-	-

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