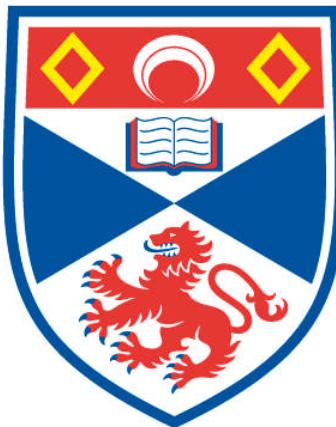


**CATALYTIC SYNTHESIS OF ORGANOPHOSPHATE PLASTICS
ADDITIVES FROM WHITE PHOSPHORUS**

Kenneth Mark Armstrong

**A Thesis Submitted for the Degree of PhD
at the
University of St Andrews**



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Catalytic Synthesis of Organophosphate Plastics Additives from White Phosphorus

A thesis submitted by

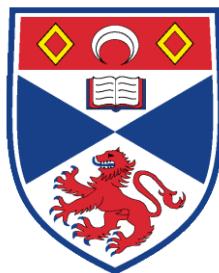
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Abstract

Triaryl phosphates were synthesized from white phosphorus and phenols in aerobic conditions and in the presence of iron catalysts and iodine. Full conversion to phosphates was achieved without the use of chlorine or chlorinated solvents, and the reactions do not produce acid waste. Triphenyl phosphate, tritolyl phosphate and tris(2,4-di-tert-butyl)phenyl phosphate were synthesized by this method with 100% conversion from P₄. Various iron(III) diketonates were used to catalyse the conversion. Mechanistic studies showed the reaction to proceed via the formation of phosphorus triiodide (PI₃), then diphenyl phosphoroiididate (O=PI(OPh)₂) before the final formation of triphenyl phosphate (O=P(OPh)₃). The nucleophilic substitution of O=PI(OPh)₂ with phenol to form O=P(OPh)₃ was found to be the rate determining step.

It was found that by modifying the reaction conditions the same catalytic systems could be used to synthesize triphenyl phosphite directly from P₄. Triphenyl phosphite was synthesized in selectivities of up to 60 %. The mechanism of these transformations was also elucidated.

Independent syntheses of the intermediate in the reaction mechanism, O=P(OPh)₂I and its hydrolysis products diphenyl phosphate (O=P(OPh)₂OH) and tetraphenyl pyrophosphate ((O)P(OPh)₂-O-P(O)(OPh)₂) were developed from PI₃. The 2,4-di-tert-butyl phenol analogues of these compounds were also prepared. Bis-(2,4-di-tert-butylphenyl) phosphoroiididate was then reacted with various alcohols to produce a series of mixed triorgano phosphates.

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Abbreviations

General Abbreviations

°C	degrees Centigrade
AIBN	azobisisobutyronitrile
acac	acetylacetone (2,4-pentandioneate)
ABS	acrylonitrile butadiene styrene
bipy	2,2'-bipyridyl
Bp	boiling point
'Bu	tertiary butyl
CAAC	cyclic alkyl amino carbene
CNDO	complete neglect of differential overlap
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
Cy	cyclohexyl
DBU	1,8-diazabicycloundec-7-ene
DFT	density functional theory
ESI	electrospray ionisation
Et	ethyl
GC	gas chromatography
IR	infra-red
LD ₅₀	median lethal dose, 50 %

MCBPA	3-chloroperoxybenzoic acid
Me	methyl
Mes*	2,4,6-tri-tert-butylphenyl
Mp	melting point
MS	mass spectrometry
NATO	North Atlantic Treaty Organisation
NMR	nuclear magnetic resonance
NHC	N heterocyclic carbene
Ph	phenyl
OTf	trifluoromethylsulfonate
<i>i</i> Pr	iso propyl
RT	room temperature
TMS	tetramethylsilane
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
UV-Vis	ultra-violet-visible
XRD	X-ray diffraction

NMR Abbreviations

d	doublet
dd	doublet of doublets
Hz	Hertz
m	multiplet
ppm	parts per million

q	quartet
quint	quintet
s	singlet
sep	septet
t	triplet

IR Abbreviations

w	weak
m	medium
s	strong
vs	very strong
FT	fourier transform

Selected Phosphorus Nomenclature

P_4	white phosphorus
$P(OR)_3$	phosphite
$O=P(OR)_3$	phosphate
$O=P(OR)_2H$	phosphonate
$P(OR)_2NR_2$	phosphoramidite
$O=P(OR)_2NR_2$	phosphoramidate
$O=P(OR)_2I$	phosphoroiodidate
$O=P(OR)_2Cl$	phosphorochloridate
$O=P(OR)_2-O-P(OR)_2=O$	pyrophosphate

1. Introduction

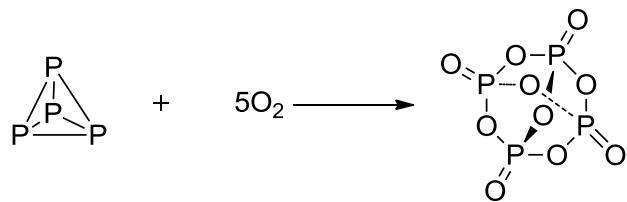
1.1 Project Aims

Our goal was to develop new, zero waste processes for the formation of organophosphate and organophosphite plastics additives. We hoped to eliminate the need for chlorine gas and phosphorus trichloride in the manufacturing processes by investigating direct reactions of white phosphorus, alcohols and air.

1.2 White Phosphorus

White phosphorus is one of the three major allotropes of the element phosphorus. It was first isolated in 1669 by Hennig Brand from urine.¹ It takes the form of a tetrahedron of 4 covalently bonded phosphorus atoms, where each phosphorus atom is bonded to each of the other three phosphorus atoms. The bond angles within the tetrahedron are all 60 ° and the P-P bond lengths are 221pm.² White phosphorus is a waxy solid which melts at 44 °C and has a boiling point of 280 °C, it usually has a yellow tint due to the presence of coloured impurities. It is extremely reactive towards air, reacting with excess oxygen to form phosphorus pentoxide P₄O₁₀. This reaction is exothermic and rapidly heats the phosphorus above its auto-ignition temperature of about 30 °C. At this point the solid phosphorus bursts into flame releasing thick clouds of white phosphorus pentoxide smoke (Scheme 1).

Scheme 1. Reaction of White Phosphorus with Air



Brand's synthesis of white phosphorus from urine was successful as urine contains phosphates. On sufficient prolonged heating in the presence of carbon the oxygen atoms are removed as carbon monoxide and the phosphorus atoms form the P₄ tetrahedron. Currently white phosphorus is produced from apatite ore. This ore largely consists of calcium phosphates (e.g. Ca₅(PO₄)₃(OH)). On heating in a submerged-arc electric furnace at 1150-1400 °C with carbon and silica white phosphorus is produced. Carbon acts as a reducing agent in this process and oxygen is removed as carbon monoxide.

1.2.1 Toxicity of White Phosphorus

Aside from its pyrophoric nature, white phosphorus is also difficult to work with due to its extreme toxicity. The United Kingdom Health and Safety Executive (HSE) set a maximum short term workplace exposure limit of 0.3 mg/m³ and a maximum long term exposure limit of 0.1 mg/m³.³ These limits refer to the maximum amount of inhalable dust or vapour that can be safely present in the atmosphere of a working environment.

The extremely corrosive properties of white phosphorus make it toxic by inhalation, ingestion and skin contact. Studies have shown the oral LD₅₀ to be 3.03-3.76 mg/kg for rats.⁴ This makes white phosphorus comparable in oral toxicity to potassium cyanide (LD₅₀ 6 mg/kg rat).⁵

Symptoms of white phosphorus exposure include lethargy, abdominal pain, loosening of teeth, jaw swelling, bone necrosis, unconsciousness and death. Mute swans given low doses of P₄ orally were found to suffer damage to the gizzard and intestinal lining and liver haemorrhage. Liver haemorrhage was the cause of death at the lethal dose.⁴

Phosphorus burns are particularly severe because white phosphorus is very lipid soluble, so the burning pieces quickly embed themselves in subcutaneous fat layers. White phosphorus will continue to burn as long as it is exposed to atmospheric oxygen and has been known to burn all the way to the bone of burn victims. Phosphorus burns are often fatal, with human fatalities recorded in people with less than 10 % of their body surface area burnt.⁶ People who suffer major white phosphorus burns are expected to later suffer the toxic effects of white phosphorus exposure.

1.2.2 Safety Precautions for Working with White Phosphorus

Due to its toxicity and flammability, working with white phosphorus requires many specific precautions to be taken. For working with white phosphorus on a laboratory scale the production of “white phosphorus sand” is recommended. This consists of 1-2 mm diameter beads of the chemical, which are prepared by the following method:-

Bulk phosphorus (stored under water) is melted at 50 °C. A small amount of molten phosphorus is then pipetted into a Schlenk flask containing warm water and a stirrer bar. There should be a flow of nitrogen through the Schlenk flask while the transfer is being

performed. The mixture is allowed to cool slowly with vigorous stirring to room temperature allowing the white phosphorus to solidify in the form of beads. The water can then be removed *in vacuo* and the “white phosphorus sand” stored in a glove box.

An alternative method of preparing white phosphorus for laboratory use is to cut small pieces of P₄ from the bulk sample. If the bulk white phosphorus (stored under water) is heated to 35 °C it becomes soft enough to cut, though importantly it will not melt. Small pieces (0.1 – 0.3 g) can then be cut away using an ordinary kitchen knife. These pieces can then be rapidly transferred into a Schlenk flask using tweezers. A flow of nitrogen must be maintained through the Schlenk flask while the transfer is being performed. After a sufficient amount of phosphorus has been transferred to the flask it is sealed and the P₄ pieces are dried *in vacuo*. These can then be transferred into a glove box and stored for further use. Both methods of white phosphorus preparation have been employed over the course of these studies. The latter ‘cutting’ method has been found to be safer and to involve much less oxidation of the P₄ during transfer.

While working with white phosphorus it is recommended to wear safety glasses, thick Kevlar gloves, a face shield, a lab coat and an aluminium clad PBI apron with sleeves and a lab coat. Reactions involving white phosphorus and a solvent should always be carried out behind a blast shield as there is a danger of explosion if the mixture is exposed to air. A large volume of copper sulfate solution and a plant spray should be kept close to hand to extinguish any fires.

To safely dispose of white phosphorus the waste should be submerged in saturated copper sulfate solution and left to stand for several days.⁷ Larger particles should be cut up under the surface of the solution so all the white phosphorus is exposed to the copper sulfate. Copper sulfate solution reacts with the white phosphorus to form copper phosphide (Cu_3P). The phosphide can then be removed from the solution by filtration and oxidized to copper phosphate (Cu_3PO_4) using 5 % sodium hypochlorite solution. This can then be disposed of as copper-containing waste.

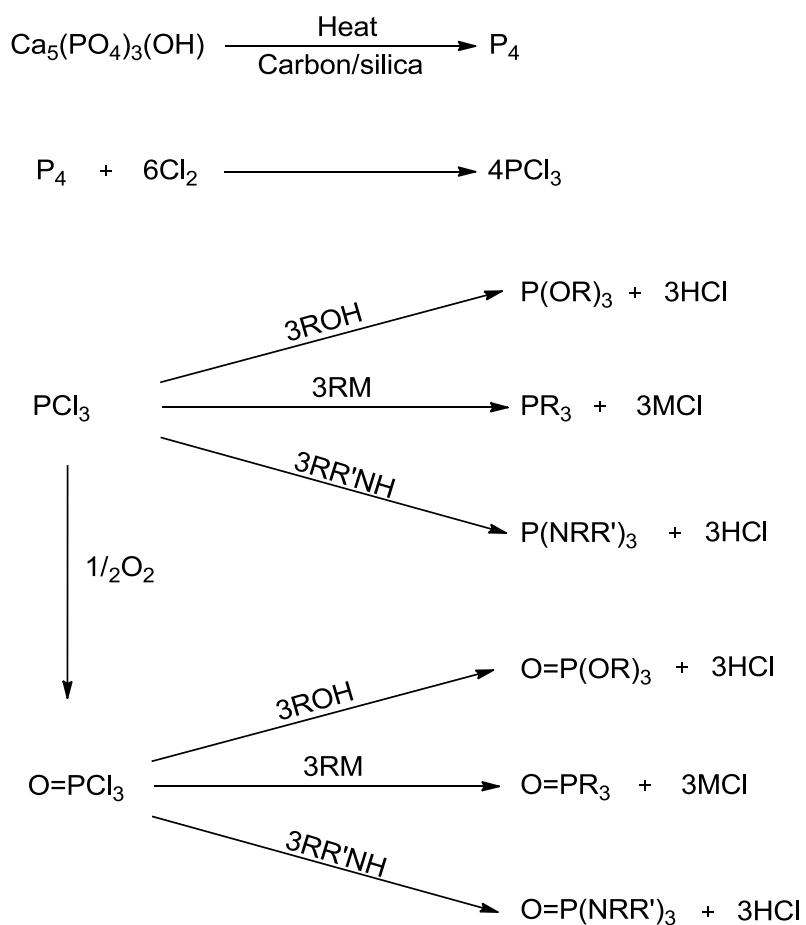
It is advisable to keep a bottle of sterile “Ben Hur Solution” on hand for the treatment of any white phosphorus burns.⁸ This is an aqueous solution of 3 % copper sulfate, 5 % sodium bicarbonate, 1 % hydroxy-ethyl-cellulose and 1 % lauryl sulfate. This should be applied to the affected area, allowing the particles of white phosphorus to be removed mechanically. This approach to treatment is somewhat controversial due to the possibility of copper poisoning when copper solutions are applied to open wounds.⁶ NATO instead recommends treating white phosphorus burns with sodium bicarbonate solution alone, to neutralise phosphoric acid and extinguish flames.⁹ The particles of white phosphorus can then be removed manually, providing the wound is constantly irrigated while this is done. This method will not destroy the white phosphorus so it is vital to ensure **all** traces of phosphorus are removed before irrigation of the wound is stopped. Fortunately neither of these procedures have proved necessary over the course of these studies.

1.3 Production of Phosphorus-Containing Compounds from White Phosphorus

White phosphorus is a major resource for the formation of phosphorus-containing chemical compounds. Most organic phosphorus chemicals are produced from white phosphorus via a halogenated phosphorus trichloride intermediate. About 300 000 tons of white phosphorus per year is converted to phosphorus trichloride, most for the purpose of further synthetic reactions. This is done because whilst white phosphorus is very reactive, getting it to react in a controlled way can be challenging. Reactions between white phosphorus and nucleophiles follow complex, often poorly understood mechanisms and can result in the formation of a wide variety of products.¹⁰

The reaction of chlorine with white phosphorus to produce phosphorus trichloride was first documented by J. B Dumas in 1859.¹¹ The reaction proceeds rapidly and gives excellent yields. Phosphorus trichloride can then react with nucleophiles in controlled nucleophilic substitution reactions to form a wide variety of phosphorus(III) compounds (Scheme 2). Phosphorus(V) compounds can be easily formed by oxidizing the phosphorus trichloride to phosphorus oxychloride before reacting with nucleophiles or by reacting nucleophiles with PCl_5 . Alternatively phosphorus(V) compounds can be made by simple oxidations of phosphorus(III) compounds. The ease with which these reactions are performed makes these attractive synthetic routes for industry.

Scheme 2. Formation of Useful Phosphorus-Containing Chemicals (Selected Examples)



1.3.1 White Phosphorus Functionalisation

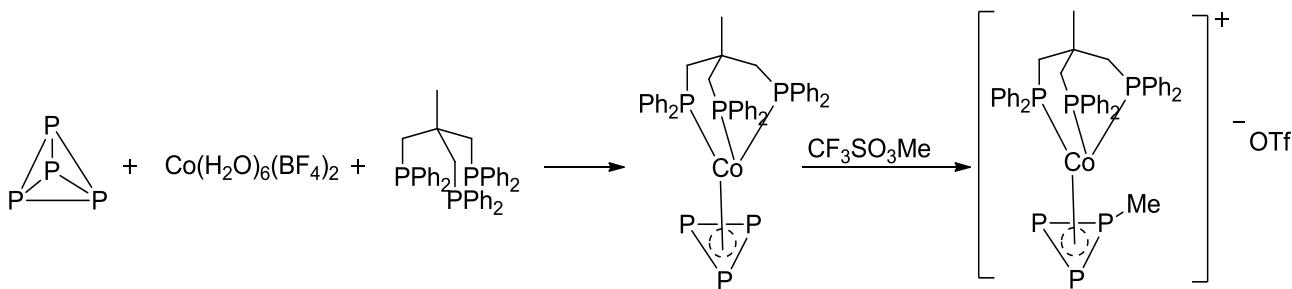
A more efficient way to make phosphorus compounds would be to control the direct reaction of P_4 with nucleophiles. This would allow products to be synthesized without using chlorine and without producing HCl waste. To this end there has been much recent work on the activation of the P_4 tetrahedron using transition metal complexes. It is hoped that by binding P_4 to a transition metal centre, the phosphorus can be activated towards selective P-O or P-C bond formation. Complexes formed from white phosphorus and

transition metal compounds have been known for some time. The first, $(\text{PPh}_3)_2\text{ClRh}(\eta^2\text{-P}_4)$, was synthesized by Ginsberg and Lindsell in 1971.¹² Since then white phosphorus has been reacted with a wide range of transition metals, most commonly Rh, Ir, Co, Mo, Ru and Fe. Examples of complexes containing P_1 , P_2 , P_3 , P_4 , P_5 , P_6 and larger units as ligands are all known.^{13, 14} Two recent reviews on the complexation of white phosphorus to transition metals have appeared in *Chemical Reviews*.^{15, 16}

Progress has been slower in using white phosphorus/transition metal complexes to form useful phosphorus-containing compounds. Recently however work has started to appear in which P-C or P-O bonds are formed from white phosphorus via a transition metal complex. Some examples of this work are given below.

An air sensitive but thermally stable cobalt triphos complex bearing a cyclo P_3 ligands was prepared from white phosphorus by Sacconi *et al.*¹⁷ by heating triphos, white phosphorus and $\text{Co}(\text{H}_2\text{O})_6(\text{BF}_4)_2$ in THF. The product crashed out of solution and other products of the reaction were not identified. Later work showed this compound could be reacted with methyl triflate or trimethyloxonium tetrafluoroborate at 0 °C to alkylate the P_3 ligand (Scheme 3).¹⁸

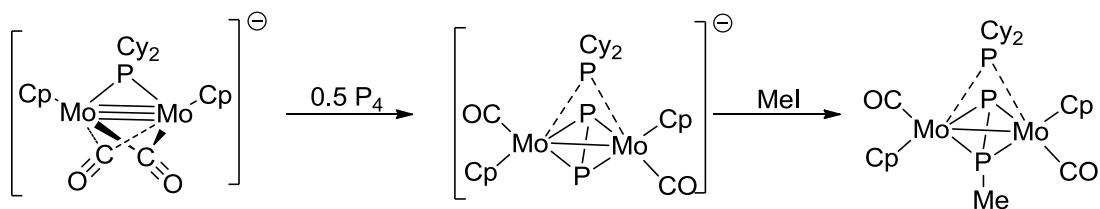
Scheme 3. Alkylation of Cobalt P₃ Ligand



This reaction was shown to work with the rhodium and iridium analogues however no further work was done to investigate whether the methylated P₃ ligand could undergo further reaction to form useful phosphorus products.

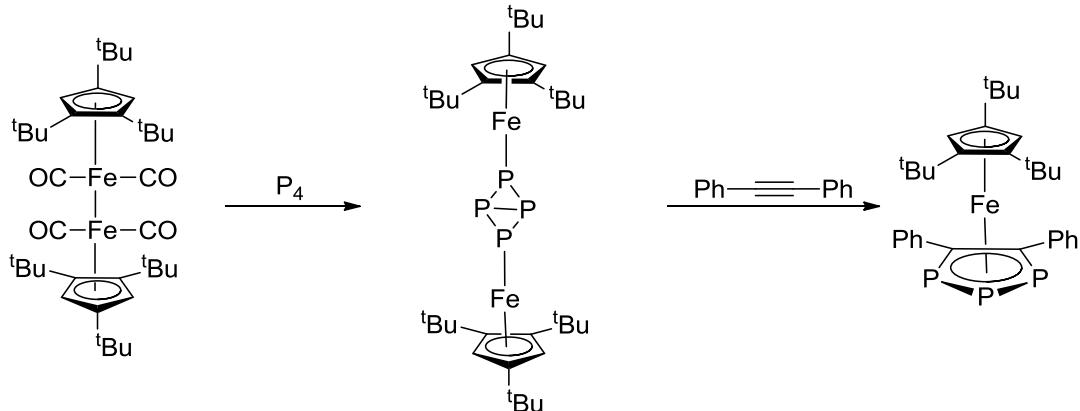
Ruiz *et al.* demonstrated the reaction of white phosphorus with the molybdenum containing anion $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2]^-$ produced a diphosphorus bridged complex at room temperature.¹⁹ The reaction of this complex with methyl iodide at room temperature resulted in methylation of one of the bridging phosphorus atoms (Scheme 4). The structure of the original diphosphorus anion was deduced from calculations and spectroscopic data and the structure of the methylated product was confirmed by X-ray diffraction.

Scheme 4. Alkylation of Molybdenum Diphosphorus Bridge



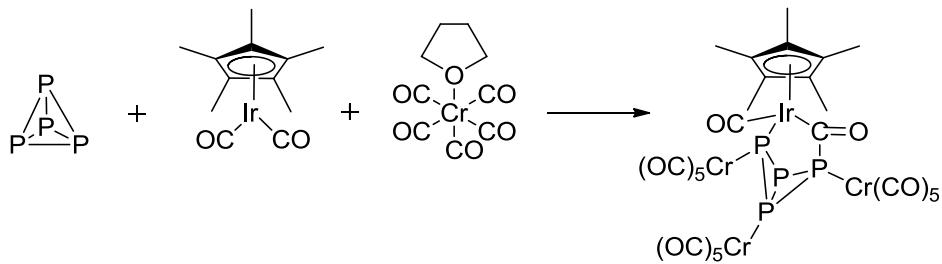
Perhaps the most well known phosphorus/transition metal complexes are the pentaphosphapherrocene derivatives. The first of these, pentamethylpentaphosphapherrocene, was first synthesized by Scherer *et al.* in 1987. By the reaction an excess of white phosphorus with $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$.²⁰ Further work from the same group showed it was possible to synthesize a so-called butterfly complex, with P_4 bound between two iron atoms (Scheme 5).²¹ This was found to react with diphenyl acetylene to form a 3 phosphorus, 2 carbon heterocycle coordinated to the iron centre.²² Similar work has been reported using mixed iron – molybdenum butterfly complexes.²³ As yet there have been no examples of separating organo-phosphorus compounds from complexes of this type.

Scheme 5. Synthesis of a Mixed C-P Ring



Carbon monoxide insertion into a phosphorus-metal bond has been demonstrated by the one pot reaction of white phosphorus with chromium and iridium carbonyl species leads to the formation of a C-P bond in the reaction shown in Scheme 6.²⁴

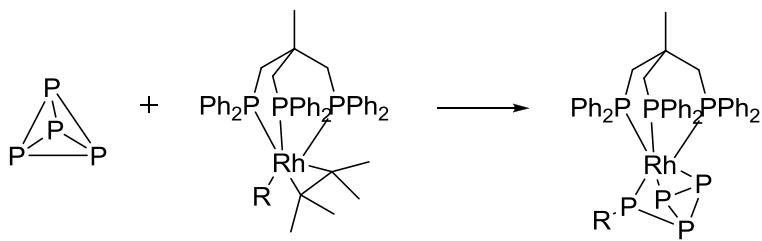
Scheme 6. CO Insertion into Ir-P bond



This reaction was found to proceed under either photochemical or thermal conditions (70 °C or 15 °C, UV) and was said to proceed via η^2 coordination of P_4 to the iridium followed by CO insertion into one of the P-Ir bonds. As yet the product of the reaction has not been reacted on further to separate phosphorus compounds from the iridium metal but the direct attachment of a carbonyl to P_4 is an interesting starting point.

Ligand transfer reactions have been documented which allow the formation of P-C bonds from P_4 without the need for an extremely electrophilic alkyl reagent. This was first shown with alkyl rhodium triphos complexes (Scheme 7).²⁵ When these complexes were reacted with P_4 the alkyl group was found to transfer onto a phosphorus atom as the P_4 bound to rhodium. It was shown to be possible to obtain a low yield of primary phosphines by reacting the resulting complexes with H_2 after the ligand transfer processes. It was also shown that electrophiles would react selectively with the already functionalized atom of the P_4 moiety. Sadly the resulting complexes were extremely unstable, limiting this as a possible synthetic route to secondary phosphines.

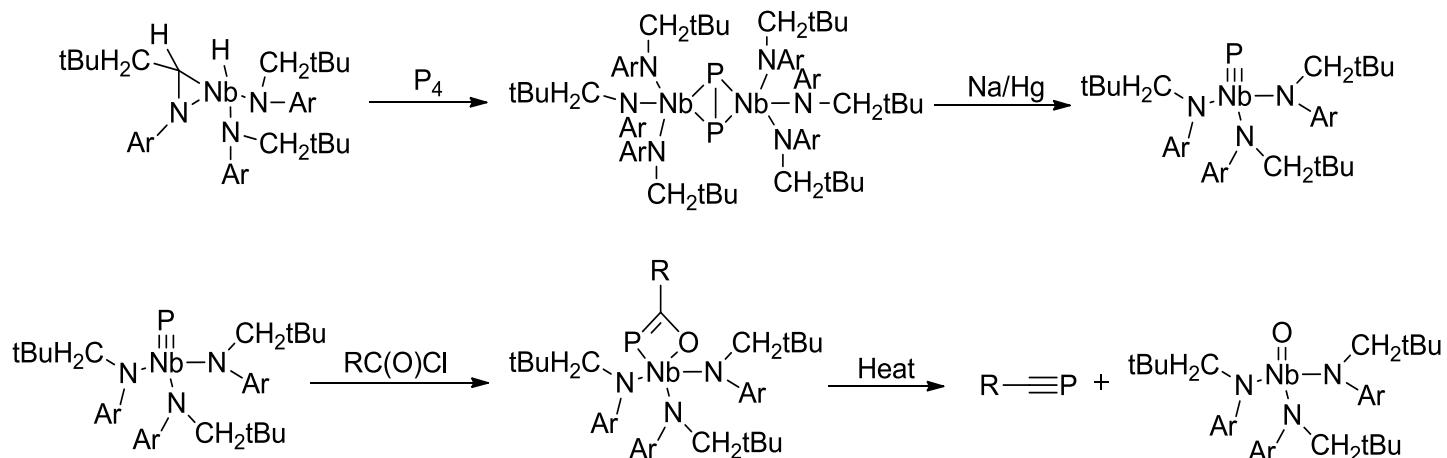
Scheme 7. Ligand Transfer Reaction. R = Me, Et, *i*Pr



A drawback of this reaction is that the alkyl rhodium species had to be generated in a separate reaction before the white phosphorus was added. If a true catalytic cycle could be developed whereby the original catalyst could be regenerated post cleaving of organophosphorus compounds this reaction could be very interesting indeed.

Recent work by Cummins *et al.* has demonstrated the synthesis of phosphaalkynes directly from white phosphorus (Scheme 8).²⁶ They reacted a niobaziridine hydride complex with P₄ to form a bridging diphosphorus diniobium complex. This complex was then reduced with 1% Na/Hg amalgam to split the dimer giving a phosphide anion with a P-Nb triple bond. Reacting this anion with pivaloyl chloride (*t*-BuC(O)Cl) and then heating to 70 °C resulted in the release of the corresponding phosphaalkyne and the formation of a niobium oxo complex.

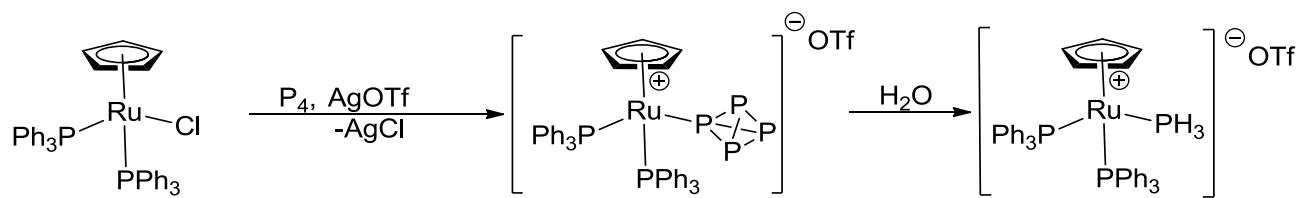
Scheme 8. Phospha-alkyne Synthesis from P₄. R = tBu



Unfortunately very few stable phosphaalkynes are known¹ so the scope of this reaction is limited. Nevertheless it is encouraging to see small organophosphorus molecules produced from P₄ and the formation of a P-C triple bond directly from P₄ is synthetically impressive. A comprehensive review of C-P bond formation reactions was published by Perruzini *et al.*²⁷

Some work has been conducted on the formation of P-O bonds from P₄/transition metal complexes. Stoppioni *et al.* published a reaction in which white phosphorus is hydrolysed after coordination to a ruthenium centre (Scheme 9).²⁸ The reaction proceeds at room temperature and yields one equivalent of ruthenium-bound PH₃ and a mixture of various phosphorus oxoacids.

Scheme 9. Hydrolysis of Ruthenium Bound P₄



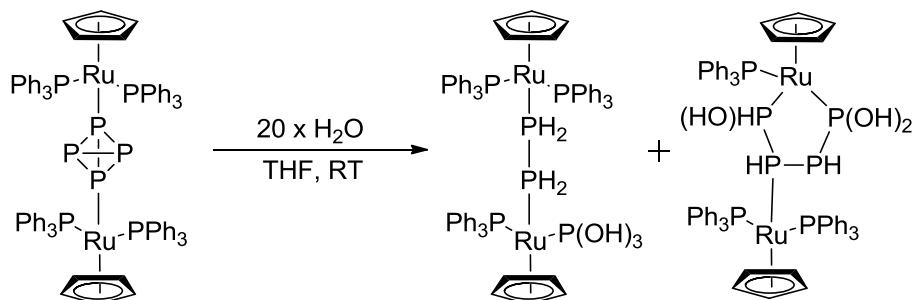
Later work by the same group showed the diruthenium butterfly complex

[{CpRu(PPh₃)₂}₂(μ,η^{1:1}-P₄)] [CF₃SO₃]₂ could be synthesized by reacting 2 equivalents of CpRu(PPh₃)₂Cl with P₄.^{29, 30} By hydrolysing this compound under various conditions several interesting P-H and P-O bond containing compounds were formed (Scheme 10).

Reacting the complex with a 100 fold excess of water formed a mixture of

CpRu(PPh₃)₂PH₃, CpRu(PPh₃)₂P(OH)₃, CpRu(PPh₃)₂PH(OH)₂ and CpRu(PPh₃)₂-P₂H₄-RuCp(PPh₃)₂. Alternatively reacting with only a 20 fold excess of water over 6 days yielded CpRu(PPh₃)₂-P₂H₄-RuCp(PPh₃)P(OH)₃ and the ring complex [{CpRu(PPh₃)₂} {RuCp(PPh₃)} {μ^{1:4:3},η^{2:1}-P(OH)₂PHPHPH(OH)}] [CF₃SO₃]₂. In both cases free phosphorus oxyacids were also formed during the process.

Scheme 10. Hydrolysis of Diruthenium P₄ Complex



It is interesting to note the degree to which the reactivity of the P₄ cluster has been modified by its coordination to ruthenium in these complexes. P₄ is stable to hydrolysis and is often stored under water, whereas the hydrolysis of these ruthenium complexes proceeds readily at room temperature.

A 1999 patent showed that complexes of a wide variety of metals were able to catalyse the reaction of water with white phosphorus to form phosphorus oxyacids without using a PCl₃ intermediate.³¹ Ag, Au, Pt, Pd, Ru, Rh, Ni, Co, Cr and Mn complexes all showed some ability to catalyse the oxidation of white phosphorus at temperatures lower than 200°C. Copper complexes were found to be particularly effective homogeneous catalysts. Heterogeneous palladium black was also an excellent catalyst and showed good selectivity for the formation of P(III) over P(V) oxyacids. These reaction systems are promising candidates for forming a wider range of compounds containing a P-O bond, providing highly efficient catalysts are identified.

Work on the functionalization of white phosphorus without the use of transition metals has also appeared in the literature. A recent review on P₄ activation by main group elements was presented by Scheer et al.³² Much of this work focuses on the formation of P-C bonds directly from P₄.

Work done in the 1960s by Rauhut and Semsel investigated the direct reaction of white phosphorus with organometallic compounds to form phenyl phosphines.³³ A 40 % yield of phenylphosphine was achieved by cautiously adding white phosphorus to a solution of

phenyl lithium in ether and then refluxing for three hours. The reaction mass was then hydrolysed with water to yield the product (Scheme 11). Whilst all the white phosphorus was consumed much of it went to form an unidentified yellow solid which did not react under alkaline hydrolysis conditions.

Scheme 11. Reaction of P₄ with Phenyllithium



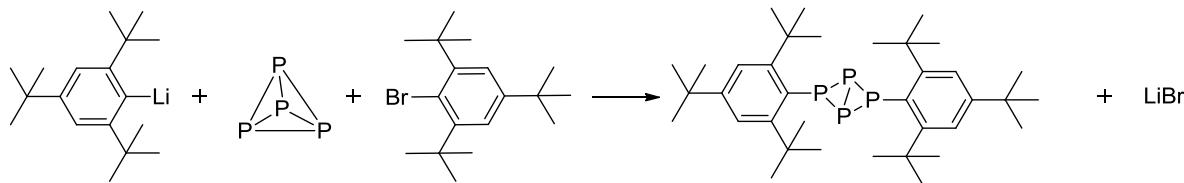
A similar result was obtained by replacing the phenyl lithium in ether with phenyl magnesium bromide in THF however the phosphine yield was lower (25 %). In a follow up paper Rauhut and Semsel went on to show that tertiary phosphines could be synthesized by adding butyl halides to the reactions outlined above. The reaction of phenyl lithium and butyl halide with white phosphorus yielded PhP(Bu)₂ (24 %), Ph₂P(Bu) (39 %) and O=PPh₂(Bu). Similarly butyl lithium was reacted with butyl bromide and white phosphorus to form tributyl phosphine in 39 % yield. This type of reaction was not attempted using other alkyl or aryl halides. Whilst the combination of expensive starting materials and poor selectivities make these reactions uninteresting from a production perspective, they do serve to illustrate that phosphines can be synthesized directly from white phosphorus.

Other reactions of P₄ with organolithium reagents are documented in the literature. Fritz and Härrer reacted white phosphorus with both methyl lithium and tert-butyl lithium.³⁴ In both reactions the products were reported as Li₃P₇, Li₂P₇R and LiP₇R₂, however the

reaction mixtures were only analysed by ^{31}P NMR. The reaction of white phosphorus and lithiumdihydrogenphosphide (PH_2Li) has also been reported.³⁵ The products of the reaction were Li_3P_7 and PH_3 , once again the reactions were monitored by ^{31}P NMR.

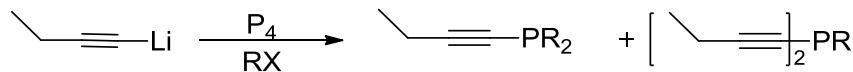
The reaction of P_4 with 2,4,6-tri-tert-butylphenyllithium and 1-bromo-2,4,6-tri-tert-butylbenzene cleaves one P-P bond and leaves a product with two Mes* groups bound to the P_4 tetrahedron (Scheme 12).³⁶ This product has been characterized by ^{31}P NMR and X-ray crystallography. It is probable that the lithiate attacks the P_4 first and the electrophilic bromide traps the intermediate phosphorus anion formed before it can reform the P-P bond. The extremely bulky nature of the Mes* substituents will stabilize the product. Sadly the yield of the reaction was only 5 %.

Scheme 12. Formation of Bis(2,4,6-tri-tert-butylphenyl)bicyclotetraphosphane



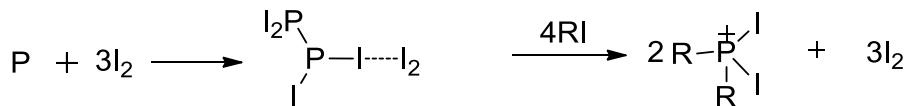
Gusarova *et al.* have successfully reacted white phosphorus with lithiated alkynes to produce phosphines (Scheme 13).³⁷ P_4 was treated with but-1-ynyllithium followed by the addition of alkyl halides (ethylbromide and propylchloride were used as examples). The reactions produced mixtures of two tertiary phosphines; one with one but-1-yne substituent and two alkyl substituents, one with one alkyl and two but-1-yne substituents. The combined yields of these products did not exceed 20 %.

Scheme 13. Reaction of P₄ with Lithium Acetylenides. R= Et, Pr



The reaction of red phosphorus with iodine and alkyl iodides has been shown to produce dialkyl phosphonic acids (R₂P(=O)H) in good yields after hydrolysis (Scheme 14).³⁸ The authors found that using 5 iodine atoms to every phosphorus atom gave the best yields and speculated that P₂I₄/I₂ complexes were the reactive species.

Scheme 14. Reaction of Red Phosphorus with Iodoalkanes. R = Me, Et, Pr, Bu, Oct

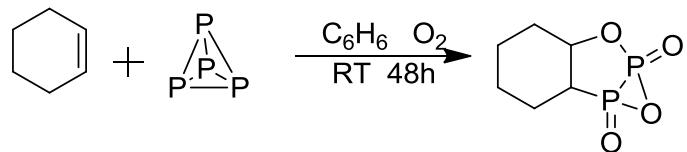


The reactions were performed using methyl, ethyl, propyl, butyl and octyl iodide. Best results were obtained with octyl iodide at 125-130 °C for 36 hours. This gave a 91 % yield of dioctyl phosphonic acid. Yields of at least 75 % were obtained with ethyl, propyl and butyl iodides as well. Whilst these reactions use red rather than white phosphorus they do show that phosphorus iodine species can be useful intermediates for P-C as well as P-O bond formation.

There are examples in the literature of one pot reactions of white phosphorus and alkenes.^{39, 40} Walling *et al.* reported that a solution of white phosphorus in benzene reacted with cyclohexene to form a ‘phosphorate’ with the molecular formula C₆H₁₀P₂O₄

(Scheme 15). This product was not well characterized, however on treatment with 40 % HNO₃ it formed phosphoric acid and C₆H₁₀PO₃H. The reaction scheme proposed by the authors is shown below.

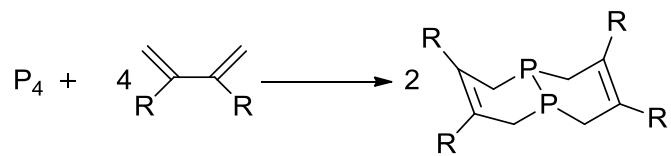
Scheme 15. Reaction of P₄ with Cyclohexene



The reaction was shown to work with various alkenes and to be accelerated by addition of a radical initiator (AIBN). The reaction products were shown to react with alcohols to form dialkyl phosphites with yields of 28-29 %. This work appears to be worthy of further investigation using modern characterization methods.

More recently Cummins et el. have demonstrated the reaction of white phosphorus with conjugated 1,3-dienes to produce diphosphanes (Scheme 16). This reaction was conducted photochemically with the starting materials dissolved in hexane at 55-60 °C and irradiated for 12 hours to facilitate the reaction. This reaction was performed using 2,3-dimethyl-1,3-butadiene and 1,3-butadiene as the starting dienes.⁴¹

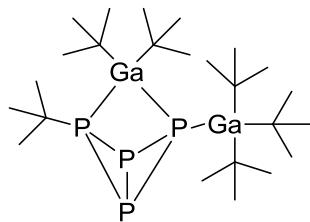
Scheme 16. Reaction of P₄ with 1,3-dienes. R = H, Me



Another direct route to P-C bond formation is the degradation of the P₄ tetrahedron by CN⁻ ions.⁴² Schmidpeter *et al.* found the reaction of [K(18-crown-6)]Na cyanides with P₄ formed P(CN)₂⁻ containing salts and P₁₅⁻ clusters. Although this is a rare good example of a small phosphorus molecule synthesis directly from P₄, P(CN)₂⁻ in itself is not hugely interesting from a synthetic standpoint.

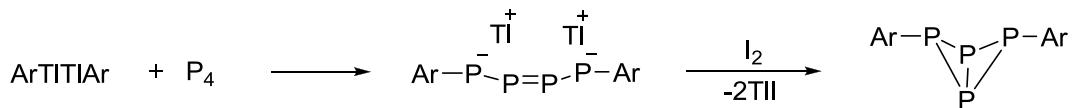
Power and Barron reacted white phosphorus with Ga^tBu₃ in pentane at room temperature.⁴³ The reaction resulted in the formation of a mixed gallium-phosphorus cage Ga₂P₄^tBu₆ (Figure 1) in an impressive 84 % yield. This molecule contains a P-C bond as one of the gallium ^tBu groups migrates onto a phosphorus atom. No attempts have been made to isolate a simple phosphorus-containing molecule from this cage.

Figure 1. Mixed Gallium-Phosphorus Cage



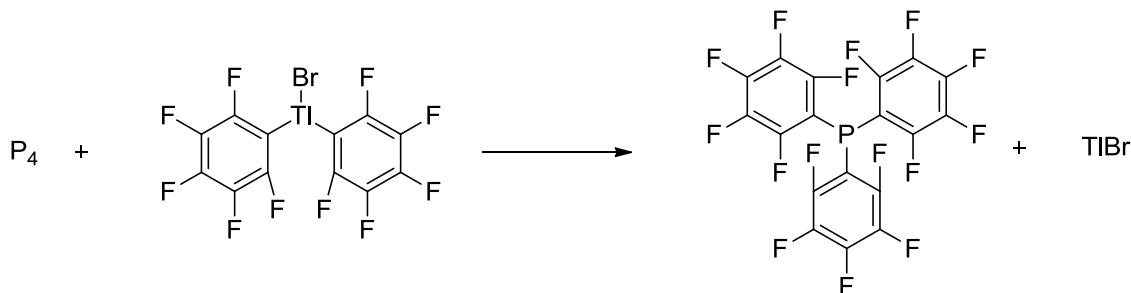
P_4 has also been reacted with the $[ArTlTlAr]$ dimer ($Ar = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$) to give a linear P-P-P-P dianionic species with thallium counter ions (Scheme 17).⁴⁴ Oxidation of this unusual compound with iodine caused one of the bonds of P_4 tetrahedron to reform, giving a neutral Ar- P_4 -Ar compound. The overall yield of this from white phosphorus was 21 %.

Scheme 17. Reaction of P_4 with $ArTlTlAr$. $Ar = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$



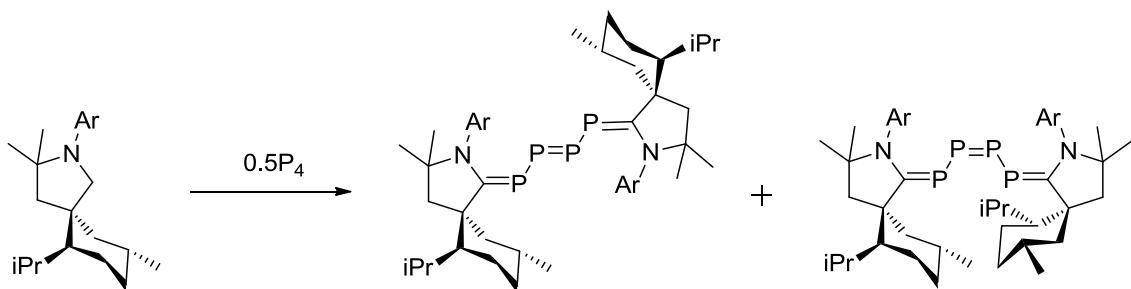
In an extremely rare example of phosphine formation directly from P_4 , Deacon and Parrot heated bromobis(pentafluorophenyl) thallium(III) with white phosphorus at 190 °C for 4 days.⁴⁵ Tris(pentafluorophenyl)phosphine was formed as the product in 70 % yield (Scheme 18). While the expensive starting material would prohibit using this kind of reaction as a large scale route to phosphines, it is heartening to see a high yielding direct reaction of white phosphorus producing a simple phosphorus-containing molecule.

Scheme 18. Direct Phosphine Formation from P₄



It is worth giving mention the work of Guy Bertrand *et al.*, who have had some success reacting P₄ with carbenes as an alternative to white phosphorus activation with transition metals.⁴⁶ The reaction of a cyclic (alkyl)-(amino)carbene (CAAC) with half an equivalent of white phosphorus caused the formation of a 4 atom P chain, connecting two CAAC units (Scheme 19).

Scheme 19. Reaction of P₄ with a CAAC

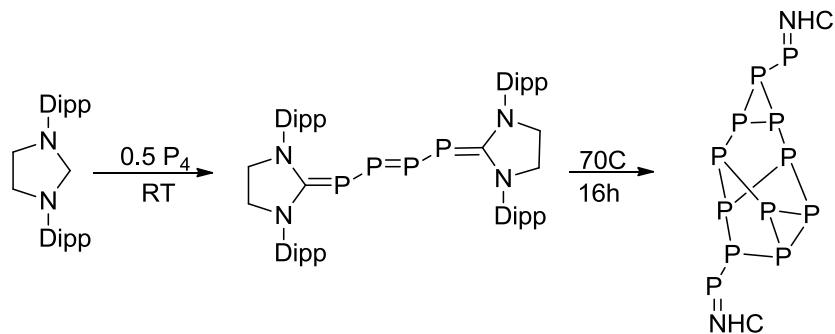


This reaction was performed under mild conditions (two hours stirring at room temperature in hexanes) and gave a decent 65 % yield. The four atom phosphorus chain was then further reacted with a dialkene in a Diels-Alder style reaction. This gave a six membered ring incorporating two of the phosphorus atoms and forming two P-C bonds.

This reaction showed 95 % diastereoselectivity. The authors hope further work with CAACs could provide an easy route to chiral organo phosphorus molecules.

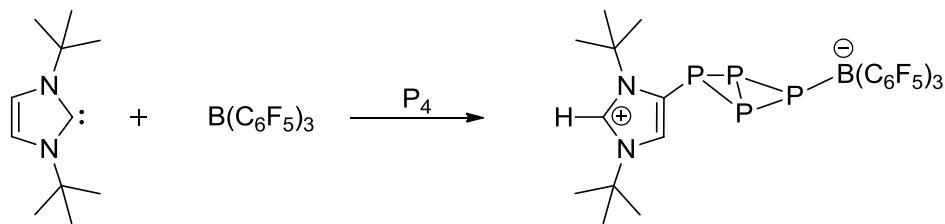
In a similar reaction Bertrand *et al.* reacted P₄ with two equivalents of an N-heterocyclic carbene (NHC).⁴⁷ At room temperature the reaction formed a tetraphosphatriene complex analogous to that formed in the reaction of P₄ with CAACs (Scheme 19). On prolonged heating at 70 °C however this compound formed an unusual 12 P cluster in 81 % yield (Scheme 20).

Scheme 20. Reaction of P₄ with an NHC



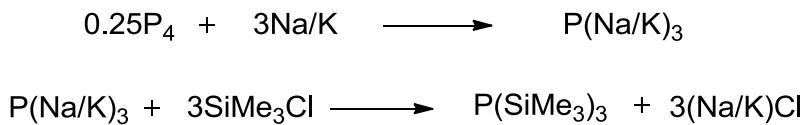
Tamm *et al.* have used a frustrated carbene borane Lewis pair to selectively cleave one phosphorus-phosphorus bond of the P₄ tetrahedron.⁴⁸ An imidazolium-4-yl type carbene and B(C₆F₅)₃ were added to white phosphorus at RT to give a product with P₄ sandwiched between the borane molecule and the carbene (Scheme 21). It is not immediately apparent how this reaction could be used to generate small molecules from P₄. It is however a synthetically impressive achievement to complex P₄ within a frustrated Lewis pair.

Scheme 21. Reaction of P₄ with a Frustrated Lewis Pair



The reduction of white phosphorus with alkali metals is known and has been used to facilitate the formation of P-Si bonds. Refluxing white phosphorus in dimethoxyethane with sodium potassium alloy produces a solution of P(K/Na)₃. The slow addition of SiMe₃Cl to this solution followed by a 24 hour reflux gives P(SiMe₃)₃ which can be isolated in 60-75 % yield (Scheme 22). Both steps of this reaction are exothermic and there are serious safety issues with refluxing solutions of white phosphorus and alkaline metals for extended periods. Nonetheless this is a rare example of a small phosphorus molecule being produced from P₄ in good yield, without the use of a halogenated intermediate.^{49, 50}

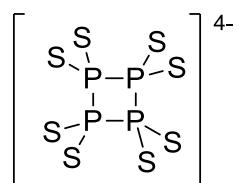
Scheme 22. Synthesis of P(SiMe₃)₃



The reaction of P₄ with chalcogens has also been reported. The reaction of P₄ with sulfur and triethylamine forms the anionic P₄S₈⁴⁻ in 50 % yield (Figure 2).⁵¹ This molecule has

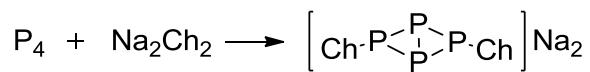
the highly unusual structural motif of four phosphorus atoms arranged in a square, with P-P-P bond angles of almost exactly 90 °.

Figure 2. $\text{P}_4\text{S}_8^{4-}$



Karaghiosoff *et al.* reacted white phosphorus with Ch^{2-} where $\text{Ch} = \text{S}, \text{Se}, \text{Te}$.⁵² The reactions were performed in N-methyl imidazole at RT, P_4 butterfly complexes with the chalcogen atoms in the exo positions were identified as products (Scheme 23). Sadly further reactivity of these complexes has not been demonstrated.

Scheme 23. Reaction of P_4 with Chalcogen Anions. $\text{Ch} = \text{S}, \text{Se}, \text{Te}$

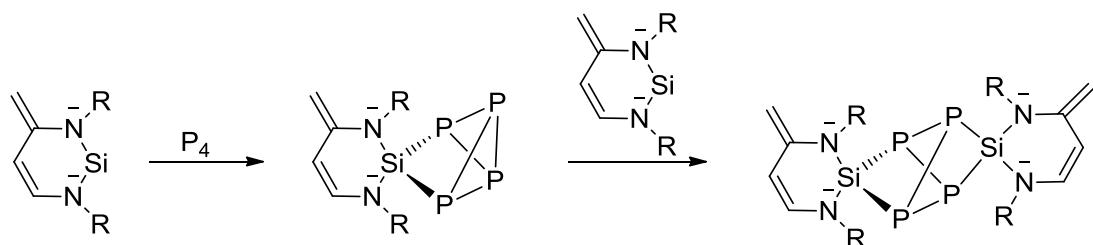


From the literature reviewed so far it appears the P_4 tetrahedron is more susceptible to nucleophilic as opposed to electrophilic attack. This trend was noted in the recent review of Scheer *et al.* mentioned earlier.³² The direct attack of unactivated P_4 with electrophiles has rarely been reported. It appears extremely forcing conditions are required to make this feasible. White phosphorus has been shown to react with trifluoriodomethane to form $(\text{CF}_3)_3\text{P}$ however reaction temperatures of over 200 °C for 48 h were required.^{53, 54}

Even under these forcing conditions the selectivity was at best 70 %, with $(CF_3)_2PI$ and $(CF_3)PI_2$ also being formed. Reactions between nucleophiles and white phosphorus on the other hand are reported extensively.⁵⁵

In an unusual case of P_4 reacting directly with an electrophilic species, Driess *et al.* reacted P_4 with one equivalent of a silylene compound at room temperature (Scheme 24).⁵⁶ Whilst silylenes are often considered nucleophilic, calculations have suggested in this case the silylene is acting as an electrophile.⁵⁷ The reaction formed an adduct with the P_4 tetrahedron η^2 bound to the silicon atom. Reaction with a further equivalent of P_4 gave a butterfly complex.

Scheme 24. Reaction of P_4 with Silylenes



The reluctance of P_4 to react with electrophilic species was noted by Wolfgang Schoeller in the computational paper mentioned above.⁵⁷ In a theoretical study calculations indicated a high activation barrier for electrophilic attack of the P-P bond. This is said to be due to the low π -character of the bonds. In the reaction of a silylene with P_4 mentioned above (Scheme 24), Schoeller showed the participation of a second P_4 molecule lowered the energy of the transition state, facilitating the unusual electrophilic attack.

Despite all this impressive synthetic work the goal of generating a catalytic way of synthesizing small phosphorus molecules has proved surprisingly elusive. A recent review noted the lack of literature examples of catalytically converting all four atoms of the P₄ tetrahedron into a single product ⁵⁸ There are few examples of useful compounds being cleaved from these complexes after P-C or P-O bond formation. Where metals have been used they have been used stoichiometrically, rather than catalytically which makes these routes unsuitable for industry. Furthermore less work has been done on P-O as opposed to P-C bond formation. This is unfortunate as efficient P-O bond formation could provide a route to phosphates and phosphites, which are of prime interest to us here.

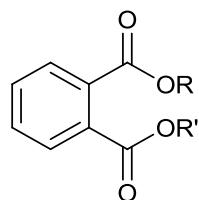
1.4 Triaryl Phosphates and Phosphites as Plastics Additives

Organophosphorus compounds are added to many plastics during processing to enhance various properties of the polymer during use. Triorgano phosphates are added to polymers to act as plasticizers and/or flame retardants. Plasticizers are added to polymers to increase their flexibility and make them easier to process. They also lower the glass transition temperature of the polymer making it more suitable for low temperature applications. The most common type of plasticizers are external plasticizers. These function by disrupting secondary bonding interactions between polymer chains; the plasticizer solvates polar sites along the polymer chains. This prevents these sites becoming points of cross chain interaction. Plasticizers are mainly used in thermoplastics

as these are much less cross linked than thermosetting resins and are required to be much less brittle.

The market for plasticizers is largely dominated by phthalates (Figure 3) however triaryl phosphates still maintain a small but significant share of the market. For some particular applications (cellulose-based polymers for example) phosphates are preferred over phthalate plasticizers due to their light stability, better rheological properties at low temperatures and flame retardant properties.⁵⁹ Indeed whilst most phosphate plasticizers are very effective flame retardants, high phthalate loading can actually increase the flammability of a polymer.⁶⁰

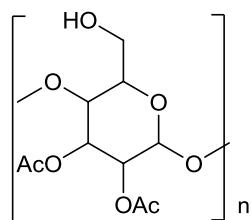
Figure 3. Phthalate Plasticizer, R/R' = various alkyl chains



Triphenyl phosphate is the most common plasticizer for cellulose acetate (Figure 4). This polymer is used in clothing, playing cards, greenhouse windows and film stock. Prior to 1940 cellulose nitrate (with camphor as a plasticizer) was used to produce film stock, however this compound is potentially explosive and extremely flammable. It can become unstable at temperatures as low as 38 °C.⁶¹ Modern cellulose acetate film is far more stable. As triphenyl phosphate is colourless it allows the production of a clear acetate film, whilst bestowing sufficient flexibility and crucially high resistance to fire. Triphenyl

phosphate is resistant to extraction with hydrocarbon oils making it an attractive plasticizer in some engineering applications.

Figure 4. Cellulose Acetate



Flame retardants are added to almost all commercially available plastics. This is because thermal decomposition of polymers releases flammable gases (hydrocarbons, carbon monoxide, etc). This presents a risk of starting a fire and helps an already existing fire spread rapidly. Flame retardants are added to minimise these risks. Halogen-containing flame retardants like tetrabromobisphenol A dominate the flame retardant market at present however health concerns have been raised about these compounds. The EU's REACH legislation which called for a gradual phase out of halogen based flame retardants came into force on the 1st of January 2007.⁶² This opens up new opportunities in the market for non halogenated flame retardants like triaryl phosphates. It is believed phosphorus based flame retardants function by facilitating polymer degradation in case of a fire. Phosphorus acid is produced by the burning flame retardant. This then reacts with the polymer to form a non flammable charred layer over the surface of the polymer. Tritolyl phosphate, triphenyl phosphate and trioctyl phosphate are all commercial flame retardants. All these molecules are easy to process, also act as plasticizers, have low

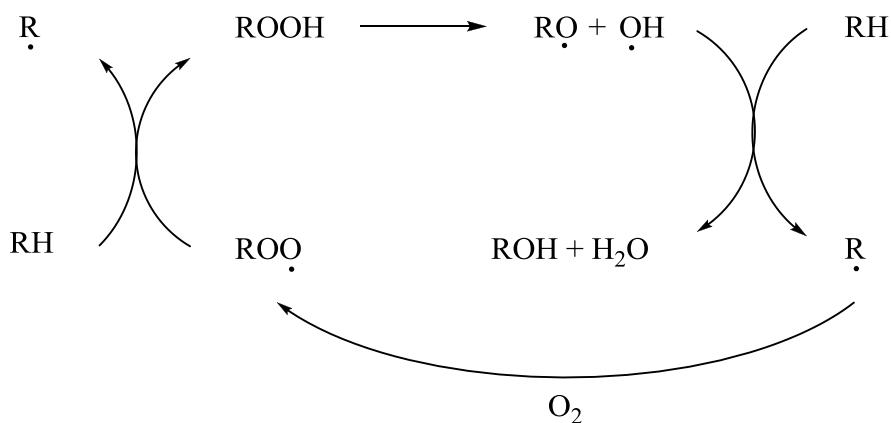
volatility and bestow excellent low temperature flexibility. Tritolyt phosphate is the most commonly used of these due to its compatibility with PVC.¹

Recent studies have shown the efficacy of triphenyl phosphate as a flame retardant is increased when used in conjunction with phenol-formaldehyde resins (novolacs). These two flame retardants form a complex charred residue when burnt. This residue is said to be less volatile than the residue produced by triphenyl phosphate alone, giving better resistance to fire. This combination has been shown to be very effective for both styrene acrylonitrile copolymers and ABS resins.^{63, 64} Use in ABS in particular would greatly enhance the demand for triphenyl phosphate.

Tritolyt phosphate is also used as an additive in leaded petrol, where it acts as a lead scavenger. Tetraethyl lead deposits in petrol engines can cause pre-ignition of the fuel before the spark plug fires. This is more problematic in engines which highly compress the fuel prior to ignition. Organophosphates convert tetraethyl lead deposits to more soluble lead phosphates, eliminating the problem.⁶⁰ Whilst leaded petrol is much less common in the western world it is still used in aviation fuel, where tetraethyl lead is added as an antiknock agent. Another application for tritolyl phosphate is as an additive for high pressure lubricants to decrease wear on metal parts.⁶⁵ Up to 3 % organophosphate can be added to jet turbine oil for example. Triphenyl phosphate is also used for this application, though to a much lesser extent.

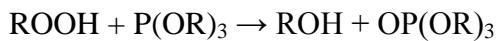
Triaryl phosphites are added to protect polymers from oxidation during processing and in general use. Plastics tend to degrade in the presence of oxygen by the chain reaction mechanism shown in the illustration below (Figure 5).⁵⁹

Figure 5. Oxidation of a Polymer



The initial radical species ($R\cdot$) is formed by heat, light or mechanical friction homolytically cleaving a bond on the polymer chain. In the presence of oxygen the radical then oxidizes to form a peroxy radical ($ROO\cdot$). The peroxy radical abstracts a hydrogen atom from the polymer creating another radical and forms a hydroperoxide ($ROOH$). The peroxide can then decompose to form more radical products, which can go on to attack the polymer chain. This degradation cycle is particularly troubling during processing when the polymer is at elevated temperatures (~200 °C for polyolefins).

Phosphite antioxidants slow this cycle by breaking down peroxide molecules into non radical products by the reaction shown below⁵⁹:

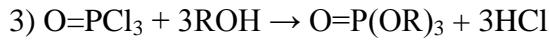
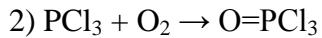
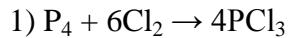


Two types of polymer antioxidants are used; primary and secondary ones. Primary antioxidants (which are radical trapping molecules) are more effective at protecting polymers during normal usage. Phosphites are secondary antioxidants, which function by removing peroxides. These antioxidants are most effective at the elevated temperatures of the polymer processing when peroxide decomposition becomes a much more rapid and therefore has more impact on polymer degradation. It is usual to add both primary and secondary antioxidants to polymers. Triorgano phosphites (P(OR)_3) are produced in huge quantities as secondary antioxidants (>90000 ton/year is produced by Chemtura's Morgantown plant alone). Amongst these production of triaryl phosphites is particularly significant. Tris(nonylphenyl) phosphite (TNPP) is one of the most commonly used secondary antioxidants.

Triaryl phosphites are also used as low cost ligands for catalysis. Perhaps the most well known example of this is the use of nickel(0) phosphite complexes for the hydrocyanation of alkenes.⁶⁶ Nickel(0) phosphites have also been shown to be effective in many catalytic systems including catalysing the cotrimerisation of 3,3-dimethylcyclopropene with methyl acrylate⁶⁷ and catalysing the coupling of aryl halides to form polyaromatic compounds.⁶⁸ Palladium(0) phosphite compounds are also known and have been shown to have applications in for catalysis.⁶⁹

1.4.1 Current Synthetic Route to Triaryl Phosphates

Like many phosphorus compounds, triaryl phosphates are produced using white phosphorus as precursor and are formed via a PCl_3 intermediate (see Scheme 2). The reaction proceeds in the 3 steps (Equations 1-3).⁷⁰



Both aliphatic and aromatic homoleptic phosphates are produced in this way. This process is atom and energy inefficient. 1.5 moles of chlorine gas are consumed for every mole of product formed and three moles of HCl waste are also produced. In the case of aromatic phosphates large amounts of aluminium trichloride are added to catalyse the final step of the reaction. This adds expense and increases the environmental risks of the process.⁷¹ Whilst the HCl waste can sometimes be sold on or used in another process this is unlikely to offset a significant part of the overall cost of the process. Significant environmental risks are involved in production and transport of chlorine gas as well as phosphorus trichloride.

Triaryl phosphites are manufactured in a similar process, where PCl_3 is reacted directly with aromatic alcohols, without the intermediate oxidation to $\text{O}=\text{PCl}_3$ first. The problems

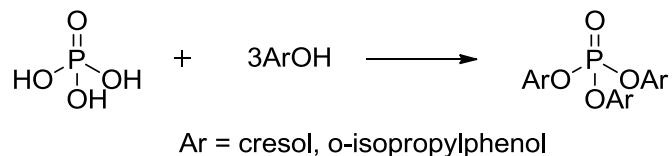
with stoichiometric chlorination and the generation of HCl waste are the same for the production of phosphites as they are for phosphates.

PCl₃ acts in these processes as a reactivity moderator, and is used in a stoichiometric manner. Because of the environmental concerns, its replacement with a catalyst, acting in a sub-stoichiometric manner, is highly desirable.

1.4.2 Alternative Synthetic Routes to Triaryl Phosphates and Phosphites

It is possible to synthesize triaryl phosphates from phosphoric acid as opposed to phosphorus oxychloride (O=PCl₃). Segall *et al.* synthesized a series of triaryl phosphates by reacting the appropriate phenols with phosphoric acid in xylene (Scheme 25).⁷¹ Various transition metal catalysts (at a loading of 0.6 wt%) were found to enhance the rate of phosphate formation. Phosphoric acid can be synthesized by treating apatite ore with sulphuric acid (wet process)⁷² so this route eliminates the need to work with white phosphorus or phosphorus trichloride. There are several drawbacks to this synthesis however. Even with water removal by Deans-Stark apparatus there was a problem with the co-formation of diaryl phosphates (O=P(OAr)₂OH) and the highest conversion to triaryl phosphate achieved was 85 %. The reaction rates were slow even in the presence of catalyst and high temperatures (150 °C) were required. Finally phosphoric acid is extremely corrosive and can corrode stainless steel. This makes it unattractive to work with on an industrial scale.

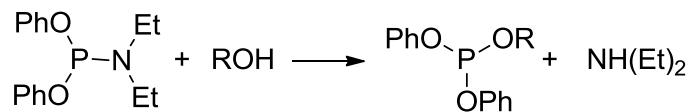
Scheme 25. Synthesis of Phosphates from Phosphoric Acid



Ilia *et al.* have developed a variation of the industrial synthetic method, in which gaseous phosphorus oxychloride in a nitrogen stream is passed through a solution of phenol and 20 % aqueous sodium hydroxide.⁷³ Sodium chloride and water are formed instead of HCl waste and phosphates are obtained in a near quantitative yield. This method still uses PCl₃ as the starting material and therefore offers no significant improvement on the existing industrial synthesis. Furthermore there is the added cost and environmental impact of sodium hydroxide to be considered.

A laboratory scale route to heteroleptic phosphates and phosphites has been developed by Perich and Johns using phosphoramidites as the source of phosphorus (Scheme 26).⁷⁴ Reaction of N, N-diethylphosphoramidite (Et₂NP(OPh)₂) with alcohols in the presence of tetrazole (CN₄H₂) and THF gave triorgano phosphites. These were oxidized to phosphates by addition of 3-chloroperoxybenzoic acid (MCPBA) *in situ*, giving near quantitative yields of the phosphates.

Scheme 26. Synthesis of Phosphites/Phosphates from Phosphoramidites



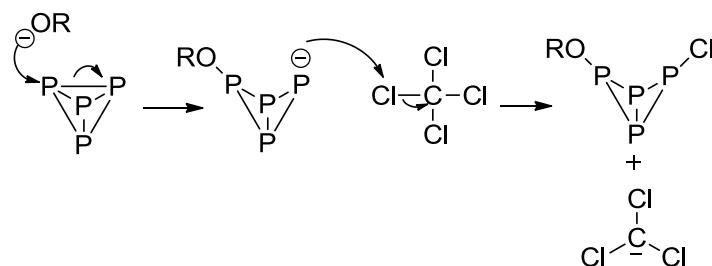
Phosphorus trichloride was used as a precursor during the preparation of the phosphoramidates. Unless a route direct from white phosphorus could be developed the use of phosphoramidates would complicate rather than simplify the production of triorgano phosphates. No examples of such a direct reaction to form phosphoramidates could be found in the literature.

Efforts have been made to develop an alternative synthesis for triorgano phosphites. As oxidation from phosphites to phosphates is often trivial, a better synthetic route to phosphites would automatically provide a better route to many phosphates as well.

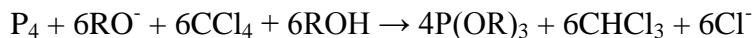
Brown and coworkers developed a one pot synthesis of trialkyl phosphites from white phosphorus, sodium alkoxide and alcohol achieving yields of up to 82 % (Scheme 27).⁷⁵

⁷⁶ The drawback of the Brown method is that an excess of tetrachloromethane was used to facilitate the reaction. The tetrachloromethane was included to trap the phosphide anion after attack of P₄ by nucleophilic RO⁻ ions.

Scheme 27. Reaction of P₄ with Alcohol and Tetrachloromethane



The products of this reaction rapidly react with ROH to yield chloroform, $P_4(OR)_2$ and Cl^- . $P_4(OR)_2$ can then suffer further attack by RO^- and subsequent reaction with more tetrachloromethane. The reaction continues by repetition of this mechanism until all the P-P bonds are broken and $P(OR)_3$ is produced. The overall reaction equation is given as:



Without the involvement of chlorine (in the form of tetrachloromethane) in the reaction the authors stated that P-P bonds were likely to reform after nucleophilic attack due to the extreme nucleophilicity of the phosphide anion.

A similar method is described in a BASF patent.⁷⁷ White phosphorus was found to react with alcohols to form phosphites. These reactions were also performed in chlorinated solvents, for the same reasons as outlined above. In the reactions described in the patent air and NO_2 were bubbled through the reaction to help oxidize the white phosphorus. Due to the toxicity of tetrachloromethane and chloroform (both are carcinogens) these routes are not significant improvements on the current industrial method. To make it practical it would be necessary to find a less harmful electrophile to trap the phosphorus anion.

The oxidation of white phosphorus with organic peroxides in the presence of alcohols has been investigated.⁷⁸ Reactions using phenol were found to be slower than those using aliphatic alcohols. It was speculated that this may be because phenol is a radical scavenger and so inhibits any radical oxidation. Toluene was found to be the best solvent

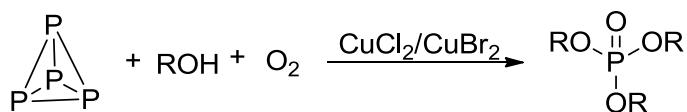
and tert-butyl peroxide the best oxidant. Phenol formed diphenyl phosphonate as the major product though conversion was never complete and unreacted P₄ was present at the end of the reactions. Also tested were similar reactions with transition metal catalysts present. Vanadyl acetylacetone was found to be the best catalyst for the oxidation of white phosphorus with dibenzoyl peroxide in phenol; upping the conversion to organophosphorus compounds from 20 to 58 %. Surprisingly this reaction was not tried with the superior tert-butyl peroxide oxidant. Obviously air is both easier to handle and cheaper than peroxides as a reagent so air would be a preferable oxidant. The reaction between white phosphorus and alcohol with air as the oxidant and vanadyl(V) acetylacetone as the catalyst is not documented in the literature. It should be noted that there would be serious safety issues involved in mixing white phosphorus and peroxide on a large scale.

A series of studies by Budnikova *et al.*, have investigated the possibility of synthesizing organo phosphorus compounds from white phosphorus by electrochemical means.^{79, 80, 81, 82} Usually these studies concentrated on the formation of trialkyl phosphates with some success. Interestingly Cu(II) and Ni(II) complexes were shown to catalyse P-O bond formation under electrochemical conditions.⁸⁰ To achieve this, aliphatic alcohols were reacted with white phosphorus in acetonitrile at 20-60 °C. Et₄NI was used as the electrolyte and the products formed after electrolysis were predominately phosphates (up to 70 % yield). These electrochemical systems were also shown to be capable of forming triphenyl phosphate in 82 % yield.⁷⁹

As the authors are keen to point out the electron is an extremely “green” reagent (zero waste) and the cost of electricity is low compared to the cost of starting chemicals.⁸¹ Despite these genuine advantages in the years since the electrochemical synthesis of triphenyl phosphate was first reported no major producer has switched to this route of production. This is most likely because the switch from non electrochemical to electrochemical synthesis requires a major redesign of the industrial reactors used. This represents a major investment which producers will be hesitant to make in a competitive market. Furthermore the increased power and maintenance costs of an electrochemical plant will serve to deter producers from making the switch. It would be more appealing to develop a route by which the same reaction can be performed with a catalyst and heat without the electrochemical input.

Abdreimova *et al.*, have been attempting to develop catalyst/phosphorus/alcohol/oxygen systems with some very interesting results.^{83, 84} It was shown that copper(II) complexes catalyse P-O bond formation and that the nature of the ligands on the metal affect the final product distribution (Scheme 28). Copper halides were found to selectively enhance the formation of phosphates whereas copper sulfate and copper acetates were found to selectively enhance the formation of phosphites. No changes in the reaction conditions other than the change of catalyst are said to be necessary to cause this remarkable change in selectivity. Whilst the reactions described all used aliphatic alcohols as starting materials, the authors describe phenol as a potential reactant.

Scheme 28. Catalytic Formation of Phosphates from P₄



For safety reasons an excess of catalyst and alcohol was always present relative to the amount of white phosphorus (the reaction of white phosphorus with oxygen can be explosive without the presence of alcohol and catalyst). Toluene was used as a solvent for these reactions for two reasons. It dissolves white phosphorus (forming a saturated solution of approximately 4 % w/v at room temperature) and it is immiscible with H₂O. It is claimed that the water of reaction forms a separate phase and is therefore less likely to hydrolyze any phosphite/phosphate product formed. The highest yield of phosphite obtained by this group was 87 %.⁸⁴ This was produced using 1-propanol and copper(II) stearate (Cu(C₁₇H₃₅CO₂)₂) as a catalyst. The highest selectivity towards phosphate was 88 %.⁸⁵ This was produced using n-butanol and copper chloride as the catalyst.

The same group expanded this work to investigate a wider range of catalysts and alcohols.^{85, 86} The catalytic formation of triphenyl phosphate was documented in these papers, using iron(III) chloride as a catalyst. The reaction was said only to proceed in the presence of iodine as an additive. Presumably in this instance the reaction proceeded via a PI₃ or P₂I₄ intermediate however even then the yield was low (28 %). This is in stark contrast to aliphatic alcohols where good yields were reported even without the addition of iodine. Possibly the phenol acts as a radical scavenger impeding the oxidation of white

phosphorus and slowing the reaction. Steric hindrance is another possible explanation as to why the reaction proves more taxing with aromatic alcohols.

In an earlier paper a similar set up was used with PdCl_2 or Ru(OH)Cl_3 as catalysts and the addition of a “co-oxidant”.⁸⁶ The reason for the selection of such an unusual ruthenium catalyst is unclear, it is possible $\text{O}=\text{Ru(H)Cl}_3$ was used and the Ru(IV) catalyst was named in error. Whilst the authors claim success, the palladium and ruthenium catalysts were ineffective when used on their own. When FeCl_3 or CuCl_2 were added as “co oxidants” the results were similar to when these metals were used as catalysts in the later study. From this we can conclude that PdCl_2 and Ru(OH)Cl_3 do not catalyse the reaction between white phosphorus and alcohol and the so called co-oxidants were responsible for all of the observed catalytic effects. The other co-oxidants trialled in this study were NaNO_2 , NaBrO_3 and benzoquinone.⁸⁷ These compounds are reduced during the reaction and may not be regenerated by oxygen. The non-catalytic nature of this reaction makes it much less interesting as a potential industrial route. Benzoquinone produced exclusively phosphite product when reacted with white phosphorus, butanol and air. NaNO_2 produced dibutyl phosphonate when it was used as an oxidant and provided a slow reaction rate (the rate order was $\text{CuCl}_2 > \text{NaNO}_2 > \text{FeCl}_2$). NaBrO_3 produced the phosphate. A summary of the catalytic systems trialled by this group is presented in the table below.

Table 1. Catalyst Trials by Abdreimova et. al.

Catalyst ^b	Alcohol	Major Product	Max Conversion ^a
CuSO₄	BuOH	phosphite	65 %
CuCl₂	Various Aliphatic	phosphate	88 %
Cu(CH₃CO₂)₂	Various Aliphatic	phosphite	93 %
Cu(C₁₇H₃₅CO₂)₂	Various Aliphatic	phosphite	82 %
Cu(C₃H₇CO₂)₂	Various Aliphatic	phosphate	85 %
Cu(NO₃)₂	i-AmOH	phosphate	63 %
NaNO₂	BuOH	phosphonate	32 %
Fe(NO₃)₃	i-AmOH	phosphonate	16 %
FeCl₃	BuOH	phosphate	73 %
FeCl₃ with I₂	PhOH	phosphate	28 %

a. By $^{31}\text{P}\{\text{H}\}$ NMR spectrum of a sample taken from the final reaction mass

b. PdCl₂ and Ru(OH)Cl₃ were also trialled as catalysts however they were only used with co-catalysts present and did not perform better than the co catalysts used alone

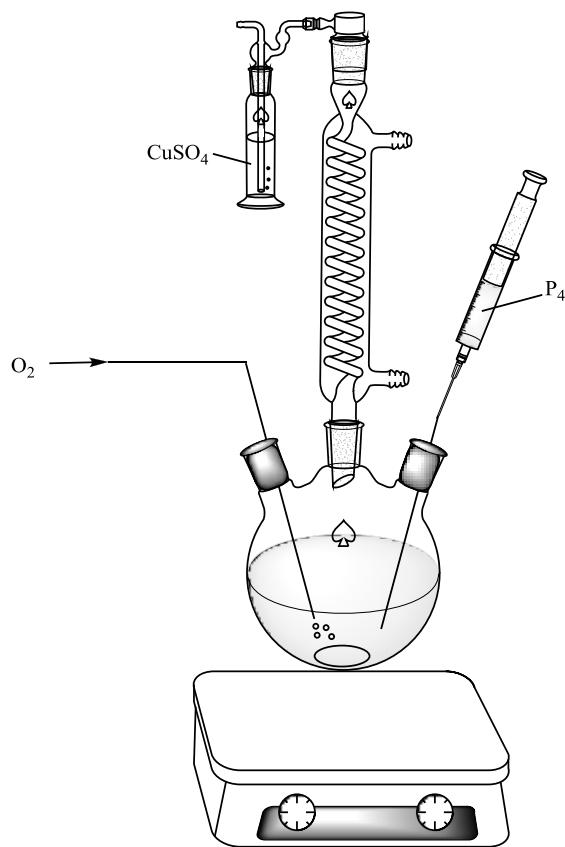
From the comprehensive literature review presented above it can be concluded that the most promising route to triaryl phosphates is the reaction of phenol, white phosphorus and air with transition metal catalysts. It is notable that only a small number of metal and ligand combinations have been tried as catalysts for this reaction system, despite the wide ranging successes complexing white phosphorus to transition metals (see above). In this study we have attempted to develop new superior catalyst systems for reactions of this type.

2. Catalyst Trials

2.1 General Experimental Setup

The apparatus used throughout for the reactions of white phosphorus with phenols is shown in Figure 6. The catalyst to be tested was charged to a 3 neck round bottomed flask. Phenol, iodine and a small volume of toluene were added to this flask. The mixture was stirred and heated to 80 °C and a solution of white phosphorus in toluene was slowly added to the reaction using a syringe pump. Air was bubbled through the reaction masses at a rate of 30-45 mL/min for around 7 hours. The composition of the dark mixture after the reaction was analysed by ^{31}P NMR. For further details of the reaction setup see the experimental section.

Figure 6. Reaction Apparatus



2.2 Copper Catalysts

Due to the success of Abdreimova *et al.* at catalysing the reaction between aliphatic alcohols and white phosphorus with copper it was hypothesized that copper species might also catalyse the reaction of white phosphorus with phenol.^{83, 84, 85, 86} Copper(II) sulfate, copper(II) chloride and copper(II) acetate were tested to this end. An equimolar amount of copper sulfate was used with respect to P_4 (P_4 : $CuSO_4$ ratio 1:1). Iodine was also added as a co catalyst (0.1 equivalents of I_2). The presence of copper sulfate served to prevent the direct reaction of P_4 with air (no phosphorus smoke was observed⁸⁸) however the

colour of the reaction mass darkened quickly as the addition of P₄ progressed. The original blue, transparent colour of the solution was not regenerated by bubbling air through the reaction mass, instead a black solid was observed to be gradually precipitating out of the solution. Powder X-ray diffraction showed the solid to contain elemental copper suggesting that the copper sulfate was oxidizing the phosphorus - however bubbling air through the reaction mixture was not affecting reoxidation of the copper catalyst. There were four singlet peaks observed in the ³¹P{¹H} NMR spectrum of a sample of the final reaction mass however none of these corresponded to expected reaction products. The peaks were observed at 13.9, 7.8, 5.3 and 1.9 ppm. Similar results were obtained for copper(II) chloride and copper(II) acetate. Solid elemental copper also precipitated from the reaction using copper(II) chloride. An unknown solid was precipitated in the reaction using copper(II) acetate. The solid could not be conclusively identified by X-ray powder diffraction. It appeared to contain copper pyrophosphate (Cu₂P₂O₇) however other species were also present. It is interesting to note that when a certain excess of P₄ with respect to copper(II) chloride was added to a reaction, this resulted in the direct oxidation of white phosphorus by air, observed as formation of white smoke above the reaction mixture. This observation strongly suggests that reoxidation of the catalyst is not occurring at the required rate if it is occurring at all. Best results for copper catalysts were obtained when pyridine was added to copper(II) chloride prior to reaction. Pyridine was added to help solubilise the catalyst however pyridine can also potentially coordinate to copper⁸⁹ and could therefore influence the redox properties of the catalyst. Results for the copper catalysed reactions are shown in Table 2.

Table 2. Copper Catalysed Reactions

Catalyst	Mol. Ratio cat:P ₄ :I ₂	Rate P ₄ addition /mmol/h/ mmolcat	³¹ P NMR of reaction mass	Solid products
CuSO₄/I₂	1:1:0.1	0.50	4 singlets δ _p = 13.9, 7.8, 5.3 and 1.9 ppm	Cu (s)
CuCl₂/I₂	1:1:0.03	0.25	Smoke observed after all Cu(II) was consumed	
CuCl₂/I₂/Py	10:1:0.03:0.5	0.21	OP(OPh) ₂ (OH) [42 %] OP(OPh) ₃ [14 %] Unknown Product δ _p = 3.4 [26 %] and further minor products.	Cu (s)
Cu(CH₃CHO₂)₂/I₂	2:1:0.3	0.11	No phosphorus peaks observed in the solution	Unidentified solid

All reactions were conducted in toluene with a 20:1 mol ratio of phenol to P₄. Reaction temperatures ranged from 60-80 °C. See experimental section 6.2.1 to 6.2.4 for details.

2.3 Iron Catalysts

The only example in the literature of a catalysed reaction between white phosphorus and phenol used an iron(III) chloride and iodine catalytic system.⁸⁵ Iron is a desirable metal for the catalysis of industrial processes due to its low toxicity, low cost and ready availability. A series of different iron catalysts were tested in the hope of improving the poor yield reported in the literature.⁸⁵ Iron(III) chloride, iron(II) bromide, ferrocene, iron(II) bipyridine dichloride, iron(II) stearate, iron(II) phosphate, iron(III) diacetate chloride, cyclopentadienyliron dicarbonyl dimer and iron(III) acetylacetonate were tested to this effect. The iron catalysts generally performed better than the copper catalysts. The

use of iron(III) chloride with iodine gave a reasonably good conversion to triphenyl phosphate which improved when a small amount of pyridine was added to the reaction and the P₄ addition rate was slightly slowed. Some phosphorus smoke formation was seen towards the end of the iron(III) chloride reactions suggesting there are problems with the rate of reoxidation of this catalyst. Iron(II) bromide was tried as a catalyst to try and eliminate the need for the iodine. This reaction had to be abandoned due to the rapid formation of phosphorus smoke. The reactions using tris(bipyridine)iron(II) chloride, iron(II) phosphate and iron(II) stearate also resulted in the formation of phosphorus smoke. Iron(III) diacetate chloride was synthesized according to the method of Lau *et al.*⁹⁰ It showed some catalytic effect, and all the white phosphorus in the reaction was consumed. The mixture formed by the end of the reaction consisted of triphenyl phosphate and an unknown compound with a ³¹P{¹H} NMR shift of -4 ppm. Whilst both these compounds were separated from the catalyst by distillation *in vacuo*, they co-distilled and therefore could not be separated from each other in this manner. Ferrocene and the cyclopentadienyliron dicarbonyl dimer facilitated complete conversion from P₄ to products, however the conversion was not selective and numerous phosphorus-containing products were observed in the ³¹P NMR spectrum of the mixture after reaction.

Iron(III) acetylacetone was selected as a more organic soluble iron catalyst. Iron(III) acetylacetone has been used as a catalyst in a variety of oxidation reactions reported previously in the literature. The wide range of oxidizing agents (and substrates) used in conjunction with it include H₂O₂ (used in stereospecific oxidations of sulfides),⁹¹ high pressure oxygen (oxidation of phenol)⁹² and air (aerobic oxidation of ethylenic bond in β-

isophorone).⁹³ The catalytic reaction (see above for reaction setup) using a ratio of 2 moles of iron(III) acetylacetone to 1 mole of P₄ gave a black oil as the product (after removal of the solvent *in vacuo* at RT). The only peak present in the ³¹P{¹H} NMR had a shift of δ_p = -17.5 ppm, corresponding to triphenyl phosphate. As there was no insoluble solid component present, this suggests all the white phosphorus had been consumed and converted to triphenyl phosphate. Distilling this oil at 160 °C (0.4 mbar) yielded triphenyl phosphate (100 % purity by ³¹P NMR, 33 % yield). As this seemed to be a particularly effective catalyst, further reactions were attempted with it – varying the reaction conditions. The isolated yield was improved to 61 % by repeating the reaction on a larger scale, with a stoichiometric amount of phenol as opposed to an excess.

Unfortunately pure iron acetylacetone could not be recovered when distillation *in vacuo* was used to separate the product from these reactions. Some non volatile black solid remained after distillation, however this appeared (by IR) to contain impurities as well as both triphenyl phosphate and iron acetylacetone. The IR spectra shows many of the peaks present in Fe(acac)₃ however strong absorbance peaks at 1164, 1492 and 1595 cm⁻¹ were also present.

Table 3. Iron Catalysed Reactions

Catalyst	Mol Ratio cat:P ₄ :X ₂ :PhOH	Rate P ₄ addition/ mmol/h/ mmolcat	³¹ P NMR of reaction mass	Isolated organophosphorus product
FeCl ₃ /I ₂	3:2:0.3:20	0.18	OP(OPh) ₃ [78 %]	
FeCl ₃ /	3:2:0.3:20	0.10	OP(OPh) ₃	OP(OPh) ₃ [19 %]

Py^a/I₂			[96 %]	
FeBr₂	3:2:0:20		Reaction abandoned due to immediate formation of phosphorus smoke	
Fe(C₁₇H₃₅CO₂)₂/I₂	2:1:0.3:12	0.11 mmol/h	Final reaction mass contained a significant amount of unreacted P ₄	
Fe(bpy)₃Cl₂/I₂	2:1:0.3:6		Smoke observed after 45 % of the P ₄ had been added.	
FeCp₂/I₂	2:1:0.3:12	0.10 mmol/h	P(OPh) ₃ [31 %] 7 minor resonances	Not worked up
[CpFe(CO)₂]₂/I₂	1:1:0.3:12	0.10 mmol/h	OP(OPh) ₃ [69 %] P(OPh) ₃ [18 %] PI ₃ [13 %]	Not worked up
FeCl(O₂CCH₃)₂/I₂	2:1:0.3:12	0.08 mmol/h	OP(OPh) ₃ [46 %] Unknown product at δ _p -4 ppm [54 %]	Nothing isolated
Fe(PO)₄·2H₂O/I₂	2:1:0.3:12	0.12 mmol/h	Final reaction mass contained a significant amount of unreacted P ₄	
Fe(acac)₃/I₂	2:1:0.3:20	0.12 mmol/h	OP(OPh) ₃ [100 %]	OP(OPh) ₃ [33 %]
Fe(acac)₃/I₂	2:1:0.3:12	0.11 mmol/h	OP(OPh) ₃ [100 %]	OP(OPh) ₃ [61 %]
Fe(acac)₃/Br₂	2:1:0.3:12	0.10 mmol/h	Reaction abandoned due to formation of phosphorus smoke	
Fe(acac)₃	2:1:0:20		Reaction abandoned due to immediate formation of phosphorus smoke	

All reactions were conducted at 80 °C for 7 hours in toluene. See experimental section 6.2.5-6.2.17 for details.

a. 1 equivalent of pyridine per mol catalyst was added

Attempts were made to recycle the catalyst from the iron(III) acetylacetonate reactions. The solid residue left behind after distillation (described above) showed some activity as a catalyst. On first reuse (alongside a fresh measure of iodine) conversions to triphenyl phosphate as high as 98 % were observed by ^{31}P NMR. The other 2 % was converted to $\text{O}=\text{P}(\text{OPh})_2\text{OH}$. Unfortunately further reuse of the catalyst led to the formation of more $\text{O}=\text{P}(\text{OPh})_2\text{OH}$ and a decrease in activity until the catalyst no longer functioned. Full results are shown in table 4 below.

Table 4. Recycled Iron Acetylacetonate Reactions

	Original Catalyst	First Reuse	Second Reuse
Run 1	100 % $\text{OP}(\text{OPh})_3$	88 % $\text{OP}(\text{OPh})_3$ 12 % $[\text{OP}(\text{OPh})_2]_2$	not attempted
Run 2	100 % $\text{OP}(\text{OPh})_3$	98 % $\text{OP}(\text{OPh})_3$ 2 % $\text{OP}(\text{OPh})_2\text{OH}$	20 % $\text{OP}(\text{OPh})_3$ 80 % $\text{OP}(\text{OPh})_2\text{OH}$
Run 3	100 % $\text{OP}(\text{OPh})_3$	44 % $\text{OP}(\text{OPh})_3$ 56 % $\text{OP}(\text{OPh})_2\text{OH}$	Phosphorus smoke observed

All reactions conducted at 80 °C for 7 hours in toluene. See experimental section 6.3 for details.

It seems that the high temperature distillation slowly damaged the catalyst, rendering it inactive after several cycles. As can be seen from Table 4 there was a large variation in the catalytic activity of the residues from different reactions. It is likely that longer distillation times did more damage to the catalyst. Attempts were made to develop a solvent extraction work up to separate the product from the catalyst. Unfortunately the similar solubilities of triphenyl phosphate and iron acetylacetonate made this impossible.

Reactions with iron(III) acetylacetonate, but without the iodine co-catalyst, did not prove successful. Both the reaction with no co-catalyst and the reaction using bromine instead of iodine had to be abandoned due to the formation of phosphorus smoke (Table 3).

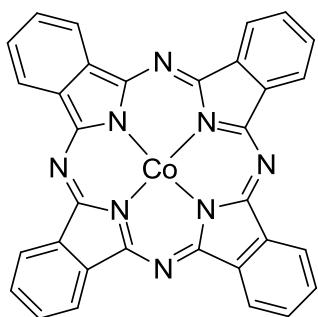
2.4 Other Transition Metal Catalysts

A selection of molybdenum, vanadium, nickel, cobalt and manganese complexes have been trialled as catalysts for the reaction of phenol with white phosphorus. In all cases no catalytic activity was observed unless a small amount of iodine was also present as an additive. MoCl_5 proved ineffective as a catalyst, phosphorus smoke was observed long before the intended amount of white phosphorus had been added. The reaction had to be abandoned, though ^{31}P NMR spectrum of the reaction mass indicated some triphenyl phosphate had been formed. It seems MoCl_5 may function as a stoichiometric oxidant but is ineffective as a catalyst. $\text{VO}(\text{acac})_2$ was trialled as a catalyst due to its usefulness in catalysing the aerobic oxidation of alcohols⁹⁴ and for its effectiveness at catalysing the oxidation of white phosphorus with peroxides (see above).^{94, 78} This proved to be much more effective than the molybdenum catalyst. All the white phosphorus reacted and triphenyl phosphate was the only product in the phosphorus NMR spectrum of the final reaction mass (though this NMR spectrum was somewhat broadened due to residual paramagnetism). Sadly only a low yield of phosphate was isolated by distillation in vacuo of the mixture at the end of the reaction. Why this was so remains unclear. No phosphorus compounds were found in the volatile fractions so presumably the remaining

phosphorus was left in the non volatile residue. It is possible the phosphate product reacted with the catalyst during the high temperature distillation.

NiCl₂Py₂ appeared to be an effective oxidant at the start of the reaction however phosphorus smoke was observed before the intended amount of white phosphorus had been added. Like MoCl₅, NiCl₂Py₂ may function as a stoichiometric oxidant. It is likely that the reduced form of this catalyst cannot be reoxidized by air at the reaction temperature, preventing true catalytic activity. The reaction mass from this reaction could not be analysed safely as it contained an appreciable quantity of white phosphorus. Cobalt phthalocyanine (Figure 7) was trialled as it has been shown to be effective at catalysing the aerobic oxidation of alcohols.⁹⁴ Cobalt phthalocyanine seemed to function as a catalyst and no phosphorus smoke was observed during the reaction. Despite this, when the final reaction mass was removed from the reaction vessel, phosphorus smoke formed and the mass had to be destroyed unanalysed for safety reasons. It is unclear how this occurred however there was a significant amount of oily liquid stuck to the sides of the reaction vessel during this reaction. It is possible this protected some unreacted white phosphorus from the air being bubbled through the reaction so its presence only became clear on work up.

Figure 7. Cobalt(II) Phthalocyanine



Mn(acac)₃ proved to be an effective catalyst and formed only triphenyl phosphate was observed in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the final reaction mixture, though an unidentified insoluble solid precipitated from the reaction. When this reaction was conducted with a much faster rate of P₄ addition, 27 % triphenyl phosphite and 73 % triphenyl phosphate were formed. Unfortunately increasing the reaction rate even further results in the formation of phosphorus smoke, so increased conversion to triphenyl phosphite is not feasible. The results obtained from the reactions using VO(acac)₂ and Mn(acac)₃ are comparable with the results obtained using Fe(acac)₃. It seems likely that the reaction system is tolerant of a wide range of catalysts with varying redox properties; and that the solubility of these transition metal catalysts in toluene solutions is a key factor in their effectiveness. Results obtained using non-iron transition metal catalysts are presented in Table 5.

Table 5. Reactions Catalysed by Other Transition Metals

Catalyst	Rate P ₄ addition (mmol/h/ mmolcat)	³¹ P NMR of reaction mass	Isolated organo- phosphorus product	solid product	Notes
MoCl₅/I₂	0.11	OP(OPh) ₃ [83 %]	-	-	-
Co(C₃₂H₁₆N₈)/ I₂	0.10		Reaction abandoned due to formation of phosphorus smoke.		
VO(acac)₂/I₂	0.13	OP(OPh) ₃ [100 %]	OP(OPh) ₃ [5 %]	Unidentified solid	-
Ni(Cl₂Py₂)/I₂	0.11		Reaction abandoned due to formation of phosphorus smoke.		
Mn(acac)₃/I₂	0.08	OP(OPh) ₃ [100 %]	OP(OPh) ₃ [11 %]	Unidentified solid	-
Mn(acac)₃/I₂	0.14	OP(OPh) ₃ [73 %] P(OPh) ₃ [27 %]	-	-	Not worked up

All reactions were performed in toluene at 80 °C with mol ratio cat:P₄:PhOH of 2:1:20. See experimental section 6.2.17-6.2.23 for details.

2.5 Heterogeneous Catalysts

Several studies have shown that heterogeneous catalysts can catalyse P-O bond formation at least in the formation of phosphorus oxyacids.^{95, 31} The possibility of a heterogeneously catalysed reaction of white phosphorus and phenol was thought worthy of further investigation. As no reaction of this type has been reported in the literature, inspiration was sought from other oxidation reactions using oxygen. Recent work has shown that supported gold nanocrystals can effectively catalyse oxidations with air or

oxygen.^{96, 97, 98}. Using the method of Enache *et al.* 2.5 % Au – 2.5 % Pd nanocrystals on a TiO₂ support were prepared.⁹⁸ This was used to catalyse a phenol/white phosphorus reaction under the same conditions as had been used for the homogeneous catalysts. The results were promising with the ³¹P NMR spectrum of the finished reaction showing just two major peaks, one for OP(OPh)₂(OH) [60 %] and one for OP(OPh)₃ [35 %]. The catalyst was recovered at the end of the reaction by filtration and was then re used for a second reaction (with the same results). It is likely that the hydrolysis to the diphenyl product is facilitated by the water of reaction. A duplicate reaction in the presence of 4A molecular sieves gave only phosphorus triiodide and diphenyl hydrogen phosphonate as products. A reaction was also performed using just Pd on TiO₂ however the resulting mass had a complicated ³¹P NMR spectrum. The largest single resonance in this spectrum, belonging to OP(H)(OPh)₂, accounted for just 40 % of the total. A trial reaction was conducted with copper(II) oxide nanocrystals prepared by the method of Zhou *et al.*⁹⁹ Unfortunately these showed no catalytic activity. Iron pyrophosphate (Fe₄O₂₁P₆) was tested as a heterogeneous iron catalyst. It also showed no catalytic activity.

Table 6. Heterogeneous Catalysed Reactions

Catalyst composition	Ratio Cat:P ₄ :I ₂ :PhOH	Rate P ₄ addition mmol/h/	³¹ P NMR of reaction mass
2.5%Au/TiO₂ 2.5%Pd/TiO₂	1:6:6:120	0.50	OP(OPh) ₃ [35 %] OP(OPh) ₂ (OH) [60 %]
2.5%Au/TiO₂ 2.5%Pd/TiO₂ (mol sieves)	1:6:6:120	0.63	OP(OPh) ₂ I [5 %] HPO(OPh) ₂ [68 %] PI ₃ [25 %]
5%Pd/TiO₂	1:6:6:120	0.37	OP(OPh) ₂ (OH) [3 %] OP(OPh)(OH) ₂ [31 %] OP(H)(OPh) ₂ [43 %] OP(OPh) ₂ I [7 %]
CuO	2:1:0.3:20		Reaction abandoned due to immediate formation of phosphorus smoke
Fe₄O₂₁P₆	1:1:0.3:12		Reaction abandoned due to immediate formation of phosphorus smoke

All reactions conducted at 80 °C for 7 hours in toluene. See experimental section 6.2.24-6.2.28 for details.

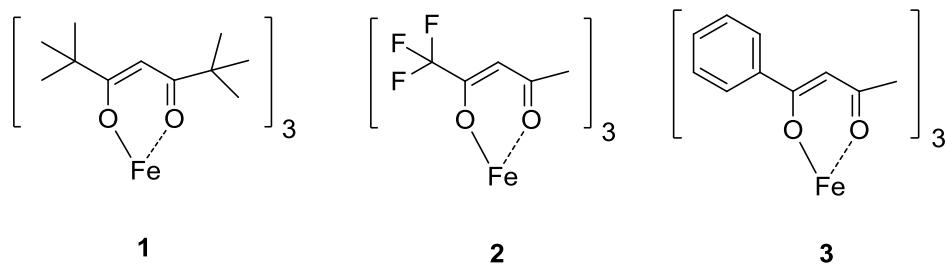
It would appear that both palladium and gold show catalytic activity in the oxidation reactions of white phosphorus. In these reaction systems they did not give the degree of product selectivity that was offered by homogeneous iron catalysts. For this reason and because of the significantly lower cost of iron; further studies have focused on optimisation of systems using iron catalysts.

3. Modification of Catalyst Ligands and Substrate Screening

3.1 Iron(III) Diketonates as Catalysts

Due to the difficulties with recovering the iron(III) acetylacetone catalyst, a series of iron(III) catalysts with modified diketonate ligands were tested in the reactions of phenols with white phosphorus. It was hoped catalytic efficacy would not be diminished by modification of the ligand, while modified solubility characteristics would allow the catalyst to be separated from the phosphate product by solvent extraction. The iron(III) complexes of 2,2,6,6-tetramethyl-3,5-heptanedione (**1**), 1,1,1-trifluoro-2,4-pentanedione (**2**) and 1-phenyl-1,3-butanedione (**3**) were tested (see Figure 8 for their structures).

Figure 8. Diketonate Catalysts Tested for Activity.



All three catalysts (**1-3**) showed some degree of catalytic activity in the aerobic reactions of white phosphorus with phenol. By gradually decreasing ratio of catalyst to phosphorus (whilst keeping the P₄ addition rate approximately the same) it was found that the parent complex Fe(acac)₃ and **1** were the most effective catalysts. As the ratio of phosphorus to catalyst increased, the formation of side products was observed. The major side product was identified as diphenyl phosphate (O=P(OPh)₂OH) by ³¹P NMR. If the P₄/catalyst

ratio was increased further, the amount of catalyst became insufficient to oxidize all of the white phosphorus at a satisfactory rate. This resulted in the formation of phosphorus smoke and the reactions had to be abandoned. By comparing the maximum phosphorus to catalyst ratio at which conversion to triphenyl phosphate was complete, an order of catalytic activity was elucidated. The results of these investigations are summarized in Table 7. The order, from most effective to least effective is $\text{Fe}(\text{acac})_3 \sim \mathbf{1}, \mathbf{2}, \mathbf{3}$. Further experiments showed that this order is the same irrespective of which phenol (i.e. substrate) is used.

Table 7. Activity of Modified Iron Diketonate Catalysts.

	Minimum catalyst loading (mol % with respect to P) to achieve 100 % selectivity	Notes
$\text{Fe}(\text{acac})_3$	25	12 % catalyst loading gives 67 % conversion to $\text{OP}(\text{OPh})_3$
$\mathbf{1}$	25	12 % catalyst loading gives 75 % conversion to $\text{OP}(\text{OPh})_3$
$\mathbf{2}$	33	Reaction starts smoking if less than 33 mol% of catalyst is used.
$\mathbf{3}$	50	Reaction starts smoking if less than 50 mol% of catalyst is used.

All reactions were conducted at 80 °C in toluene. See experimental section 6.4 for details.

Of the alternative catalysts $\mathbf{1}$ appeared to be the most effective, with similar catalytic activity to iron(III) acetylacetone. Separation of products and recovery of catalyst by

extraction was tackled successfully for the reaction with **1** as a catalyst. In the reaction using phenol, the separation was achieved by removing the toluene *in vacuo* at RT, then extracting the residue with a 50/50 mixture of toluene and hexane. Addition of a small volume of water to this mixture resulted in the formation of two distinct layers. The organic layer was found to contain catalyst **1**, which appeared pure by IR spectroscopy and had a melting point of 158-160 °C (lit. 162-164 °C¹⁰⁰). The dried weight of catalyst recovered was 92 % of the starting mass. The aqueous layer contained a light brown solid, which was identified as triphenyl phosphate by IR and NMR spectroscopy. The isolated yield of triphenyl phosphate was 82 %.

The recovered catalyst was reused in a further reaction to verify its catalytic activity had not been diminished by the solvent extraction process. Once again a 25 % loading of the recycled catalyst was found to be sufficient to facilitate complete conversion of P₄ to triphenyl phosphate. This shows solvent extraction to be a better method of catalyst recovery than removal of the product by distillation (see Table 4). The solvent extraction workup also gave a better isolated yield of the triphenyl phosphate product (82 % as opposed to 61 % isolated by distillation).

3.2 Reactions Using Higher Substituted Phenols

3.2.1 Reactions with 2,4-Di-tert-butylphenol

It is often considered desirable for plastics additives of all types to be of high molecular weight. This is because large organic molecules tend to be more soluble in molten

polymer and tend to leach less from the surface of the plastics during use.¹⁰¹ Therefore it is common to use substituted phenols rather than phenol itself to manufacture plastics additives, as this is a cheap and efficient way to increase molecular weight without significantly affecting functionality.

Bearing this in mind, it is surprising that only one example can be found in the literature of reacting white phosphorus with higher substituted phenols and that this is an electrochemical rather than a catalytic synthesis.¹⁰² To address this gap, we have chosen to use bulky 2,4-di-tert-butylphenol as another substrate in our catalytic reactions. It was expected that formation of the phosphate from this bulky phenol would be challenging, since the tris(2,4-di-tert-butylphenyl) phosphate molecule is significantly crowded.

Initially, the reactions using the 2,4-di-tert-butylphenol substrate were performed with iron(III) acetylacetone and iodine, since Fe(acac)₃ was shown to be an effective catalytic system in the reactions with phenol. However, at the usual rate of P₄ addition a significant decrease in selectivity towards triaryl phosphate was observed (Table 8). The ³¹P NMR spectrum showed that the resulting reaction mass contained only 30 % of tris(2,4-di-tert-butylphenyl) phosphate, which was identified by comparison with a standard sample prepared by oxidizing tris(2,4-di-tert-butylphenyl) phosphite.¹⁰³ The other 70 % was accounted for by tetrakis(2,4-di-tert-butylphenyl) pyrophosphate – (2,4-*t*Bu₂C₆H₃O)₂(O=)P-O-P(=O)(O₂,4-*t*Bu₂C₆H₃)₂. When this reaction was repeated in the presence of 4A molecular sieves the distribution of the two products was altered. In this case 67 % phosphate and only 33 % pyrophosphate was formed.

Increasing the reaction temperature to 110 °C (refluxing toluene) without molecular sieves resulted in only pyrophosphate being produced (100 % conversion). Decreasing the reaction temperature to 60 °C slowed the reaction rate and led to the co-formation of (2,4-di-tert-butylphenyl) phosphoriodidate O=PI(2,4-*t*BuC₆H₃)₂. This product was synthesized separately and was fully characterized by ³¹P, ¹H, ¹³C NMR, IR and MS (see experimental section 6.12.3 for details).

Catalysts **1**, **2** and **3** have also been tested with 2,4-di-tert-butylphenol as substrate (Table 8) and the product mixtures were analysed by ³¹P NMR. Catalyst **2** does not catalyse the reaction at a sufficient rate; white smoke was observed immediately when the reaction was attempted under the usual conditions. Catalyst **3** showed some catalytic effect, however the only product of the reaction was the pyrophosphate, even when the ratio of phosphorus atoms to catalyst was only 2:1. Using catalyst **1**, however, the reaction gave solely the desired tris(2,4-di-tert-butylphenyl) phosphate. As expected, to achieve the desired selectivity towards triorgano phosphate, 2,4-di-tert-butylphenol requires higher catalyst loadings (i.e. a more effective catalytic system) than phenol.

Table 8. Catalytic Reactions with 2,4 Di-tert-butylphenol

Catalyst	Rate of P ₄ addition/ mmol/h/ mmolcat	Reaction Temp / °C	Composition of products mixture (analysed by ³¹ P NMR)
Fe(acac)₃	0.09	80	70 % (2,4- <i>t</i> Bu ₂ C ₆ H ₃ O) ₂ OP-O-PO(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂ 30 % OP(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₃
Fe(acac)₃/ mol sieves	0.10	80	33 % (2,4- <i>t</i> Bu ₂ C ₆ H ₃ O) ₂ OP-O-PO(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂ 67 % OP(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₃
Fe(acac)₃	0.28	110	100 % (2,4- <i>t</i> Bu ₂ C ₆ H ₃ O) ₂ OP-O-PO(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂
Fe(acac)₃	0.18	60	50 % O=PI(2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂ 24 % (2,4- <i>t</i> Bu ₂ C ₆ H ₃ O) ₂ OP-O-PO(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂ 18 % OP(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₃ 8 % unknown minor products
1	0.13	80	100 % OP(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₃
2	0.21	80	Smoked
3	0.08	80	100 % (2,4- <i>t</i> Bu ₂ C ₆ H ₃ O) ₂ OP-O-PO(O-2,4- <i>t</i> Bu ₂ C ₆ H ₃) ₂

In all cases the ratio of P/catalyst/I₂/2,4-*t*Bu₂C₆H₃OH was 2:1:0.6:12. All reactions were conducted in toluene over approx. 7 hours, see experimental section 6.5.1-6.5.7 for details.

3.2.2 Reactions with *o*-Cresol

The phosphate of cresol is a useful industrial chemical (see section 1.4). The tritoly phosphorus used in industry is a mixture of the *ortho*, *meta* and *para* isomers. In this study *o*-cresol was used as a substrate because it was anticipated to be the most difficult isomer with which to achieve the desired reactivity towards triaryl phosphate. This is because of the steric hindrance caused by the presence of methyl group ortho to the oxygen atom. *O*-cresol was reacted aerobically with white phosphorus using iron(III) acetylacetone and **1** as the catalyst (Table 9). These catalysts were chosen as they were by far the most effective catalysts for the reactions using phenol and 2,4-di-*tert*-butyl phenol. Complete conversion to tritoly phosphorus was achieved with each catalyst as judged by ^{31}P NMR.

Table 9. Catalytic Reactions with *o*-Cresol

Catalyst	Ratio P/catalyst/I ₂ / <i>o</i> -cresol	Rate of P ₄ addition / mmol/h/mmolcat	Composition of products mixture (analysed by ^{31}P NMR)
Fe(acac)₃	2/0.5/0.6/24	0.19	100% O=P(OC ₆ H ₄ <i>o</i> -Me) ₃
Fe(acac)₃	2/0.5/0.6/24	0.21	88% O=P(OC ₆ H ₄ <i>o</i> -Me) ₃ 12% (i-MeC ₆ H ₄ O) ₂ OP-O-PO(OC ₆ H ₄ <i>o</i> -Me) ₂
1	2/1/0.6/24	0.10	100% O=P(OC ₆ H ₄ <i>o</i> -Me) ₃

All reactions were conducted at 80 °C in toluene over approx. 7 hours. See experimental section 6.5.8-6.5.10 for details.

In the reactions using 2,4-di-tert-butyl phenol the pyrophosphate was formed when insufficient catalyst loadings were used. The analogous process was also observed in the case of cresol substrate. When the rate of phosphorus addition was increased the tetra-*o*-tolyl pyrophosphate was formed. This is notably different from the reactions using phenol, where O=P(OPh)₂OH was more commonly observed as the byproduct when the catalyst loading was too low.

Separation of the phosphate product from the mixture after the reaction using catalyst 1 was attempted. A similar solvent extraction technique to that used to separate triphenyl phosphate (above) was utilized. The reaction solvent was removed *in vacuo* at RT and the residue was extracted with a 50/50 mixture of toluene and hexane. The extract was filtered through a sinter and the filtrate was transferred to a separating funnel. The phosphate product was washed out of this mixture using 4 portions of a warmed (50 °C) 50/50 mixture of methanol and water. The solvent was removed from the aqueous wash *in vacuo* to give tritolyl phosphate in 20 % yield. The product was found to be pure by ³¹P and ¹³C NMR. Removing the solvent from the organic layer produced an orange oil, which seemed to consist largely of the catalyst by IR spectroscopy although some other species were clearly present.

Both the yield of product and the purity of the recovered catalyst are lower than those achieved by the analogous process in the triphenyl phosphate forming reaction. This is believed to be due to the increased solubility of tritolyl phosphate in hexane. To date a superior work up for the reaction has not been developed.

3.2.3 Reactions with Resorcinol

Resorcinol bis-diphenyl phosphate is a commonly used flame retardant. The presence of its OH groups, capable of hydrogen bonding and its high molecular weight make it less volatile than other triaryl phosphate flame retardants. It also does not share the plasticizing properties of triphenyl phosphate and tritolyl phosphate. Chemtura, who market resorcinol bis-diphenyl phosphate as Reofos RDP recommends it for use in modified polyphenylene oxide, polycarbonate ABS blends and polyurethane foams.¹⁰⁴

It was thought interesting to see how resorcinol would react in our catalytic reactions with white phosphorus. Iron(III) acetylacetone and iodine was used as the catalytic system, with a 25 % loading of the iron catalyst with respect to P₄. All the white phosphorus added was consumed in the reaction (as evidenced by ³¹P NMR of the final reaction mass). The sole product of the reaction was a black paste which precipitated from the solution as the white phosphorus was added. This paste was insoluble in all common laboratory solvents and therefore very difficult to characterize. High temperature distillation *in vacuo* of the paste yielded only a small amount of resorcinol, whilst the bulk of the paste was involatile. It can be speculated that the two functional groups on resorcinol leads to the formation of polymers/oligomers on its reaction with phosphorus.

A second reaction was attempted in which 0.5 equivalents of resorcinol per P atom and two equivalents of phenol were reacted. This is the correct stoichiometry for the

formation of resorcinol bis-diphenyl phosphate. The reaction conditions were otherwise identical to the reaction outlined above. Once again all the white phosphorus added to the reaction was consumed and a black paste precipitated from the solution. In this reaction triphenyl phosphate was found to be present in the solution and once again the solid was insoluble and could not be characterized. Perhaps unsurprisingly, it seems resorcinol and phenol reacted separately with the P₄, and no evidence of combined products was observed.

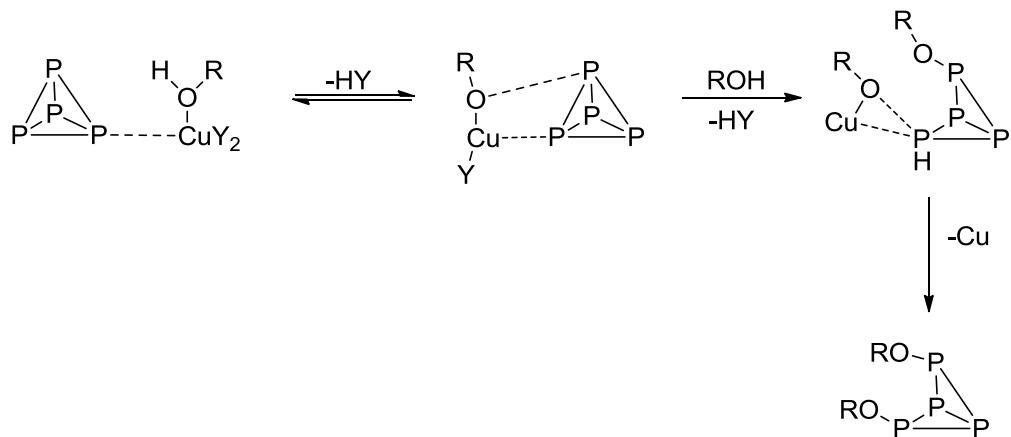
4. Mechanistic Studies

4.1 Mechanistic Studies of Related Reactions in the Literature

As the work of Abdreimova *et al.* is the closest literature precedent to our reactions their mechanistic studies seem worthy of consideration. They made some efforts to elucidate the mechanism of their phosphate forming reactions using copper catalysts (see section 1.4.1). They believe the initial step is the coordination of P₄ to the copper centre and that this coordination is bidentate where possible (η^2).⁸³ They also observed that higher coordinated copper complexes were less effective catalysts and argued this was because they were only capable of η^1 coordination.

By use of calculations based on the CNDO (complete neglect of differential overlap) method (see Santry *et al.* for a description of this method)¹⁰⁵ it was argued that the reaction proceeded via a series of P₄ insertions into Cu-OR bonds. Each of these insertions results in the opening of one P-P bond. The insertions proceed until all P-P bonds are broken and only molecules of P(OR)₃ remain. This mechanism is shown in Scheme 29.

Scheme 29. Reaction of P₄ with CuY₂ and Alcohol



Kinetic data and redox potential measurements are put forward in support of the suggested reaction mechanism.⁸⁴ Redox measurements showed rapid formation of Cu(I) and Cu(0) when an arene solution of white phosphorus was added to an alcohol solution of copper (II) catalyst. If oxygen is present in the reaction atmosphere, these reduced species are reoxidized to Cu(II). In an argon atmosphere the reduced compounds remain. Based on the rate of O₂ consumption the reoxidation of reduced copper species by air appeared to be the rate determining step. In our reactions with white phosphorus and phenol using copper catalysts, the reoxidation of the copper by air seemed to be problematic (see section 2.2). This would support the view that copper reoxidation is likely to be the rate limiting step in the Abdreimova reactions.

The same paper also put forward various other pieces of evidence to support the mechanism above. It showed that decreasing the alcohol to white phosphorus ratio to less than 20:1 inhibited the reaction. The authors put this down to the formation of Cu(I) phosphite complexes stopping the alcohol entering the coordination sphere of copper.

The evidence given for this hypothesis is a lack of free phosphite peaks and the presence of peaks in the region of 6-10 ppm in the $^{31}\text{P}\{\text{H}\}$ NMR spectra of the reaction mixtures. Given the low chemical shift these products are unlikely to be phosphite species as the authors state. Phosphonates are more probable candidates. The addition of water to the reaction was found to dramatically reduce the yield of phosphates and phosphites. It was argued that this may be because water can coordinate to copper more easily than alcohol. The hydrolysis of any phosphite formed may present an alternative explanation for this, although the rate of this hydrolysis would not normally be expected to be high, the copper(II) may catalyse this process as well. The variation of the rate of these reactions with temperature allowed Abdreimova *et al.*, to calculate activation energies and entropies. They argued that the low activation energy of the reaction and the negative entropy of activation both supported the mechanism shown in Scheme 29 (above). This evidence does all seem to support a mechanism in which white phosphorus coordinates to copper; however both P_4 insertion into Cu-OR bonds and OR insertion into Cu-P bonds (with P_4 coordinated to the copper) seem to be equally plausible mechanisms. In a later paper by the same group it was claimed that Fe(III) catalysts function by the same coordination mechanism as Cu(II) catalysts.⁸⁵ Similar reaction results when using these metals as catalysts seems to be the entirety of the evidence presented to support this proposal.

An ab initio study into a similar system was published by Tamuliene and coworkers in 2002.¹⁰⁶ Their aim was to clarify the mechanism of the reaction between white phosphorus and alcohol in the presence of copper (II) chloride reported by Abdreimova *et*

al. (see above).⁸³ This study used $[\text{CuCl}_2(\text{NH}_3)(\text{CH}_3\text{OH})]$ as a model copper complex. It was claimed that quantum chemical investigations showed white phosphorus does not enter the coordination sphere of this complex. Instead it was argued that the dipole on the complex induces a dipole on the white phosphorus weakening the P-P bonds. By comparison with $[\text{CuCl}(\text{NH}_3)_2(\text{CH}_3\text{OH})]$ and $[\text{Cu}(\text{NH}_3)_3(\text{CH}_3\text{OH})]$ it was argued that the halide ligands “do not directly participate in the oxidative P-O coupling but they are active components of the reaction providing nucleophilic assistance to the deprotonation step of the alcohol” (i.e. they help in the formation of alkoxide ions).

It has been claimed that pentavalent reaction products, $\text{P}(\text{O})(\text{OR})_3$ and $\text{P}(\text{O})(\text{H})(\text{OR})_2$ are formed via a phosphite intermediate which is then rapidly oxidized to the phosphate or dealkylated to the phosphonate.^{85, 86} This notion is supported by a Borg-Warner Chemicals patent of 1982.¹⁰⁷ In this patent triphenyl phosphite was shown to oxidize to triphenyl phosphate with oxygen in the presence of iodine and transition metal catalysts under mild conditions (50-100 °C, atmospheric pressure). The oxidation did not proceed if the iodine was not present. Iron(III), cerium(IV), copper(II) manganese(III) were shown to be effective catalysts for the oxidation. The oxidation was said to give excellent conversion with aromatic alcohols yet poor conversion with aliphatic alcohols. No mention of the drying of reagents is given in the patent. In these circumstances it is likely that water and iodine are responsible for the oxidation of the phosphite, with HI produced as a byproduct.

4.2 Experimental Mechanistic Studies

A series of reactions were performed to investigate the mechanism of the aerobic reaction of white phosphorus and phenol, using iron acetylacetonate as a catalyst.

4.2.1 Oxidation of Phosphite to Phosphate

The initial mechanistic investigations focused on the intermediacy of phosphorus(III) species, most importantly whether phosphite was the initial product and oxidation to phosphate occurred *in situ*. For this purpose the kinetics of the oxidation of the phosphite to the phosphate was investigated with and without the presence of $\text{Fe}(\text{acac})_3$ and iodine as a catalyst. In both cases phosphite was dissolved in toluene and held at 80 °C with air bubbling through the mixture. In the case of triphenyl phosphite very little conversion to phosphate was observed without iodine present, with or without $\text{Fe}(\text{acac})_3$. When both $\text{Fe}(\text{acac})_3$ and iodine were present a steady conversion to phosphate was observed. After 6 h at 80 °C only triphenyl phosphate could be observed in the NMR. Dry solvent and dry reagents were used in these experiments, indicating the oxidation of phosphite with air in these conditions is also possible. This result is supported by the US patent by Dibella on the oxidation discussed in section 4.1.¹⁰⁷

When these experiments were repeated with 2,4-di-tert-butylphenol phosphite the oxidation reaction appeared to be less favoured. Once again very little conversion occurred without iodine present. In the oxidation with both iodine and $\text{Fe}(\text{acac})_3$ there was approximately 25 % conversion to phosphate after 6 hours (the broad nature of the

NMR spectrum makes precise measurement of the conversion impossible). Increased steric hindrance around the central phosphorus atom is likely to account for the slower oxidation of this phosphite.

It seems that in the case of triphenyl phosphite oxidation is sufficiently rapid that any phosphite formed could be oxidized to phosphate under our reaction conditions. It is possible the phosphate products of the reactions are formed by oxidation of phosphite intermediates.

Table 10. Aerobic Oxidation of Phosphites

Starting Phosphite	Amount I ₂ /mmol	Amount Fe(acac) ₃ /mmol	Conversion to Phosphate after 6 hours
Triphenyl phosphite (1.3 M)	1.08	3.23	100 %
Triphenyl phosphite (1.3 M)	0	3.23	0 %
Triphenyl phosphite (1.3 M)	0	0	0 %
Tri-2,4-di-tert-butylphenyl phosphite (0.3 M)	0.51	1.54	23 %
Tri-2,4-di-tert-butylphenyl phosphite (0.3 M)	0	1.54	0 %
Tri-2,4-di-tert-butylphenyl phosphite (0.3 M)	0	0	0 %

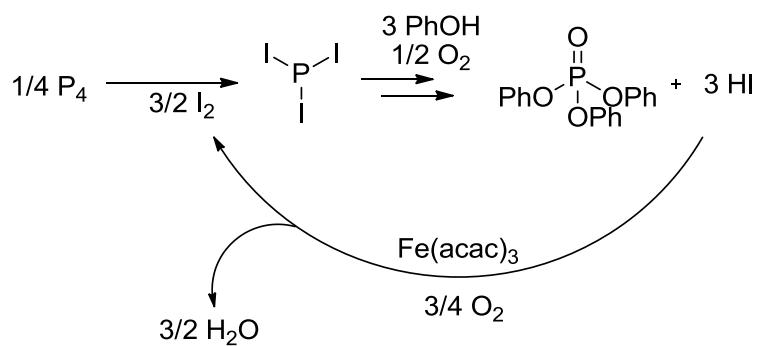
Reactions were conducted at 80 °C in toluene. See experimental section 6.6 for details.

4.2.2 Initial Steps of the Catalytic Cycle

In order to identify the initial step of the transformation, solutions of white phosphorus in toluene were reacted with iron acetylacetone or iodine in *anaerobic* conditions. The reactions were followed by ^{31}P NMR spectroscopy. Due to the paramagnetic nature of iron(III) acetylacetone samples were reduced by shaking with sodium sulfite before NMR measurements were taken. It was shown that iron(III) acetylacetone does not react with white phosphorus even at 80 °C. In a similar experiment a solution of P_4 was slowly added to a solution of I_2 with vigorous stirring. Iodine was found to react exothermically with P_4 instantly to form a mixture of P_2I_4 and PI_3 even at room temperature. This is an expected result as iodine and P_4 are known to react to form PI_3 when stirred together in carbon disulfide solutions.¹⁰⁸

Attempts to react white phosphorus and phenol in the presence of air using iodine alone resulted in the rapid formation of smoke after a stoichiometric amount of P_4 to form PI_3 was added. The reaction towards phosphates therefore requires an additional catalyst as well as iodine. It appears that iodine is responsible for the initial rapid oxidation of white phosphorus to PI_3 and P_2I_4 , which after phenolysis and further oxidation gives the triaryl phosphate. It appears that iron(III) acetylacetone and air chiefly function to reoxidise the HI byproduct (formed at the latter stages of the reaction) back to I_2 , thus forming a catalytic cycle (Scheme 30). However, additional experiments have shown that the iron catalyst also plays an important role in the latter stages of the reaction (see below).

Scheme 30. Catalytic Role of Iodine



4.2.3 Oxidation of HI

Oxidation of HI(aq) with oxygen to I_2 is thermodynamically feasible, however the uncatalysed reaction is very slow on kinetic grounds.¹⁰⁹ To investigate the effect of iron acetylacetone on the rate of this reaction, air was bubbled through an aqueous solution of 6 M HI at 80°C . The concentration of I_2 formed was monitored by titration against sodium thiosulfate. The initial concentration of I_2 in commercially available 6 M HI solution was found to be 0.30 M (4.5 %). As air was bubbled through 10 mL of the solution at a rate of 40 mL/minute, this concentration gradually increased to 0.52 M (7.8 %) over 5 hours. When this experiment was repeated using a 0.5 M solution of HI , the initial concentration of I_2 was measured as 0.020 M (4.2 %). After 5 hours of oxidation in the same conditions as above, the concentration of I_2 was 0.026 M (5.5 %). The oxidation is slow in both cases and substantially slower at the lower concentration of aqueous HI solution. The slow rate of $\text{HI} \rightarrow \text{I}_2$ oxidation observed in the reactions of HI(aq) does imply the iron catalyst used in our reaction system increases the rate of HI oxidation

significantly; it is likely that without additional catalyst iodine would not reform in these reaction systems rapidly enough.*

To test whether the oxidation rate of HI increases measurably in the presence of iron catalyst, a similar experiment was performed in the presence of iron(III) acetylacetone. Air was bubbled through a 0.2 M solution of HI in methanol at 65 °C for 4 hours.† This experiment was performed twice, once with a 0.2 M concentration of iron(III) acetylacetone and once with a 1.2 M concentration of iron(III) acetylacetone. The oxidizing nature of Fe(III) catalyst made titration against sodium thiosulfate an inappropriate way to monitor the reaction. Instead the solutions were titrated against 0.2 M sodium hydroxide to determine the remaining concentration of HI. The end point was determined by monitoring the titration with a pH meter. Results of the titrations are plotted in

Figure 9 and Figure 10.

* Note that only a catalytic amount of iodine is required in the iron complex catalysed reaction (ca. 0.33 moles of iodine per mole of P₄).

† Aqueous methanol (ca 2.5% water) was used as the iron catalyst is soluble in methanol but not water

Figure 9. Neutralisation of HI(aq) after Oxidation in the Presence of 0.2 M Fe(acac)₃

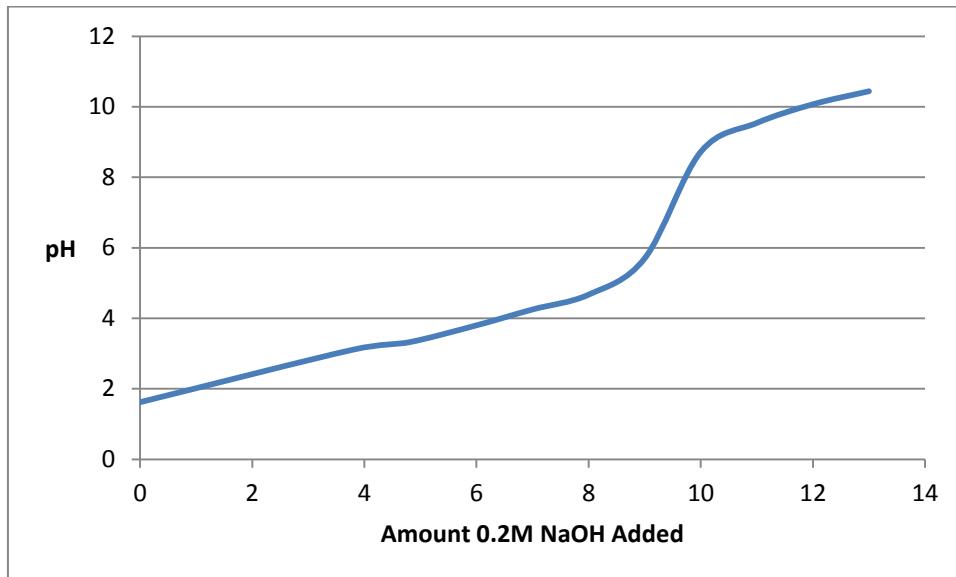
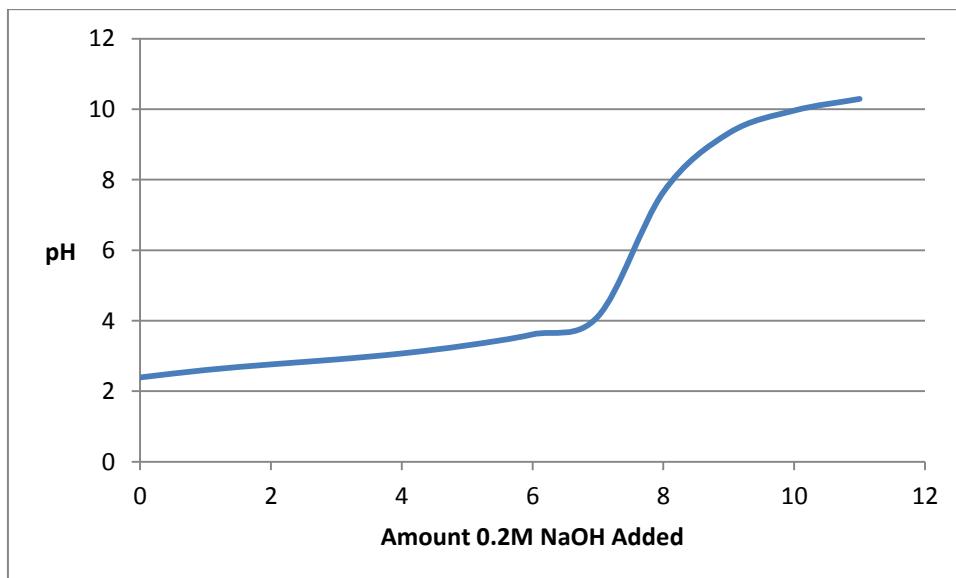


Figure 10. Neutralisation of HI(aq) after Oxidation in the Presence of 1.2 M Fe(acac)₃



When a 0.2 M concentration of iron(III) acetylacetone was used the solution became neutral after 9.4 mL of 0.2 M NaOH was added. This shows 0.00188 mol of the original 0.002 mol of HI was not oxidized -

$$\frac{0.2}{1000} \times 9.4 = 0.00188$$

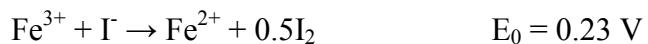
This is 94 % of the initial amount of HI indicating a 6 % conversion to I₂.

When the concentration of iron(III) acetylacetone was 1.2 M the solution became neutral after only 7.7 mL of 0.2 M NaOH was added. This shows 0.00154 mol of the original 0.002 mol of HI was not oxidized -

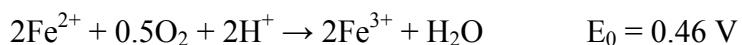
$$\frac{0.2}{1000} \times 7.7 = 0.00154$$

This is 77 % of the initial amount of HI indicating 23 % conversion to I₂. The higher concentration of iron better mimics the situation in the phosphate reactions where the concentration of iron is always significantly higher than the concentration of HI, which forms *in situ*. This experiment indicates iron(III) acetylacetone significantly increases the rate of the reoxidation of HI in the phosphate-forming reaction systems.

The effect of the Fe(acac)₃ can be rationalized by considering the redox potentials of the various components of the reaction system. The I⁻/I₂ couple has a standard reduction potential of 0.54 V.¹⁰⁹ Fe(acac)₃ has a surprisingly low Fe(III)/Fe(II) reduction potential of -0.42 V¹¹⁰ and could not oxidize the I⁻ formed in our reaction systems back to I₂. Free Fe(III) ions on the other hand have a much higher Fe(III)/Fe(II) reduction potential of 0.77 V¹⁰⁹ and can easily oxidize I⁻ to I₂ by the half reaction:



It is likely that in the high temperature, acidic conditions of the catalytic white phosphorus reactions there is at least partial dissociation of the acetylacetonate ligands and the HI is oxidized by these dissociated species. In acidic solutions, the Fe(II) formed by this process can be oxidized back to Fe(III) by oxygen, according to the equation below:¹¹¹



It should be noted that these figures are for aqueous solutions at room temperature and can only be taken as rough guides to the situation in our reaction systems, where acidic toluene solutions are held at 80 °C.

It may also be possible that the rate of HI oxidation is affected by the presence of other compounds in the reaction system. The combination of red phosphorus and HI is well known as a reducing reagent in organic chemistry. It has been argued that the presence of the phosphorus increases the reducing power of HI. This effect is thought to be caused by the reaction of red phosphorus with iodine to form PI₃ and P₂I₄.¹¹² This constant removal of iodine drives the oxidation of HI. An analogous process is likely to happen in our systems with HI and white phosphorus.

4.2.4 Reactions of Phosphorus Iodides with Phenol

To gain further insight into the mechanism of the phosphate-producing reactions, solutions of $\text{PI}_3/\text{P}_2\text{I}_4$ in toluene were reacted with phenol at various reaction conditions, with and without the presence of iron catalyst. The results are summarized in Table 11. The reactions were monitored by ^{31}P NMR.

Table 11. Reactions of PI_3 with Phenol

Entry	Reaction Time	Air flow	Fe(acac) ₃ catalyst loading	Product
1	5h	40 mL/min	None	$\text{O}=\text{PI}(\text{OPh})_2$
2	3h	40 mL/min	Fe(acac) ₃ (100 mol%)	$\text{O}=\text{P}(\text{OPh})_3$
3	5h	None	None	PI_3
4	5h	None	Fe(acac) ₃ (100 mol%)	PI_3

All reactions were performed with 1:3 stoichiometric ratio of PI_3 : PhOH, reaction temperature was 80 °C. See experimental section 6.7 for details.

In the aerobic reaction of PI_3 with PhOH with no catalyst added (Entry 1 in Table 11), diphenyl phosphoriodidate ($\text{O}=\text{PI}(\text{OPh})_2$) was formed in quantitative yield. Diphenyl phosphoriodidate was previously reported in the literature,¹¹³ and its identity was confirmed by comparison of $^{31}\text{P}\{^1\text{H}\}$ NMR data. As expected, the aerobic reaction of PI_3

with PhOH in the presence of the iron(III) catalyst yielded triphenyl phosphate as the sole product (Entry 2 in Table 11). No reaction took place between PI₃ and phenol when it was performed anaerobically (Entry 3 in Table 11). Repeating this reaction in the presence of Fe(acac)₃ did not have any effect, PI₃ was still the only phosphorus-containing species at the end of the reaction (Entry 4 in Table 11). ‡

Since the first reaction in Table 11 showed the formation of the intermediate O=PI(OPh)₂ to be essentially stoichiometric, we speculated that it is also formed as an intermediate in the catalysed phosphorus and phenol reactions. The formation of O=PI(OPh)₂ does not require catalyst. However, in the presence of the catalyst, it is quickly consumed in the reaction which affords triaryl phosphate as an end product (as seen in Entry 2, Table 11). Thus the catalyst appears to play dual role in the phosphate-forming reaction system, i.e. it catalyses the oxidation of HI back to I₂ (as described above), as well as increasing the rate of the nucleophilic substitution reaction O=PI(OPh)₂ → O=P(OPh)₃. To verify this hypothesis, O=PI(OPh)₂ was reacted with one equivalent of phenol in toluene at 80 °C, with and without metal catalyst. The reactions were performed under nitrogen to avoid hydrolysis of O=PI(OPh)₂ with air moisture, however a small amount of water may have been present in the phenol used. Results of these experiments are shown in Table 12, the product mixtures were analysed by ³¹P NMR.

‡ This reaction proved difficult to monitor as treatment with sodium sulfite is required to reduce the paramagnetic Fe(III) before NMR measurements can be taken. Unfortunately treatment with sulfite can decompose PI₃, however by limiting the length of the sodium sulfite shake to ca. 30 second a reasonable quality NMR spectrum was obtained. Unreacted PI₃ was the only product observed in this spectrum.

Table 12. Reactions of O=PI(OPh)₂ with Phenol

Concentrations of O=PI(OPh) ₂ and phenol (molar ratio 1 : 1)	Fe(acac) ₃ catalyst loading	Reaction time till all O=PI(OPh) ₂ was consumed	Phosphorus-containing products
0.63 M	none	20 h	66 % O=P(OPh) ₂ OH, 4 % O=P(OPh) ₃ 30 % (PhO) ₂ (O)P-O-P(O)(OPh) ₂
0.62 M	25 mol%	3 h	O=P(OPh) ₃

Reactions were conducted in toluene at 80 °C in anaerobic conditions. See experimental section 6.8 for details.

Without catalyst only a small amount of O=P(OPh)₃ (ca. 4 %) was produced after twenty hours. The rest of the starting material hydrolyzed to form pyrophosphate (PhO)₂(O)P-O-P(O)(OPh)₂ and O=P(OPh)₂OH. Notably, related pyrophosphates were formed as side products in our reactions using 2,4-di-tert-butyl phenol and cresol with low catalyst loadings (Table 8 and Table 9 above). In the presence of iron acetylacetone, quantitative conversion to triphenyl phosphate was achieved anaerobically within 3 hours (Table 12). Clearly the catalyst vastly increases the rate and selectivity in the formation of O=P(OPh)₃ from the O=PI(OPh)₂ intermediate.

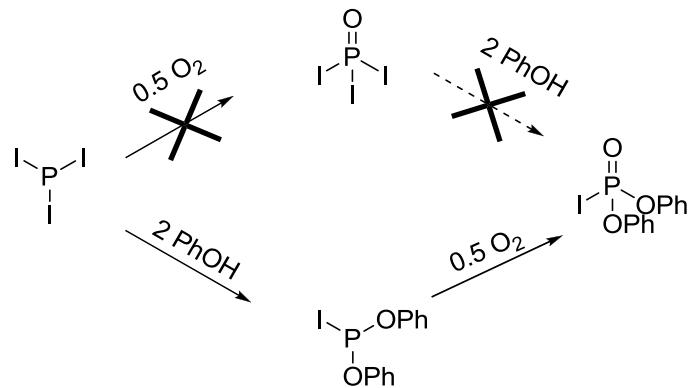
4.2.5 Formation of Diphenyl Phosphoriodidate from Phosphorus Triiodide

It was thought useful to investigate the mechanism of O=PI(OPh)₂ formation in the PI₃/phenol/air system. One of the possible pathways towards O=PI(OPh)₂ (with or without catalyst) involves formation of O=PI₃ from PI₃ and air. Similar oxidation of

phosphorus chloride to O=PCl₃ is known to proceed readily.¹¹⁴ On the other hand, the difficulty of synthesizing O=PI₃ in comparison to O=PCl₃ has been reported in the literature.¹¹⁵ To verify this at conditions used in our experiments, a solution of PI₃ in toluene was heated to 80 °C, while air was bubbled through this solution for 3 hours. After this time no conversion to O=PI₃ was observed and none of the PI₃ was consumed. This reaction was repeated in the presence of iron acetylacetonate (at a molar ratio of iron: phosphorus, 1:1). Once again no conversion to O=PI₃ was observed. It is therefore very unlikely that the O=PI(OPh)₂ intermediate is formed via O=PI₃.

An alternative route to O=PI(OPh)₂ would be the nucleophilic substitution of PI₃ with one or two equivalents of phenol before it is oxidized to P(V) (Scheme 31).

Scheme 31. Reaction of PI₃ with Oxygen and Phenol

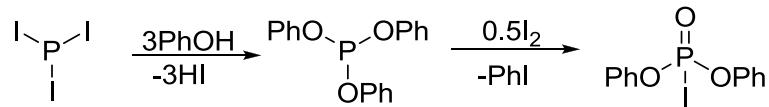


PI₃ was found not to react with phenol in anaerobic conditions without catalyst (Entry 3, Table 11), whilst rapid reaction took place in aerobic conditions, giving O=PI(OPh)₂ (Entry 1, Table 11). Presumably in aerobic conditions, rapid removal of initially formed

$\text{PI}(\text{OPh})_2$ or $\text{PI}_2(\text{OPh})$ by oxidation to $\text{O}=\text{PI}(\text{OPh})_2$ or $\text{O}=\text{PI}_2(\text{OPh})$ drives the otherwise slow $\text{P}-\text{I} \rightarrow \text{P}-\text{OPh}$ substitution reaction. To investigate this we attempted to synthesize $\text{P}(\text{OPh})_2\text{I}$ from $\text{P}(\text{OPh})_2\text{Cl}$ and sodium iodide to investigate its reactivity towards oxygen. Only partial conversion to $\text{P}(\text{OPh})_2\text{I}$ was observed, however the $\text{P}(\text{OPh})_2\text{I}$ produced was found to oxidize to $\text{O}=\text{P}(\text{OPh})_2\text{I}$ very rapidly when exposed to air. This indicates the involvement of $\text{P}(\text{OPh})_2\text{I}$ as an intermediate before its rapid oxidation *in situ* is possible. Rapid oxidation would also explain why no P(III) (i.e. phosphite) intermediates have been observed when these reactions were monitored by ^{31}P NMR.

Another possible route for the formation of $\text{O}=\text{P}(\text{OPh})_2\text{I}$ is via the reaction of triphenyl phosphite with iodine, followed by an Arbuzow rearrangement to the product (Scheme 32).

Scheme 32. Alternative Mechanism for the Formation of $\text{O}=\text{P}(\text{OPh})_2\text{I}$



To test the possibility of such a mechanism being operable, a toluene solution of triphenyl phosphite was reacted with iodine. After stirring for 3 h under nitrogen at RT a low conversion to $\text{O}=\text{P}(\text{OPh})_2\text{I}$ was observed by ^{31}P NMR (5 %). This indicates that the reactions shown in Scheme 32 are also a possible but unlikely route to $\text{O}=\text{P}(\text{OPh})_2\text{I}$. To investigate this route further, the reaction mass from the aerobic reaction of PI_3 with phenol (Entry 1, Table 11) was analysed by GCMS. If the Arbuzow route was

responsible for the formation of O=P(OPh)₂I we would expect to see the iodobenzene side product in the final reaction mass. Iodobenzene would not be present if the reaction proceeded by the substitution/oxidation route depicted in Scheme 31.

Samples of the final reaction mass were compared by GCMS to samples of dilute iodobenzene in toluene (500 ppm) and a sample of the final reaction mass spiked with 200 ppm of iodobenzene. Both the dilute iodobenzene and the spiked reaction sample showed a sharp peak at 8.2 minutes in the GC, which had a mass of 204 ($C_6H_5I^+$ has a m/z of = 203.94). The peak for iodobenzene was not present in the final reaction mass. This shows that iodobenzene is not formed during the reaction, indicating the Arbuzow route does not occur.

To further confirm that the mechanism depicted in Scheme 31 was more likely to account for the formation of O=P(OPh)₂I, two further experiments were performed. In the first, PI₃ was reacted with three equivalents of phenol in the presence of iodine but not air. In the second PI₃ was reacted with phenol in the presence of air but not iodine.

Table 13. Studies into the Formation of O=P(OPh)₂I.

Reaction mixture composition	Equivalents Iodine	Air Flow	Product
PI₃ + 2PhOH	1	None	70 % unreacted PI ₃
			20 % O=P(OPh) ₂ I
			10 % O=P(OPh) ₃
PI₃ + 2PhOH	0	40 mL/min	O=P(OPh) ₂ I

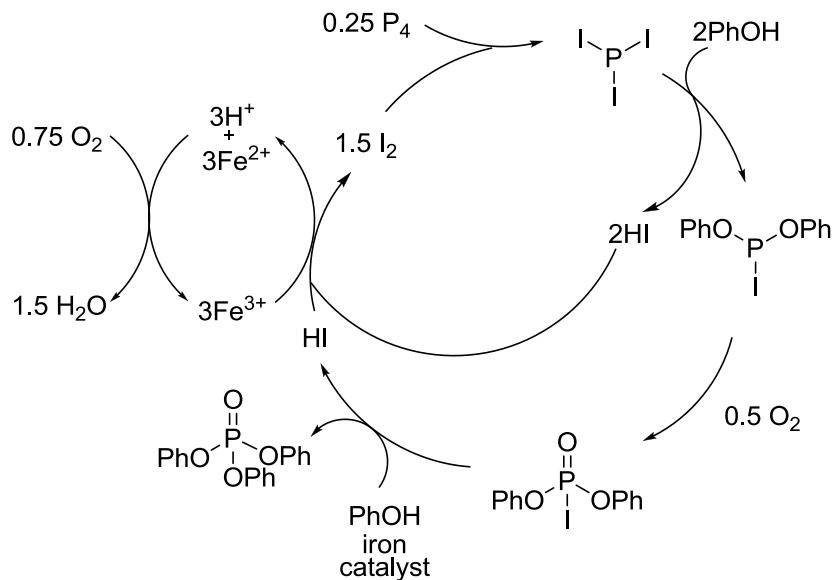
Reactions were performed in toluene at 80 °C, reaction time was 4 hours. See experimental section 6.9 for details.

The aerobic reaction with no extra iodine (Entry 2 in Table 13) rapidly and selectively produced the phosphoriodidate product. All of the starting phosphorus triiodide was converted to product within the 4 hour reaction time. In the anaerobic reaction with extra iodine only 20 % of the PI₃ was converted to the phosphoriodidate. The reaction mixture was heated to 80 °C for a further 4 hours, however no further conversion of PI₃ was observed. These results also indicate that the Arbuzow route (Scheme 32) is not responsible for the formation of O=P(OPh)₂I in our reactions. The pathway including rapid oxidation of phosphoriodidite intermediates (Scheme 31) is the more likely mechanism.

4.2.6 Proposed Reaction Scheme

An overall reaction mechanism of phosphate formation shown in Scheme 33 was deduced from the reactions detailed above.

Scheme 33. Overall Scheme of Catalysed Aerobic Reaction of P₄ with Phenol



Iodine is believed to be entirely responsible for the initial oxidation of P₄ to PI₃.

Phosphorus triiodide reacts with two equivalents of phenol and half an equivalent of O₂ to form O=PI(OPh)₂. This stage of the reaction is believed to proceed via rapid oxidation of P(OPh)₂I or P(OPh)I₂. This oxidation can be achieved by oxygen or by the reaction of phosphite with iodine and H₂O. In the presence of iron(III) acetylacetonate O=PI(OPh)₂ reacts with a further equivalent of phenol to form triphenyl phosphate. This final stage of the reaction is in competition with the hydrolysis of this intermediate to form (PhO)₂(O)P-O-P(O)(OPh)₂ and O=P(OPh)₂OH. The hydrolysis is facilitated by the water of reaction (as HI is reoxidized to I₂ and H₂O). Alkaline hydrolysis of triorgano phosphates is well known however hydrolysis with water alone is less well documented.¹¹⁶ The aqueous hydrolysis of phosphorus–halogen bonds on the other hand is well documented.^{117, 118} It is likely that the combination of the good iodine leaving group and the elevated reaction temperature help facilitate the hydrolysis. The

pyrophosphate-forming reaction appears only to proceed slowly at 80 °C (see Table 12), however it becomes an issue if insufficient catalyst is used.

4.2.7 Kinetic Study

The data collected in this study was used to determine how quickly the reactions could produce triphenyl phosphate without reducing selectivity. The efficacy of industrial catalysts is often measured in terms of turn over frequency (TOF). This is the number of moles of product which can be produced by one mole of catalyst per unit time.¹¹⁹ Kinetic data obtained with the standard reaction setup is presented in Table 14.

Table 14. White Phosphorus Conversion with Varying Amounts of Catalyst and Iodine.

Entry	Rate of P ₄ addition / mmol/h	Amount of Fe(acac) ₃ / mmol	Rate P ₄ addition per mmol Fe(acac) ₃ / mmol/h	Amount of I ₂ / mmol	Rate P ₄ addition per mmol of I ₂ / mmol/h	Phosphorus containing products (by ³¹ P NMR)
1	0.73	4.35	0.17	1.45	0.50	100 % O=P(OPh) ₃
2	0.75	2.50	0.30	1.66	0.44	67 % O=P(OPh) ₃ 33 % O=P(OPh) ₂ OH
3	1.04	3.02	0.34	0.49	2.10	Reaction smoked

Reactions were conducted at 80 °C in toluene. See experimental section 6.10 for details.

For the reaction with phenol, white phosphorus can be added to a reaction mixture at a maximum rate of 0.17 mmol/h, per mmol of $\text{Fe}(\text{acac})_3$ at 80 °C (see Entry in Table 14). At this rate of addition, 100 % conversion to triphenyl phosphate is observed. If the addition rate per mmol of catalyst is increased, the hydrolysis product is observed in the final reaction mass. For example, at a white phosphorus addition rate of 0.30 mmol/h, per mmol of catalyst, the reaction produces approximately 33 % of the hydrolysis product (Entry 2 in Table 14). In this case, the conversion of $\text{O}=\text{PI}(\text{OPh})_2$ to triphenyl phosphate is the rate limiting step of the reaction. If the amount of iodine present is drastically reduced, the rate determining step is altered (Entry 3 in Table 14). Under these low iodine conditions, the rate at which the iron catalyst reoxidises HI back to I_2 is too slow. Therefore the reaction mixture became iodine-deficient and the formation of smoke was observed, indicating the direct reaction of P_4 with air.

The maximum rate of addition for 100 % selectivity (0.17 mmol/h/mmol) equates to a TOF of 0.68 /h. This is far below the standard expected of industrial catalysts, where turn over frequencies range from 0.01-100 /s. It is hoped that this rate could be dramatically improved through further study, perhaps by using separate catalysts for the reoxidation of HI and the substitution of $\text{O}=\text{P}(\text{OPh})_2\text{I}$ to form $\text{O}=\text{P}(\text{OPh})_3$.

In summary, the work outlined above has shown the iron catalyst performs at least two key functions in the reaction of phenol, air and white phosphorus. Firstly it enhances the rate of triphenyl phosphate formation from $\text{O}=\text{PI}(\text{OPh})_2$, favouring this reaction over hydrolysis. Secondly it increases the rate of reoxidation of HI to form iodine. Meanwhile

the iodine serves to oxidise white phosphorus to phosphorus(III) (in the form of phosphorus triiodide). Bubbling air through the reaction serves two purposes. The first is to oxidize the phosphorus(III) to phosphorus(V) when phosphorus triiodide reacts with phenol. The second is the reoxidation of HI byproduct back to iodine.

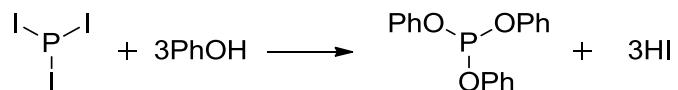
4.3 Catalytic Synthesis of Triphenyl Phosphite from White Phosphorus

Using the mechanistic knowledge gained from the reactions described in this chapter, attempts were made to modify our catalytic process to yield triphenyl phosphite as a product. As previously noted in the introduction, triphenyl phosphite is of great use as an antioxidant in various plastic materials.

Triphenyl phosphite has been shown to slowly oxidize to phosphate in iron acetylacetone and iodine-containing systems (Table 10). Therefore to successfully synthesize phosphites with these or similar systems the reactions must be conducted rapidly to minimize the amount of oxidation which can occur.

We have shown that PI_3 will not react with phenol unless air is bubbled through the reaction system, where the rapid oxidation of $\text{P}(\text{OPh})_2\text{I}$ to $\text{O}=\text{P}(\text{OPh})_2\text{I}$ drives the substitution reaction (Scheme 33). To facilitate the formation of triphenyl phosphite it was clear that another way of driving the PI to $\text{P}(\text{OPh})$ substitution reaction, without oxidation of the product, would have to be devised (Scheme 34). As the reaction produces HI as a byproduct methods of rapidly removing the HI were focused upon.

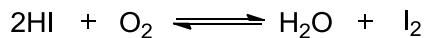
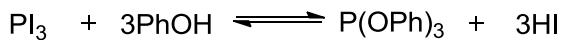
Scheme 34. Desired Reactivity of PI₃ with Phenol



To this end the aerobic reaction of P₄ with phenol in the presence of iodine and DBU was attempted. It was hoped the presence of a base would remove the protons from HI and this would encourage the formation of phosphites. A catalytic amount of iron(III) acetylacetone was added in the hope that the oxidation of I⁻ back to I₂ would be possible. The reaction was unsuccessful as white phosphorus smoke was observed after sufficient P₄ had been added to form PI₃. It is likely that the significant change of pH of the reaction mixture leads to a change of redox potentials, resulting in an inability of the air/iron acetylacetone system to oxidize I⁻ back to I₂.

An alternative way of removing the HI would be to increase the rate of oxidation of HI to I₂. It has been shown that the presence of iron(III) acetylacetone increases the rate of this oxidation. It was hoped that if a way could be found to further increase the rate of this oxidation, the faster removal of HI would encourage P-I to P-OPh substitution. As the oxidation of HI produces water as a byproduct the removal of water could reasonably be expected to increase the rate of HI removal (Scheme 35).

Scheme 35. HI Reaction Equilibria



The removal of water will also help to inhibit the oxidation of phosphites to phosphates.

The reaction of triphenyl phosphite with water and iodine has been shown to form triphenyl phosphate and HI.¹²⁰ If this mechanism is contributing to the oxidation of P(III) to P(V) in our reaction systems, the removal of water could both encourage the substitution of $\text{P(OPh)}_2\text{I}$ to form P(OPh)_3 and inhibit its oxidation to $\text{O=P(OPh)}_2\text{I}$.

To test this hypothesis the reaction of phosphorus triiodide with phenol was attempted in the presence of 3Å molecular sieves. It has previously been shown that the aerobic reaction of PI_3 with phenol without molecular sieves produces quantitative conversion to $\text{O=P(OPh)}_2\text{I}$ and that in an anaerobic environment no reaction occurs (Table 11).

Table 15. Reactions of PI_3 with Phenol in the Presence of Molecular Sieves

	Air Flow	Product
1	0	PI_3
2	40 mL/min	P(OPh)_3 [67 %], $\text{P(OPh)}_2\text{I}$ [5 %] O=P(OPh)_3 [9 %] $\text{O=P(OPh)}_2\text{I}$ [10 %]

Reactions were conducted in toluene at 80 °C over 4 hours. The ratio of PI_3 to phenol was 1:3. See experimental section 6.11 for details.

The anaerobic reaction of PI_3 with phenol in the presence of molecular sieves did not produce any phosphorus-containing products. Only unreacted starting material was observed in the ^{31}P NMR spectra after 4 hours stirring at 80 °C (Entry 1, Table 15). This result is unsurprising as the oxidation of HI is not possible without a supply of air so molecular sieves are not expected to influence the reaction. The aerobic reaction (4 hours at 80 °C) on the other hand was significantly affected by the presence of molecular sieves (Entry 2, Table 15). Diphenyl phosphoriodidate, the major product of the reaction without molecular sieves, was observed in only 10 % conversion from PI_3 . The major product was triphenyl phosphite which was formed in 67 % conversion from PI_3 . Triphenyl phosphate, diphenyl phosphoriodidite and unreacted PI_3 were also observed in the ^{31}P NMR spectrum of the mixture at the end of the reaction. The ratio of phosphite to phosphate of the reaction products was 3.8:1.

The results indicate the removal of water does help favour substitution of $\text{P}(\text{OPh})_2\text{I}$ to form $\text{P}(\text{OPh})_3$, over oxidation to $\text{O}=\text{P}(\text{OPh})_2\text{I}$. This is a promising result and implies catalytic synthesis of triphenyl phosphites may be possible.

Catalytic reactions of P_4 with phenol were attempted in the presence of molecular sieves. As aerobic Fe(III)/ I_2 systems were being used to catalyse the oxidation of P_4 the reactions were conducted relatively quickly. It was hoped that this would limit the time any phosphite product formed had to oxidize to phosphate.

In the first reaction attempted white phosphorus was added to the reaction at a rate of 0.50 mmol/h per mmol iron acetylacetonate (Entry 1, Table 16). At the end of this addition the reaction mass was found to contain 50 % triphenyl phosphite, 45 % triphenyl phosphate and 5 % white phosphorus. The observed formation of phosphite supports the argument that the presence of molecular sieves facilitates the nucleophilic substitution of PI_3 to form triphenyl phosphite. It was hoped that increasing the rate of P_4 addition could improve the selectivity of phosphite over phosphate formed in the reaction. To conduct a reaction with a much faster rate of P_4 addition a higher than usual iodine loading was used, to prevent the direct reaction of P_4 with air (ratio $\text{P}_4:\text{I}_2$, 1:1). When the reaction was performed with a P_4 addition rate of 1.60 mmol/h per mmol $\text{Fe}(\text{acac})_3$ the final ratio of phosphite to phosphate was more than 6:1 (Entry 3, Table 16). Unfortunately even with the higher iodine loading there was a build up of P_4 in the reaction, and the mixture at the end of the reaction contained unreacted P_4 .

Best results were obtained using an intermediate P_4 addition rate of 0.80 mmol/h per mmol of catalyst (Entry 2, Table 16). The higher iodine loading was used, and an excess of phenol was added. It was hoped that the presence of excess phenol would further favour the substitution reaction. The mixture after reaction contained 60 % phosphite and 40 % phosphate by $^{31}\text{P}\{\text{H}\}$ NMR. No white phosphorus peak was observed, indicating complete conversion from P_4 to products. It is pleasing to see some selectivity towards triphenyl phosphite. Unfortunately further improvement on this 60 % selectivity will likely prove difficult due to the tendency of iron to catalyse phosphite oxidation, and the build up of white phosphorus at faster rates of addition.

Table 16. Reactions of P₄ with Phenol in the Presence of Molecular Sieves

Catalyst	Ratio P ₄ :I ₂ :Cat:PhOH	Rate of P ₄ Addition per mmol Catalyst	Products
Fe(acac)₃	1:0.3:0.5:12	0.50 mmol/h	O=P(OPh) ₃ [45 %] P(OPh) ₃ [50 %] P ₄ [5%]
Fe(acac)₃	1:1:0.5:24	0.80 mmol/h	O=P(OPh) ₃ [40 %] P(OPh) ₃ [60 %]
Fe(acac)₃	1:1:0.5:12	1.60 mmol/h	O=P(OPh) ₃ [9 %] P(OPh) ₃ [57 %] P ₄ [34 %]

Reactions were conducted at 80 °C in toluene. See experimental section 6.11 for details.

Unfortunately 60 % appears to be the highest selectivity towards phosphite that can be obtained using these systems. Perhaps by the use of a different catalyst system, which is less prone to oxidize phosphites, a direct route to these compounds from P₄ can be obtained. It is hoped the work demonstrated here on phosphate and phosphite formation will inspire more work on the catalytic reactions of P₄ with alcohols.

5. Independent Syntheses and Reactions of Intermediates

Over the course of our mechanistic investigations several species were identified which could be of synthetic interest in their own right. Specifically the reaction intermediates diaryl phosphoriodidate ($O=P(OAr)_2I$) and the hydrolysis products of these, diaryl phosphate ($O=P(OAr)_2OH$) and tetra-aryl pyrophosphate ($(ArO)_2P(O)-O-P(O)(OAr)_2$) are of interest. To further investigate these compounds their direct synthesis from PI_3 was attempted and the chemistry of the phosphoriodidates in particular was investigated further.

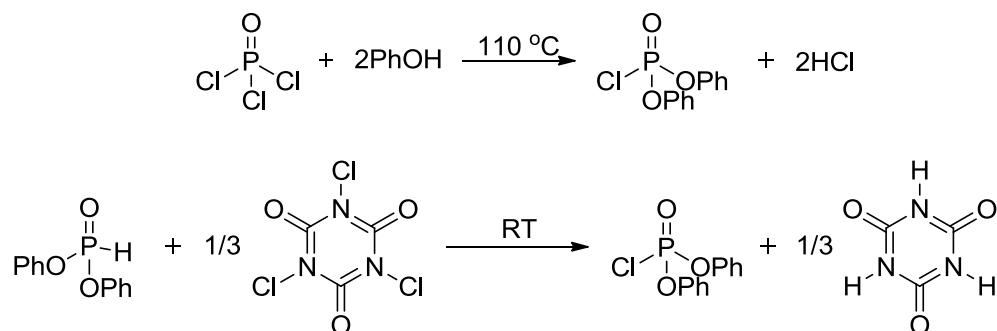
5.1 Introduction

Diphenyl phosphoriodidate was previously synthesized by Stawinski *et al.* by the reaction of diphenyl-H-phosphonate ($O=PH(OPh)_2$) with iodine.¹¹³ Stirring at room temperature for 5 minutes was said to give 90 % conversion to the phosphoriodidate. This was then reacted with pyridine *in situ* to give tetraphenyl pyrophosphate. The reaction was monitored by ^{31}P NMR and the product was not isolated or characterized further. The chemistry of this molecule does not seem to have been previously investigated.

By contrast the closely related compound, diphenyl phosphorochloridate, is well characterized. The reactivity of this compound, mainly as a phosphorylating agent, is well understood. This molecule was first synthesized by Gustav Jacobsen in 1875.¹²¹ The

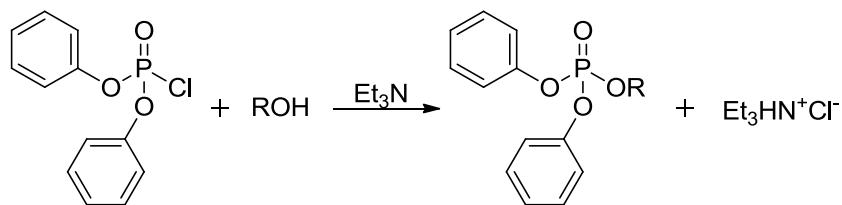
early synthesis was performed by refluxing two equivalents of phenol with phosphorus oxychloride (Scheme 36). The product was separated by reduced pressure fractional distillation. A more recent method of preparing this compound is by the reaction of diphenyl-H-phosphonate with trichloroisocyanuric acid.¹²² The reaction produces a quantitative yield of diphenyl phosphorochloridate in 15 minutes at room temperature. The isocyanuric acid byproduct can be removed by filtration.

Scheme 36. Synthetic Routes to Diphenyl Phosphorochloridate



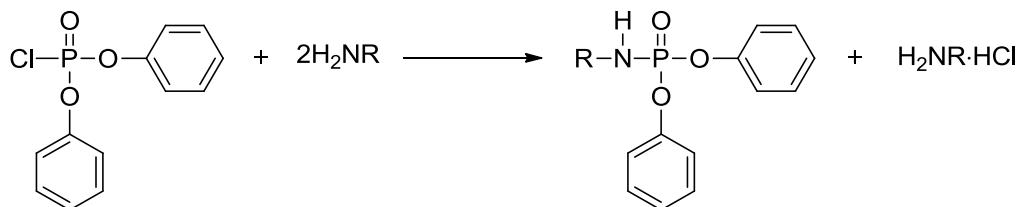
In a 1997 patent Saindane documented the synthesis of a series of mixed phosphates from diphenyl phosphorochloridate.¹²³ A series of diaryl phosphorochloridates were reacted with primary alcohols in triethylamine (Scheme 37). The reactions were conducted at room temperature over 20 hours and yields of up to 97 % were recorded. Polyethylene glycol diphenyl phosphate and methoxy-polyethylene glycol diphenyl phosphate were synthesized by this method. It was claimed that the same reactions would work using diphenyl phosphoroiodidate instead of diphenyl phosphorochloridate however no examples are given in the patent.

Scheme 37. Synthesis of Mixed Phosphates from Diphenyl Phosphorochloridates



The reaction of diphenyl phosphorochloridate with amines to form phosphoramides is also well documented. Audrieth and Toy reacted diphenyl phosphorochloridate with a series of primary and secondary amines (Scheme 38).¹²⁴ The reactions were conducted by adding the phosphorochloridate to chloroform solutions of amines at 0 °C. Methyl amine, cyclohexylamine, aniline and morpholine were successfully reacted in this manner.

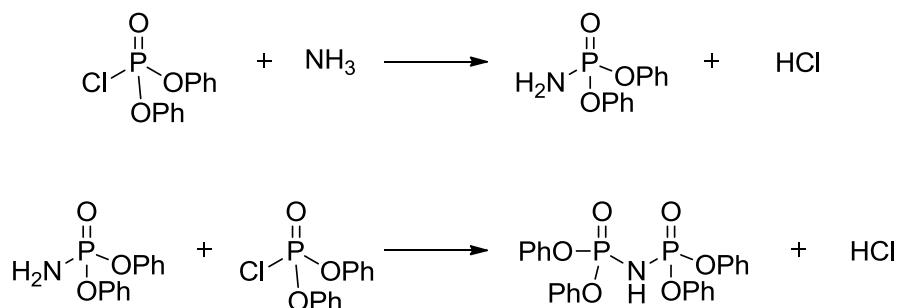
Scheme 38. Synthesis of Phosphoramides from Diphenyl Phosphorochloridate



Diphenyl phosphorochloridate has also been used for the phosphorylation of sugars.¹²⁵ Foster et. al. investigated the reactions of diphenyl phosphorochloridate and like the researchers above, noted it readily reacted with both alcohols and amines. By using various galactoside and deoxy-galactosides as the sources of hydroxyl functionality, phosphorylation of these sugars was easily achieved.

A more recent application of the phosphorylating abilities of phosphorochloridates can be seen in the work of Woollins *et al.*¹²⁶ In this paper diphenyl phosphorochloridate was reacted with ammonia to produce diphenyl phosphoramidate (Scheme 39). This was then reacted with another equivalent of diphenyl phosphorochloridate in the presence of base to form a P-N-P ligand. By using chlorosulfates and chloroselenates as well as the phosphates a series of mixed P-N-P ligands were synthesized.

Scheme 39. Formation of P-N-P Ligands from Diphenyl Phosphorochloridate



Given the wide range of chemistry possible with diaryl phosphorochloridates it was hoped similar reactions with phosphoroiodidates would prove feasible.

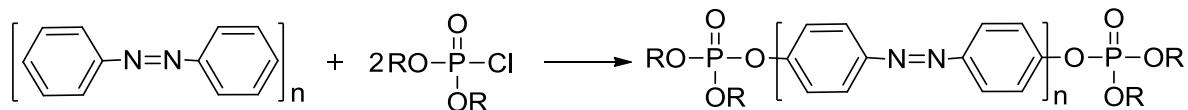
5.1.1 Mixed Phosphates as Flame Retardants

There has been some recent interest in the development of mixed phosphates for use as flame retardants. High molecular weight molecules are preferred due to their lower volatility during fires and their resistance to leaching from the polymer. Compounds like resorcinol-bis(diphenyl) phosphate are used as flame retardants for these reasons however they are viscous liquids which makes their even blending throughout the polymer resin

difficult.¹²⁷ Solid high molecular weight phosphates would be preferable to these molecules. Ideally a phosphate flame retardant should combine the rheological properties of triphenyl phosphate with a higher molecular weight and equal or greater ability to combat the spread of a fire.

In light of this and because of a desire to minimize the use of halogenated flame retardants, several flame retardant manufacturers are actively seeking to develop new, high molecular weight, solid phosphate molecules for use as flame retardants. With the intent of preparing new flame retardants, Kannan and Kishore synthesized a series of polyaryl azophosphate esters by the reaction of 4,4'-dihydroxyazobenzene with various phosphorochloridates (Scheme 40).¹²⁸

Scheme 40. Synthesis of Polyazophosphate Flame Retardants



Delobel *et al.* formed new, bis(PEPA)phosphate flame retardants for polypropylene.¹²⁹ The new molecule combined 2 equivalents of the known phosphate flame retardant PEPA ($\text{HOCH}_2\text{-C}(\text{CH}_2\text{O})_3\text{P=O}$, Figure 11) with a bridging phosphate to form a new molecule (Figure 12). The new flame retardant is of significantly higher molecular weight than PEPA and the phosphate functionality is retained.

Figure 11. PEPA

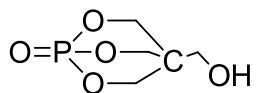
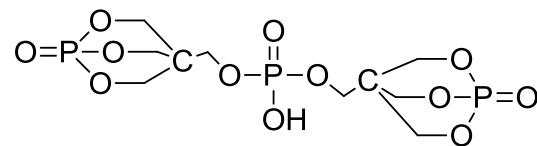


Figure 12. Bis(PEPA)phosphate



In a similar vein resorcinol and phloroglucinol have been used to attach multiple phosphates functionalities onto the same molecule (Figure 13 and Figure 14 respectively).^{130, 131} The reaction of these alcohols with diphenyl phosphorochloridate produces molecules with two and three phosphate moieties respectively.

Figure 13. Resorcinol Bis-Diphenyl

Phosphate

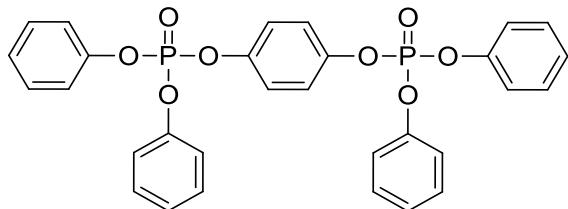
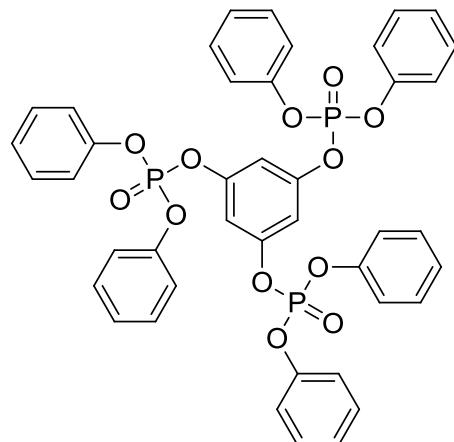


Figure 14. Phloroglucinol Phosphate



Further illustrating the industrial relevance of these species, a 2004 Azko-Nobel paper reported the discovery of a new phosphorus ester flame retardant, though the structure of the compound was not revealed.¹³²

5.2 Results

5.2.1 Independent Synthesis of Diaryl Phosphoroiodidates

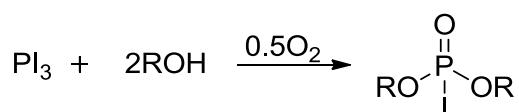
The synthesis of diphenyl phosphoroiodidate ($O=P(OPh)_2I$) from PI_3 was conducted as part of our studies into the phosphate forming reactions (section 4.2.3). It was thought interesting to synthesise and characterize the *o*-cresol and 2,4-di-*tert*-butyl phenol analogues of this molecule. Whilst diphenyl phosphoroiodidate is a known compound, the more sterically hindered analogues have not been reported.

Diphenyl phosphoroiodidate and ditolyl phosphoroiodidate were both prepared in their crude forms by the aerobic reaction of PI_3 with the corresponding alcohols. The reactions were conducted at 80 °C over 5 hours, and in both cases complete conversion to phosphoroiodidate was observed. On evaporation of the volatiles *in vacuo* crude diphenyl phosphoroiodidate was isolated as a yellow oil in 51 % yield. Ditolyl phosphoroiodidate was isolated as a red oil in 44 % yield. The darker colour of the products is believed to be due to small amounts of iodine contaminating the samples. Unfortunately purification by column chromatography on silica proved impossible as the products were prone to hydrolysis to diaryl phosphates.

Bis(2,4-di-*tert*-butyl phenyl) phosphoroiodidate was synthesized by a slightly different method. PI_3 was reacted with 2,4-di-*tert*-butyl phenol at 60 °C over 24 hours. Fortunately the product was slightly more resistant to hydrolysis than its analogues. After the removal of the solvent *in vacuo* the crude product was purified by column chromatography on

silica gel (eluent 3:1 hexane:ether). The product of this reaction is still somewhat moisture sensitive and rapid elution was required to prevent hydrolysis on the column. The pure product was isolated in 13 % yield and was characterized by NMR (^1H , ^{31}P , ^{13}C), IR and mass spectrometry (including exact mass determination).

Scheme 41. Synthesis of Phosphoriodidates. R = Phenol, *o*-cresol, 2,4-di-*tert*-butyl phenol

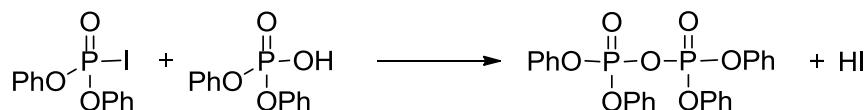


5.2.2 Independent Synthesis of Tetraphenyl Pyrophosphate

Tetraphenyl pyrophosphate was formed during our mechanistic studies when diphenylphosphoriodidate was reacted with phenol without the presence of the iron(III) acetylacetone catalyst (Table 12, section 4.2.3). Its equivalents were also formed when insufficient catalyst loadings were used in the phosphate forming reactions using *o*-cresol and 2,4-di-*tert*-butyl phenol (sections 3.2.1 and 3.2.2). From this data it was believed that the pyrophosphate was a partial hydrolysis product of the phosphoriodidate, forming when insufficient water was present to facilitate complete hydrolysis to diaryl phosphates. This is similar to the hydrolysis of diphenyl phosphorochloridate with 0.5 equivalents of water¹³³ and to the reaction of diphenyl phosphorochloridate with diphenyl phosphate in the presence of base,¹³⁴ both of which have been shown to produce tetraphenyl pyrophosphate.

In analogy with the latter reaction, diphenyl phosphoroiiodide was reacted with a small excess of diphenyl phosphate in anhydrous conditions under nitrogen. After 4 hours of reflux in dry toluene the solution was analysed by ^{31}P NMR. The starting materials were found to have combined to form tetraphenyl pyrophosphate, the excess of diphenyl phosphate was the only other signal in the ^{31}P NMR spectrum.

Scheme 42. Synthesis of Tetraphenyl Pyrophosphate



Though interesting, as a means of synthesising tetraphenyl pyrophosphate this preparation offers no advantage over existing laboratory preparations (i.e. the condensation of two molecules of diphenyl phosphate¹³⁵).

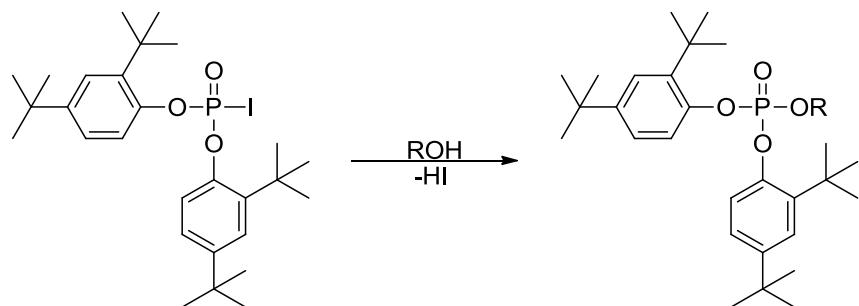
5.3 Reactions of Bis(2,4-di-tert-butylphenyl) Phosphoroiiodidate with Alcohols

As can be seen from the introduction to this chapter, there is much current interest in the synthesis of high molecular weight, solid phosphates for use as flame retardants in plastics. Many of the efforts to form these new compounds have used diphenyl phosphorochloridate as a starting material. It was hoped that phosphoroiiodidates would provide access to mixed phosphates that may not be synthesized easily from phosphorochloridates.

It also should be noted that the chlorine analogue of bis(2,4-di-tert-butylphenyl) phosphoroiiodide is not a known compound. This means that this iodine containing compound provides a potential route to 2,4-di-tert-butylphenyl containing phosphates that could not be synthesized from phosphorochloridates. Tert-butyl groups are a simple way of adding molecular weight to a compound without changing the functional groups. Furthermore the presence of tert-butyl groups is known to often encourage crystallization so phosphates formed from this phosphoroiiodide are more likely to solidify.

Bis(2,4-di-tert-butylphenyl) phosphoroiiodide was reacted with a series of alcohols to produce mixed tertiary organophosphates in quantitative yields (Scheme 43). The alcohols chosen for these reactions were methanol, ethanol and 2-propanol. More forcing conditions were required for the reaction using 2-propanol. This is probably due to the increased steric hindrance around the central phosphorus atom of the product.

Scheme 43. Reaction of Bis(2,4-di-tert-butylphenyl) Phosphoroiiodide with Alcohols. R = Me, Et, *i*Pr



To synthesize bis(2,4-di-tert-butylphenyl)methyl phosphate, bis(2,4-di-tert-butylphenyl) phosphoroiodidate was reacted with a large excess of methanol. Complete conversion was achieved in one hour of stirring at room temperature. Unlike similar reactions using phosphorochloridates¹²³ the addition of base was not required to facilitate the reaction. After removing the excess methanol *in vacuo* the product was purified by column chromatography (eluent DCM then methanol) to give bis(2,4-di-tert-butylphenyl)methyl phosphate as a clear, viscous liquid in 52 % yield. The product was characterized by NMR (¹H, ³¹P, ¹³C), IR and mass spectrometry (including exact mass determination).

Bis(2,4-di-tert-butylphenyl)ethyl phosphate was prepared by the same method, using excess ethanol as both a reagent and the solvent. After purification the product was isolated as a clear oil in 43 % yield. The product was characterized by NMR (¹H, ³¹P, ¹³C), IR and mass spectrometry (including exact mass determination).

The reaction of bis(2,4-di-tert-butylphenyl) phosphoroiodidate with an excess of 2-propanol at RT resulted in a much slower conversion to bis(2,4-di-tert-butylphenyl)-*i*-propyl phosphate. Even after stirring for six hours some starting material could be observed in the ³¹P NMR. When the reaction was repeated in refluxing 2-propanol complete conversion to the product was observed after 1 h. After cooling to RT and removing the 2-propanol *in vacuo* the product was purified by column chromatography. Bis(2,4-di-tert-butylphenyl)-*i*-propyl phosphate was obtained as a clear oil in 57 % yield. The product was characterized by NMR (¹H, ³¹P, ¹³C), IR and mass spectrometry (including exact mass determination).

To further gauge the scope of these reactions, the reaction of bis(2,4-di-tert-butylphenyl) phosphoroiiodate with triphenylmethanol was attempted. No reaction occurred, even after refluxing for 24 h in toluene. Triethylamine base was added to facilitate the reaction, however this had no discernable effect. It would appear the triphenylmethanol group is simply too bulky to form mixed phosphates of this type. The reaction of bis-1,1'-naphthol with two equivalents of bis(2,4-di-tert-butylphenyl) phosphoroiiodate was also unsuccessful.

5.4 Reactions of Bis(2,4-di-tert-butylphenyl) Phosphoroiiodate with Amines

As can be seen from the literature reviewed at the beginning of this chapter, the reactions of amines with diphenyl phosphorochloridate are well known.^{124, 126} It was thought interesting to react phosphoroiiodates with amines to verify the reactivity of phosphoroiiodates in this type of reaction. The phosphoramidates formed from such reactions could be potentially of interest to the pharmaceutical industry, as phosphoramidates have been shown to increase glutamate receptor function in mammals.¹³⁶ To this end the reaction of bis(2,4-di-tert-butylphenyl) phosphoroiiodate with selected amines was investigated.

Bis(2,4-di-tert-butylphenyl)-dimethyl phosphoroamidate was successfully synthesized by reacting bis(2,4-di-tert-butylphenyl) phosphoroiiodate in an excess of dimethyl amine at 0 °C for 1 hour. Complete conversion to product was observed in the ^{31}P NMR after this time. The product was isolated by removing the dimethyl amine *in vacuo* and extracting

the residue with dichloromethane. The organic phase was then washed with water to remove Me₂NH₂I. The organic layer was separated, dried with magnesium sulfate and evaporated to give the product as a white solid in 72 % yield. The product was unstable with respect to hydrolysis so further purification by column chromatography was not possible. The product was characterized by NMR (¹H, ³¹P, ¹³C) IR and mass spectrometry (including exact mass determination).

6. Experimental

The compounds used in these experiments were supplied by Sigma Aldrich, Alfa Aesar or Acros Organics and were used without further drying or purification unless stated otherwise. Toluene was dried using an MBraun SPS 800 solvent drying system and degassed by thorough nitrogen bubbling. White phosphorus was supplied by Thermphos International and was used as received without further purification. Molecular sieves 3Å (1-2 mm diameter pellets) were purchased from Alfa Aesar and used after activation *in vacuo* at 250 °C. IR spectra were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer 2000 FTIR/Raman spectrometer. NMR measurements were taken on a Bruker Avance II 400 spectrometer or Jeol EX 270 spectrometer and performed at 25 °C unless otherwise indicated; 85% H₃PO₄ was used as external standard in ³¹P NMR; ¹H and ¹³C NMR shifts are relative to TMS (internal standard). All NMR shift values are given in parts per million (ppm) throughout. Assignment of signals were assisted by the collection of ¹H{³¹P}, ³¹P, ¹³C DEPT-q, H-C HSQC, H-C HMBC and H-H DFQ COSY experiments. Powder X-ray diffraction patterns were recorded on a Stoe STADI/P diffractometer using CuKα₁ radiation. The GCMS system used in this study comprised of an Agilent 6890 series GC system and an Agilent 5973 Network Mass Selective Detector. This spectrometer uses electron impact ionisation (EI) detection. MS spectra were obtained on Micromass LCT (ES) and Micromass GCT (EI, CI). Microanalysis was performed by the University of St Andrews microanalysis service.

N. B. Note on Safety

White phosphorus is pyrophoric and extremely toxic. Reactions involving a flammable solvent, white phosphorus and air also present a significant risk of explosion. As such it is vital that the white phosphorus reactions documented here are performed behind a blast field and that adequate personal protection equipment is worn. A large volume of copper sulphate solution and a powder fire extinguisher should be kept close on hand in case of a fire. For further information on working with white phosphorus please consult section

1.2.2

Table 17. ^{31}P NMR Shifts of Compounds Identified in this Study

	$\text{R} = \text{phenol}$	$\text{R} = o\text{-cresol}$	$\text{R} = 2,4\text{-ditertbutylphenol}$
$\text{O}=\text{P}(\text{OR})_3$	-17.4 ^[137]	-16.1 ^[137]	-19.9
$\text{O}=\text{P}(\text{OH})(\text{OR})_2$	-9.1 ^[138]	-	-
$\text{O}=\text{P}(\text{OR})_2\text{I}$	-47.0 ^[113]	-	-60.0
$(\text{RO})_2(\text{O})\text{P-O-P(O)(OR)}_2$	-24.9 ^[139]	-24.0	-27.1

6.1 Preparation of Catalysts

Catalysts tested which are not listed in this section were purchased from Sigma Aldrich and used as received. Iron(III) stearate, iron(II) sulfate monohydrate, iron(III) 2,2,6,6-tetramethyl-3,5-heptanedioneate, and iron(III) 1,1,1,-trifluoro-2,4-pentanedioneate are known compounds however an alternative preparative method described below were used

for their syntheses here. Other catalysts were prepared by the literature methods cited below.

6.1.2 Synthesis of Iron(III) Stearate

Iron(III) chloride (2.52 g, 0.02 mol) and sodium hydroxide (2.40 g, 0.06 mol) were dissolved in 60:40 ethanol:water (50 mL). The solution was charged to a round bottomed flask and heated to 60 °C. A solution of stearic acid (17.04 g, 0.06 mol) in 200 mL of warm ethanol (200 mL) was added slowly to the reaction. The reaction mass was then allowed to cool to room temperature. A brown precipitate formed which was filtered off and washed with three 50 mL portions of water and three 50 mL portions of cold ethanol. The solid was then dried under vacuum to yield brown iron stearate powder (10.8 g, 60 %). The IR spectrum of the compound was found to be in excellent agreement with the literature.^{100, 140} M.p. 100-102 °C.

6.1.3 Synthesis of [Fe(2,2'-bipy)₃]Cl₂

Tris(bipyridine)iron(II) chloride was synthesized by the method of Sawyar *et al.* from iron(II) chloride.¹⁴¹ The compound was isolated in 48 % yield and its identity was confirmed by mass spectrometry.

6.1.4 Synthesis of Iron(II) Sulfate Monohydrate

Iron(II) chloride tetrahydrate (8.00 g, 0.04 mol) and sulphuric acid (7.84 g, 0.08 mol) were stirred in 100 mL of water for 16 h at room temperature. The solvent and HCl byproduct were removed at 70 °C *in vacuo* to yield 6.44 g iron(II) sulfate monohydrate

(6.44 g, 95 %). The IR spectrum of the compound was found to be in excellent agreement with the literature.¹⁴² M.p. > 300 °C

6.1.5 Synthesis of Iron(III) Diacetate Chloride

Iron(III) diacetate chloride was synthesized by the method of Lau *et al.*⁹⁰ The compound was isolated in 20 % yield. Its identity was confirmed by mass spectrometry.

6.1.6 Synthesis of Iron(III) 2,2,6,6-tetramethyl-3,5-heptanedioneate (1)

2,2,6,6-Tetramethyl-3,5-heptanedione (9.90 g, 0.054 mol), iron(III) chloride (2.92 g, 0.018 mol) and sodium acetate (4.42 g, 0.054 mol) were dissolved in 50 mL of 50:50 ethanol:water. The solution was heated to 60 °C for 1 hour with stirring. An orange precipitate crashed out on cooling with an ice bath. The solid was collected by filtration and washed with 25 mL of water. Drying the solid *in vacuo* yielded **1** (10.3 g, 95 %) as an orange powder. The IR spectrum and melting point of the compound (163-164 °C) were found to be in excellent agreement with the literature.¹⁴³

6.1.7 Synthesis of Iron(III) 1,1,1,-trifluoro-2,4-pentanedioneate (2)

1,1,1,-Trifluoro-2,4-pentanedione (10.00 g, 0.0648 mol), iron(III) chloride (3.70 g, 0.0216 mol) and sodium acetate (8.80 g, 0.0648 mol) were dissolved in 50 mL of 50:50 ethanol:water. The solution was heated to 60 °C for 1 hour with stirring. A red precipitate crashed out on cooling with an ice bath. The solid was collected by filtration and washed with 25 mL of water. Drying the solid *in vacuo* yielded **2** (10.90 g, 44 %) as a red

powder. The IR spectrum was found to be in excellent agreement with the literature.¹⁴⁴
M.p. 110-114 °C.

6.1.8 Synthesis of Gold and Palladium Nanocrystals on TiO₂ Support

Gold and palladium nanocrystals were synthesized by the method of Enache *et al.* by the calcination of auric acid and palladium chloride on a titanium dioxide support.⁹⁸

6.1.9 Synthesis of Copper Oxide Nanocrystals

Copper oxide nanocrystals were prepared by the method of Zhou *et al.* by the calcination of copper (II) nitrate in oxygen.⁹⁹

6.1.10 Synthesis of Palladium Nanocrystals on TiO₂ Support

Palladium nanocrystals were synthesized by the method of Enache *et al.* by the calcination of palladium chloride on a titanium dioxide support.⁹⁸

6.2 Catalyst Trials

The reactions reported in this section and the following sections were typically analysed by ³¹P NMR. Where paramagnetic catalysts were used, these samples were prepared by transferring an aliquot amount (typically 1 mL) of the mixture after reaction to another flask, shaking it with solid sodium sulphite (0.2 g) and filtering the mixture using a sinter. A small amount of CDCl₃ (0.4 mL) was added for locking purposes.

6.2.1 Reaction Using Copper(II) Sulfate

Anhydrous copper(II) sulfate (0.43 g, 2.7 mmol), phenol (7.63 g, 0.0811 mol), iodine (0.08g, 0.3 mmol) and toluene (10 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. Two of the necks of the flask were sealed with suba seals and the third was fitted with an air condenser with a copper sulfate bubbler outlet. The reaction was heated to 60 °C with vigorous stirring. Once the reaction mass had reached the required temperature, a flow of air was bubbled through the reaction mass at a rate of 40 mL/min. A solution of P₄ (0.335g, 2.7 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.5 mL/h using a syringe pump. The air and white phosphorus solution were introduced through needles inserted in the septa in the necks of the flask, making sure that needle tips were placed under the level of the liquid mixture. The air supply was from a compressed air cylinder, and was regulated by a needle valve and a flow meter. The reaction was continued for one hour after the addition of P₄ was completed to ensure all the white phosphorus was consumed. The reaction was left to cool and then filtered to leave a clear liquid and a black solid. The solid was dried *in vacuo*. Powder X-ray diffraction identified the solid as copper metal. The liquid part was analysed by ³¹P NMR however the peaks did not correspond to expected reaction products and were not identified.

³¹P NMR (109.4 MHz, CDCl₃): δ 1.9 (s), 5.3 (s), 7.8 (s), 13.9 (s)

6.2.2 Reaction Using Copper(II) Chloride

Anhydrous copper(II) chloride (0.43 g, 3.2 mmol), phenol (9.09 g, 0.097 mol), iodine (0.025g, 0.1 mmol) and toluene (20 mL) were charged to a 100 mL 3-neck round

bottomed flask under nitrogen. A solution of P₄ (0.40 g, 3.2 mmol) in toluene (20 mL) was added to the reaction at a rate of 2.8 mL/h using a syringe pump. The reaction was conducted using the same set up and conditions as Reaction 6.2.1. The phosphorus addition had to be stopped frequently due to the formation of white phosphorus smoke and was restarted when the smoke subsided. The final reaction mass was left to cool and then filtered to leave a clear liquid and a black solid. Powder X-ray diffraction identified the solid as copper metal. The liquid part was analysed by ³¹P NMR however the peaks did not correspond to expected reaction products and were not identified.

³¹P NMR (109.4 MHz, CDCl₃): 2.2 (s), 2.4 (s), 5.7 (s), 8.1 (s), 14.4 (s)

6.2.3 Reaction Using Copper(II) Chloride and Pyridine

Anhydrous copper(II) chloride (0.36 g, 2.9 mmol), phenol (8.16 g, 0.087 mol), iodine (0.025 g, 0.1 mmol), pyridine (0.12 g, 1.5 mmol) and toluene (20 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.36 g, 2.9 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.4 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.1. The final reaction mass was left to cool and then filtered to leave a clear liquid and a black solid. Powder X-ray diffraction could not conclusively identify the solid. The liquid part was analysed by ³¹P NMR.

³¹P NMR (109.4 MHz, CDCl₃): δ -24.9 ((O)P(OPh)₂-P(O)(OPh)₂, 3 %), -22.5 (unknown, 13 %), -16.7 (O=P(OPh)₃, 14 %), -9.0 (O=P(OPh)₂OH, 42 %), 2.0 (unknown, 2 %), 3.4 (unknown, 26 %)

6.2.4 Reaction Using Copper(II) Acetate

Anhydrous copper(II) acetate (1.26 g, 6.3 mmol), phenol (5.97 g, 0.063 mol), iodine (0.27 g, 1.1 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.39 g, 3.2 mmol) in toluene (20 mL) was added to the reaction at a rate of 5 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.1. with the higher reaction temperature of 80 °C. The final reaction mass was left to cool and then filtered to leave a clear liquid and a grey solid. Powder X-ray diffraction indicated the solid contained Cu₂P₂O₇. The liquid was analysed by ³¹P NMR however it did not appear to contain any phosphorus.

6.2.5 Reaction Using Iron(III) Chloride

Anhydrous iron(III) chloride (0.51 g, 3.2 mmol), phenol (3.95 g, 0.042 mol), iodine (0.15 g, 0.59 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.26 g, 2.1 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.5 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P NMR (109.4 MHz, CDCl₃): δ -47.6 (O=P(OPh)₂I, 11 %), -24.9 ((O)P(OPh)₂-P(O)(OPh)₂, 3 %), -17.0 (O=P(OPh)₃, 78 %), 3.6 (unknown, 9 %)

6.2.6 Reaction Using Iron(III) Chloride and Pyridine

Anhydrous iron(III) chloride (0.39 g, 2.4 mmol), phenol (3.03 g, 0.032 mol), iodine (0.12 g, 0.46 mmol), pyridine (0.19 g, 2.4 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.15 g, 1.2 mmol) in

toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4, however it was stopped after about 75 % of the phosphorus had been added due to the formation of white phosphorus smoke. The final reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3): δ -16.6 ($\text{O}=\text{P}(\text{OPh})_3$, 96.5 %), 126.0 ($\text{P}(\text{OPh})_3$, 3.5 %)

6.2.7 Reaction Using Iron(II) Bromide

Anhydrous iron(II) bromide (0.66 g, 4.9 mmol), phenol (6.12 g, 0.065 mol), iodine (0.27 g, 1.1 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.40 g, 3.2 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.5 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after 1.5 hours due to the formation of white phosphorus smoke.

6.2.8 Reaction Using Iron(III) Stearate

Anhydrous iron(III) stearate (4.42 g, 7.1 mmol), phenol (4.01 g, 0.043 mol), iodine (0.30 g, 1.2 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.44 g, 3.6 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass contained unreacted P_4 and was destroyed by the addition of a large volume of copper sulphate solution.

6.2.9 Reaction Using Tris(bipyridine)iron(II) Chloride

Anhydrous tris(bipyridine)iron(II) chloride (2.27 g, 3.8 mmol), phenol (4.10 g, 0.044 mol), iodine (0.30 g, 1.2 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.45 g, 3.6 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after about 75 % of the phosphorus had been added due to the formation of white phosphorus smoke.

6.2.10 Reaction Using Ferrocene

Anhydrous ferrocene (0.90 g, 4.8 mmol), phenol (2.73 g, 0.029 mol), iodine (0.21 g, 0.8 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.30 g, 2.4 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P NMR (109.4 MHz, CDCl₃): δ -50.5 (OP(OPh)₂I, 6 %), -21.8 ((O)P(OPh)₂-P(O)(OPh)₂, 19 %), -17.5 (OP(OPh)₃, 37 %), 129.6 (P(OPh)₃, 31 %)

6.2.11 Reaction Using Cyclopentadienyliron Dicarbonyl Dimer

Cyclopentadienyliron dicarbonyl dimer (0.72 g, 2.0 mmol), phenol (2.23 g, 0.024 mol), iodine (0.17 g, 0.7 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.25 g, 2.0 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the

same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3): δ -17.6 ($\text{OP}(\text{OPh})_3$, 69 %), 128.1 ($\text{P}(\text{OPh})_3$, 18 %), 173.4 (PI_3 , 13 %)

6.2.12 Reaction Using Iron(III) Diacetate Chloride

Iron(III) diacetate chloride (1.34 g, 6.4 mmol), phenol (3.65 g, 0.039 mol), iodine (0.27 g, 1.1 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.40 g, 3.2 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.3 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3): δ -17.4 ($\text{OP}(\text{OPh})_3$, 46 %), -3.8 (unknown compound, 54 %)

6.2.13 Reaction Using Iron(II) Phosphate Dihydrate

Iron(II) phosphate dihydrate (0.54 g, 2.90 mmol), phenol (1.64 g, 0.017 mol), iodine (0.12 g, 0.46 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.18 g, 1.5 mmol) in toluene (10 mL) was added to the reaction at a rate of 1.7 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass contained unreacted P_4 and was destroyed.

6.2.14 Reaction Using Iron(III) Acetylacetone (excess phenol)

Iron(III) acetylacetone (2.48 g, 6.97 mmol), phenol (6.55 g, 0.070 mol), iodine (0.29 g, 1.10 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.43 g, 3.5 mmol) in toluene (18 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was found to contain 100 % O=P(OPh)₃ by ³¹P NMR. After cooling to RT the solvent was removed *in vacuo*. The dark oil which remained was distilled at 0.4 mbar using a Kugelrohr short path distillation apparatus. The excess phenol and iodine were removed as the first fraction at 80 °C. The distillation was continued to 160 °C whereupon triphenyl phosphate was removed as a light brown solid (1.5 g, 4.6 mmol, 33 %)

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -17.4 (OP(OPh)₃)

¹H NMR (270.2 MHz, CDCl₃): δ 7.10-7.40 (m)

¹³C{¹H} NMR (67.9 MHz, CDCl₃): δ 121.4 (s, *p*-C), 126.8 (s, *m*-C), 131.1 (s, *o*-C), 151.7 (s, *i*-C)

IR (KBr disc): 3069 cm⁻¹(m, Ar-H), 1589 (s, Ar-C=C), 1489 (s, Ar-C=C), 1382 (s), 1299 (s, P=O), 1188 (s, P-O-Ar), 1025 (m), 1010 (m), 960 (s), 776 (s, Ar-H), 735 (s, Ar-H), 688 (m), 579 (m), 518 (m)

6.2.15 Reaction Using Iron(III) Acetylacetone

Iron(III) acetylacetone (2.08 g, 5.84 mmol), phenol (3.30 g, 0.035 mol), iodine (0.24 g, 0.87 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.36 g, 2.9 mmol) in toluene (20 mL) was added to the

reaction at a rate of 4.4 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was found to contain 100 % O=P(OPh)₃ by ³¹P NMR. After cooling to RT the solvent was removed *in vacuo*. The dark oil which remained was distilled at 0.4 mbar using Kugelrohr short path distillation apparatus. The unreacted phenol and iodine was removed as the first fraction at 80 °C. The distillation was continued to 160 °C whereupon triphenyl phosphate was removed as a light brown solid (1.73 g, 5.3 mmol, 61 %). The product was characterized be ³¹P NMR, ¹³C NMR and IR spectroscopy (see experiment 6.2.14).

6.2.16 Reaction Using Iron(III) Acetylacetone (without iodine)

Iron(III) acetylacetone (1.18 g, 3.30 mmol), phenol (1.86 g, 0.020 mol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.16 g, 1.3 mmol) in toluene (10 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after about 2 hours due to the formation of white phosphorus smoke.

6.2.17 Reaction Using Iron(III) Acetylacetone (with bromine)

Iron(III) acetylacetone (1.03 g, 2.91 mmol), phenol (1.64 g, 0.017 mol), bromine (0.08 g, 0.48 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.18 g, 1.45 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up

and conditions as Reaction 6.2.4. The reaction had to be abandoned after about 2.5 hours due to the formation of white phosphorus smoke.

6.2.18 Reaction Using Molybdenum(V) Chloride

Anhydrous molybdenum(V) chloride (1.86 g, 6.8 mmol), phenol (6.41 g, 0.068 mol), iodine (0.28 g, 1.1 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.42 g, 3.41 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.2 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after about 40 % of the phosphorus had been added due to the formation of white phosphorus smoke.

6.2.19 Reaction Using Cobalt(II) Phthalocyanine

Anhydrous Cobalt(II) Phthalocyanine (3.78 g, 6.62 mmol), phenol (6.23 g, 0.066 mol), iodine (0.28 g, 1.1 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.41 g, 3.31 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.2 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass contained unreacted P₄ and was destroyed.

6.2.20 Reaction Using Vanadyl Acetylacetonate

Vanadyl acetylacetonate (1.08 g, 4.08 mmol), phenol (3.84 g, 0.041 mol), iodine (0.17 g, 0.68 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask

under nitrogen. A solution of P₄ (0.25 g, 2.04 mmol) in toluene (20 mL) was added to the reaction at a rate of 2.8 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was found to contain 100 % O=P(OPh)₃ by ³¹P NMR. After cooling to RT the solvent was removed *in vacuo*. The dark oil which remained was distilled at 0.4 mbar using Kugelrohr short path distillation apparatus. The excess phenol was removed as the first fraction at 80 °C. The distillation was continued to 160 °C whereupon triphenyl phosphate was removed as a light brown solid (0.14g, 0.43 mmol, 5 %). The product was characterized by ³¹P NMR.

6.2.21 Reaction Using Dipyridine Nickel(II) Chloride

Dipyridine Nickel(II) Chloride (1.97 g, 6.84 mmol), phenol (6.44 g, 0.068 mol), iodine (0.43 g, 1.7 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.42 g, 3.41 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.2 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction was abandoned after 2 hours due to the formation of white phosphorus smoke.

6.2.22 Reaction Using Manganese(III) Acetylacetonate

Manganese(III) acetylacetonate (1.20 g, 3.42 mmol), phenol (3.22 g, 0.034 mol), iodine (0.22 g, 0.86 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.21 g, 1.71 mmol) in toluene (10 mL) was added to the reaction at a rate of 3.6 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was found to

contain 100% O=P(OPh)₃ by ³¹P NMR. After cooling to RT the solvent was removed *in vacuo*. The dark oil which remained was distilled at 0.4 mbar using Kugelrohr short path distillation apparatus. The excess phenol was removed as the first fraction at 80 °C. The distillation was continued to 160 °C whereupon triphenyl phosphate was removed as a light brown solid (0.25 g, 0.77 mmol, 11 %). The product was characterized by ³¹P NMR.

6.2.23 Reaction Using Manganese(III) Acetylacetone (rapid addition)

Manganese(III) acetylacetone (2.19 g, 6.15 mmol), phenol (5.79 g, 0.062 mol), iodine (0.26 g, 1.02 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.38 g, 3.08 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.7 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by

³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃) {Weak Spectra}: δ -17.6 (O=P(OPh)₃, 73 %), 128.2 (P(OPh)₃, 27 %)

6.2.24 Reaction Using 2.5 % Gold and 2.5 % Palladium on a TiO₂ Support

Gold/palladium nanocrystals prepared in Reaction 6.1.8 (1.70 g, 0.22 mmol Au/ 0.40 mmol Pd), phenol (5.78 g, 0.061 mol), iodine (0.47 g, 1.85 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.38 g, 3.08 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h.

The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -47.5 ($\text{O}=\text{P}(\text{OPh})_2\text{I}$, 5 %), -17.7 ($\text{O}=\text{P}(\text{OPh})_3$, 35 %), -0.1 ($\text{O}=\text{PH}(\text{OPh})_2$, 60 %)

6.2.25 Reaction Using 2.5 % Gold and 2.5 % Palladium on a TiO_2 Support (with mol sieves)

Gold/palladium nanocrystals prepared in Reaction 6.1.8 (1.90 g, 0.25 mmol Au/ 0.45 mmol Pd), phenol (6.53 g, 0.069 mol), iodine (0.59 g, 2.31 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.43 g, 3.43 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -47.8 ($\text{O}=\text{P}(\text{OPh})_2\text{I}$, 2 %), -24.9 ($(\text{PhO})_2\text{OP}-\text{PO}(\text{OPh})_2$, 1 %), -17.0 ($\text{O}=\text{P}(\text{OPh})_3$, 4 %), 1.4 ($\text{O}=\text{PH}(\text{OPh})_2$, 68 %), 183.3 (PI_3 , 25 %)

6.2.26 Reaction Using Copper Oxide Nanocrystals

Copper oxide nanocrystals prepared in Reaction 6.1.9 (0.30 g, 3.72 mmol), phenol (3.50 g, 0.037 mol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.5 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after 1 hour due to the formation of white phosphorus smoke.

6.2.27 Reaction Using 5 % Palladium on a TiO₂ Support

Palladium nanocrystals prepared in Reaction 6.1.10 (1.04 g, 0.49 mmol), phenol (1.05 g, 0.011 mol), iodine (0.07 g, 0.26 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.14 g, 1.11 mmol) in toluene (10 mL) was added to the reaction at a rate of 3.3 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -48.2 (O=P(OPh)₂I, 6 %), -10.0 (P(OPh)₂OH, 3 %), -3.3 (unknown, 8 %), 1.3 (O=PH(OPh)₂, 31 %), 5.7 (O=PH(OH)₂, 43 %), 8.7 (unknown, 2 %), 14.1 (unknown, 4 %)

6.2.28 Reaction Using Iron(II) Pyrophosphate

Iron(II) Pyrophosphate (0.74 g, 0.99 mmol), phenol (2.23 g, 0.024 mol), iodine (0.17 g, 0.68 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.25 g, 1.98 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after 2.5 hours due to the formation of white phosphorus smoke.

6.3 Attempts to Reuse Iron(III) Acetylacetonate Catalysts Recovered by Distillation

The reactions catalysed by iron(III) acetylacetonate and iodine (Reactions 6.2.13, 6.2.14) afforded triphenyl phosphate as the sole product after distillation. After the distillation was complete a black non-volatile solid remained, which appeared to contain at least

some iron(III) acetylacetone (by IR spectroscopy). Attempts were made to use this recovered solid to catalyse further reactions between white phosphorus and phenol.

6.3.1 Run 1 – 1st Reuse

Recovered iron(III) acetylacetone (1.08 g), phenol (3.57 g, 0.037 mol), iodine (0.10g, 0.39 mmol) and toluene (10 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -24.7 (OP(OPh)₂-O-P(O)(OPh)₂, 12 %). -17.1 (OP(OPh)₃, 88 %)

6.3.2 Run 2 – 1st Reuse

Recovered iron(III) acetylacetone (1.34 g), phenol (1.66 g, 0.018 mol), iodine (0.12g, 0.46 mmol) and toluene (10 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.19 g, 1.54 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.1 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): -17.7 (OP(OPh)₃, 98 %), -9.3 ([OP(OPh)₂]₂, 2 %).

The volatiles were removed from the reaction *in vacuo* (see Reaction 6.2.14). The non-volatile solid remaining after distillation was used to catalyse Reaction 6.3.3.

6.3.3 Run 2 – 2nd Reuse

Recovered iron(III) acetylacetone (1.32 g), phenol (1.66 g, 0.018 mol), iodine (0.12 g, 0.46 mmol) and toluene (10 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.19 g, 1.54 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.1 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -17.7 (OP(OPh)₃, 20 %), -9.4 (OP(OPh)₂OH, 80 %)

6.3.4 Run 3 – 1st Reuse

Recovered iron(III) acetylacetone (1.00 g), phenol (3.46 g, 0.037 mol), iodine (0.26 g, 1.02 mmol) and toluene (20 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.38 g, 3.08 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -17.3 (OP(OPh)₃, 43 %), -9.6 (OP(OPh)₂OH, 57 %). The volatiles were removed from the reaction *in vacuo* (see Reaction 6.2.14). The non-volatile solid remaining after distillation was used to catalyse Reaction 6.3.5.

6.3.5 Run 3 – 2nd Reuse

Recovered iron(III) acetylacetone (1.00 g), phenol (3.46 g, 0.037 mol), iodine (0.26 g, 1.02 mmol) and toluene (20 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.38 g, 3.08 mmol) in toluene (20 mL) was added to the

reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned due to the formation of white phosphorus smoke.

6.4 Reactions Using Modified Iron Diketonate Catalysts

The successful phosphate forming reactions were repeated using a series of iron(III) catalysts with modified diketonate ligands. Catalyst loadings were varied to test the limits of catalytic activity. The catalysts were either prepared as described in section 6.1 or purchased from Sigma Aldrich and used as received.

6.4.1 Reaction Using Iron(III) Acetylacetone

Iron(III) acetylacetone (1.55 g, 4.35 mmol), phenol (4.91 g, 0.052 mol), iodine (0.37 g, 1.45 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.54 g, 4.35 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.3 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was found to contain 100 % O=P(OPh)₃ by ³¹P NMR.

³¹P NMR (109.4 MHz, CDCl₃): δ -16.9 (OP(OPh)₃

6.4.2 Reaction Using Iron(III) Acetylacetone (low catalyst loading)

Iron(III) acetylacetone (0.89 g, 2.50 mmol), phenol (5.65 g, 0.060 mol), iodine (0.42 g, 1.66 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.62 g, 5.0 mmol) in toluene (30 mL) was added to the

reaction at a rate of 4.6 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -17.0 ($\text{OP}(\text{OPh})_3$, 67 %), -9.1 ($\text{OP}(\text{OPh})_2\text{OH}$, 33 %)

6.4.3 Reaction Using Iron(III) 2,2,6,6-tetramethyl-3,5-heptanedione (1)

Catalyst **1** (1.13 g, 1.86 mmol), phenol (2.10 g, 0.022 mol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -17.7 ($\text{OP}(\text{OPh})_3$, 100 %). The toluene was removed *in vacuo* and the residue was extracted with a 50/50 mixture of toluene and hexane. Addition of a small volume of water to this mixture resulted in the formation of two distinct layers. The organic layer was evaporated and found to contain catalyst **1** (Characterized by m.p. and IR, yield 92 %). Triphenyl phosphate was removed from the aqueous layer by filtration as a light brown solid (1.99 g, 6.10 mmol, 82 %). The product was characterized by IR and NMR spectroscopy (see Reaction 6.2.14).

6.4.4 Reaction Using Catalyst 1 (low catalyst loading)

Catalyst **1** (0.56 g, 0.93 mmol), phenol (2.10 g, 0.022 mol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the

reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3): δ -48.8 ($\text{OP}(\text{OPh})_2\text{I}$, 25 %), -17.2 ($\text{OP}(\text{OPh})_3$, 75 %)

6.4.5 Reaction Using Iron(III) 1,1,1-trifluoro-2,4-pentanedione (2)

Catalyst **2** (5.50 g, 8.08 mmol), phenol (4.56 g, 0.049 mol), iodine (0.34 g, 1.35 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.50 g, 4.04 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -17.4 ($\text{OP}(\text{OPh})_3$)

6.4.6 Reaction Using Catalyst 2 (low catalyst loading)

Catalyst **2** (1.83 g, 3.55 mmol), phenol (4.01 g, 0.043 mol), iodine (0.30 g, 1.18 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.44 g, 3.55 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.2 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after 3 hours due to the formation of white phosphorus smoke.

6.4.7 Reaction Using Iron(III) 1-Phenyl-1,4-butanedione (3)

Catalyst **3** (1.66 g, 3.07 mmol), phenol (1.74 g, 0.019 mol), iodine (0.13 g, 0.51 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under

nitrogen. A solution of P₄ (0.19 g, 1.54 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -17.7 (OP(OPh)₃)

6.5 Reactions Using Higher Substituted Phenols

The successful iron catalysts were tested in phosphate forming reactions using 2,4-di-tert-butyl phenol, *o*-cresol and resorcinol. All three substrates were purchased from Sigma Aldrich and used as received.

6.5.1 Reaction Using Iron(III) Acetylacetone and 2,4-Di-tert-butyl Phenol

Iron(III) acetylacetone (2.76 g, 7.75 mmol), 2,4-di-tert-butyl phenol (9.68 g, 0.046 mol), iodine (0.37 g, 1.44 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.48 g, 3.87 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.6 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P NMR (109.4 MHz, CDCl₃): δ -28.0 ((2,4-*t*Bu₂C₆H₃O)₂OP-O-PO(O-2,4-*t*Bu₂C₆H₃)₂, 70 %), -20.8 (OP(O-2,4- *t*Bu₂C₆H₃)₃, 30 %)

6.5.2 Reaction Using Iron(III) Acetylacetone and 2,4-Di-tert-butyl Phenol (mol sieves)

Iron(III) acetylacetone (2.13 g, 6.00 mmol), 2,4-di-tert-butyl phenol (7.44 g, 0.036 mol), iodine (0.25 g, 0.99 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck

round bottomed flask under nitrogen. A solution of P₄ (0.37 g, 2.99 mmol) in toluene (20 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -25.6 ((2,4-*t*Bu₂C₆H₃O)₂OP-O-PO(O-2,4-*t*Bu₂C₆H₃)₂, 33 %), -19.0 (OP(O-2,4- *t*Bu₂C₆H₃)₃, 67 %)

6.5.3 Reaction Using Iron(III) Acetylacetone and 2,4-Di-tert-butyl Phenol (reflux)

Iron(III) acetylacetone (0.66 g, 1.85 mmol), 2,4-di-tert-butyl phenol (4.53 g, 0.022 mol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4, however the reaction was heated to reflux rather than 80 °C. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -26.8 ((2,4-*t*Bu₂C₆H₃O)₂OP-O-PO(O-2,4-*t*Bu₂C₆H₃)₂)

6.5.4 Reaction Using Iron(III) Acetylacetone and 2,4-Di-tert-butyl Phenol (60 °C)

Iron(III) acetylacetone (0.53 g, 1.85 mmol), 2,4-di-tert-butyl phenol (3.71 g, 0.018 mol), iodine (0.13 g, 0.50 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 1.8 mL/h. The reaction was conducted using

the same set up and conditions as Reaction 6.2.4, however the reaction was only heated to 60 °C. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -59.6 ($\text{OP(O-2,4-}t\text{Bu}_2\text{C}_6\text{H}_3)_2\text{I}$, 50 %), -25.6 ((2,4- $t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{OP-O-PO(O-2,4-}t\text{Bu}_2\text{C}_6\text{H}_3)_2$, 24 %), -19.2 ($\text{OP(O-2,4-}t\text{Bu}_2\text{C}_6\text{H}_3)_3$, 18 %)

6.5.5 Reaction Using Catalyst 1 and 2,4-Di-tert-butyl Phenol

Catalyst **1** (2.54 g, 4.20 mmol), 2,4-di-tert-butyl phenol (5.44 g, 0.025 mol), iodine (0.18 g, 0.71 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.26 g, 2.10 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.5 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -18.0 ($\text{OP(O-2,4-}t\text{Bu}_2\text{C}_6\text{H}_3)_3$)

6.5.6 Reaction Using Catalyst 2 and 2,4-Di-tert-butyl Phenol

Catalyst **2** (1.92 g, 3.72 mmol), 2,4-di-tert-butyl phenol (4.60 g, 0.022 mol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.1 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned after 3 h due to the formation of phosphorus smoke.

6.5.7 Reaction Using Catalyst 3 and 2,4-Di-tert-butyl Phenol

Catalyst **3** (4.46 g, 8.00 mmol), 2,4-di-tert-butyl phenol (9.90 g, 0.048 mol), iodine (0.34 g, 0.13 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.50 g, 4.04 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.3 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -27.4 ((2,4-*t*Bu₂C₆H₃O)₂OP-O-PO(O₂,4-*t*Bu₂C₆H₃)₂, 100 %)

6.5.8 Reaction Using Iron(III) Acetylacetone and *o*-Cresol

Iron(III) acetylacetone (0.63 g, 1.78 mmol), *o*-cresol (2.31 g, 0.021 mol), iodine (0.15 g, 0.59 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.22 g, 1.78 mmol) in toluene (10 mL) was added to the reaction at a rate of 1.7 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -16.1 (OP(O-*o*-MeC₆H₄)₃, 100%)

6.5.9 Reaction Using Iron(III) Acetylacetone and *o*-Cresol (fast addition)

Iron(III) acetylacetone (1.20 g, 3.38 mmol), *o*-cresol (4.39 g, 0.041 mol), iodine (0.29 g, 1.13 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.42 g, 3.38 mmol) in toluene (20 mL) was added to the reaction at a rate of 3.8 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -24.1 ($(o\text{-MeC}_6\text{H}_4\text{O})_2\text{OP-O-PO(O-}o\text{-MeC}_6\text{H}_4)_2$, 12 %), -15.9 ($\text{OP(O-}o\text{-MeC}_6\text{H}_4)_3$, 88 %)

6.5.10 Reaction Using Catalyst 1 and *o*-Cresol

Catalyst **1** (2.05 g, 3.38 mmol), *o*-cresol (2.20 g, 0.020 mol), iodine (0.15 g, 0.59 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.21 g, 1.69 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -16.1 ($\text{OP(O-}o\text{-MeC}_6\text{H}_4)_3$)

6.5.11 Reaction Using Iron(III) Acetylacetone and Resorcinol (3 equivalents)

Iron(III) acetylacetone (0.60 g, 1.69 mmol), resorcinol (2.23 g, 0.020 mol), iodine (0.15 g, 0.59 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.21 g, 1.69 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass consisted of a light brown liquid and a black paste. The brown liquid was analysed by ^{31}P NMR and found not to contain any significant quantity of phosphorus. The black paste was washed with hot methanol to yield a black solid (2.77 g). This solid was found to be insoluble in water and all common organic solvents.

6.5.12 Reaction Using Iron(III) Acetylacetonate with Resorcinol and Phenol

Iron(III) acetylacetonate (0.66 g, 1.86 mmol), resorcinol (0.41 g, 3.72 mmol), iodine (0.16 g, 0.62 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.23 g, 1.86 mmol) in toluene (10 mL) was added to the reaction at a rate of 2.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass consisted of a light brown liquid and a black paste. The brown liquid was analysed by ³¹P NMR and found contain triphenyl phosphate. The black paste was washed with hot methanol to yield a black solid (1.11 g). This solid was found to be insoluble in water and all common organic solvents.

6.6 Oxidation Reactions of Phosphites

The triphenyl phosphite and tris-2,4-di-tert-butyl phosphite used in these reactions were purchased from Sigma Aldrich and used as received.

6.6.1 Oxidation of Triphenyl Phosphite

Triphenyl phosphite (2.00 g, 6.45 mmol) and toluene (5 mL) were charged to a 50 mL round bottomed flask. The solution formed was heated to 80 °C and air was bubbled through the reaction at a rate of 40 mL/min. After 6 hours the reaction was stopped and the solution was analysed by ³¹P NMR. This reaction was repeated twice; once in the presence of iron(III) acetylacetonate (1.15 g, 3.23 mmol) and once in the presence of iodine (0.27 g, 1.08 mmol) and iron(III) acetylacetonate (1.15 g, 3.23 mmol). The results of these reactions are presented in Table 10.

6.6.2 Oxidation of Tris-2,4-Di-tert-butyl Phosphite

Tris-2,4-di-tert-butyl phosphite (1.00 g, 1.51 mmol) and toluene (5 mL) were charged to a 50 mL round bottomed flask. The solution formed was heated to 80 °C and air was bubbled through the reaction at a rate of 40 mL/min. After 6 hours the reaction was stopped and the solution was analysed by ^{31}P NMR. This reaction was repeated twice; once in the presence of iron(III) acetylacetone (0.55 g, 1.54 mmol) and once in the presence of iodine (0.13 g, 0.51 mmol) and iron(III) acetylacetone (0.55 g, 1.54 mmol). The results of these reactions are presented in Table 10.

6.7 Reactions of Phosphorus Triiodide with Phenol

The PI_3 used in these reactions was prepared by the slow addition of toluene solutions of white phosphorus to toluene solutions of iodine. The addition was performed under nitrogen and the resulting solutions were stirred vigorously for 1 hour. The molar ratio of P to I atoms was 1:3 and complete conversion to PI_3 was consistently observed in the ^{31}P NMR. This process is an adaption of the process of Germann and Traxler, which is the usual synthetic route to PI_3 .¹⁴⁵ In this study toluene has been used as a solvent instead of carbon disulphide, as PI_3 in toluene was required for further reactions. The PI_3 solutions thus formed were used without further purification.

6.7.1 Aerobic Reaction without Catalyst

A solution of PI_3 (1.46 g, 3.56 mmol) in toluene (10 mL) was prepared in a 100 mL Schlenk flask. Phenol (1.01 g, 0.0107 mol) was also added to the flask and the mixture was heated to 80 °C with stirring. After the reaction temperature was reached air was bubbled through the flask at a rate of 40 mL/min for 5 hours. Air was introduced via a

needle inserted through a septum in the neck of the flask. The Schlenk tap was connected to a copper sulfate bubbler outlet. The final reaction mass was analysed by ^{31}P NMR.
 $^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -47.0 ($\text{O}=\text{P}(\text{OPh})_2\text{I}$, 97 %), -24.0 ($\text{O}=\text{P}(\text{OPh})_2\text{-O-P(O)(OPh)}_2$, 1%), -16.5 ($\text{O}=\text{P}(\text{OPh})_3$, 2%)

6.7.2 Aerobic Reaction with Iron(III) Acetylacetone

A solution of PI_3 (2.60 g, 6.32 mmol) in toluene (20 mL) was prepared in a 100 mL Schlenk flask. Phenol (1.79 g, 0.019 mol) and iron(III) acetylacetone (0.56 g, 1.57 mmol) were also added to the flask. The reaction was conducted using the same set up and conditions as Reaction 6.7.1 although the reaction was halted after 3 hours. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -16.6 ($\text{O}=\text{P}(\text{OPh})_3$)

6.7.3 Anaerobic Reaction without Catalyst

A solution of PI_3 (1.46 g, 3.56 mmol) in toluene (10 mL) was prepared in a 100 mL Schlenk flask. Phenol (1.01 g, 0.0107 mol) was added to the flask and the mixture was heated to 80 °C with stirring. The reaction was held at this temperature for five hours. The final reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ 174.1 (PI_3)

6.7.4 Anaerobic Reaction with Iron(III) Acetylacetone

A solution of PI_3 (1.53 g, 3.72 mmol) in toluene (10 mL) was prepared in a 100 mL Schlenk flask. Phenol (1.05 g, 0.011 mol) and iron(III) acetylacetone (0.08 g, 0.23

mmol) were also added to the flask. The reaction was conducted using the same set up and conditions as Reaction 6.7.3. The final reaction mass was analysed by ^{31}P NMR.
 $^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ 103.4 (P_2I_4), 174.3 (PI_3)

6.8 Reactions of Diphenyl Phosphoriodidate with Phenol

The $\text{O}=\text{P}(\text{OPh})_2\text{I}$ used in these reactions was prepared by the method described in Reaction 6.7.1, however two rather than three equivalents of phenol to phosphorus triiodide were used.

6.8.1 Reaction using Iron(III) Acetylacetone

A solution of diphenyl phosphoriodidate (4.41 g, 0.0126 mol) in toluene (20 mL) was prepared in a 100 mL round bottomed Schlenk flask under nitrogen. Phenol (1.19 g, 0.0126 mol) and iron(III) acetylacetone (1.12 g, 3.15 mmol) were also charged to the flask and the mixture was heated to 80 °C. The reaction was held at this temperature with vigorous stirring for 3 hours after which time the reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -16.6 ($\text{O}=\text{P}(\text{OPh})_3$)

6.8.2 Reaction without Catalyst

A solution of diphenyl phosphoriodidate (4.29 g, 0.0123 mol) in toluene (20 mL) was prepared in a 100 mL round bottomed Schlenk flask under nitrogen. Phenol (1.16 g, 0.0123 mol) was charged to the flask and the mixture was heated to 80 °C. The reaction was held at this temperature with vigorous stirring for 20 hours. After 11 hours there was still a large amount of unreacted $\text{O}=\text{P}(\text{OPh})_2\text{I}$ in the ^{31}P NMR spectrum of the reaction

mixture (49 % by integration). After 20 hours all the starting material had been consumed and the reaction mass was analysed by ^{31}P NMR.

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -24.8 ($\text{O}=\text{P}(\text{OPh})_2\text{-O-P(O)(OPh)}_2$, 30 %), -17.3 ($\text{O}=\text{P}(\text{OPh})_3$, 4 %), -9.2 ($\text{O}=\text{P}(\text{OPh})_2\text{OH}$, 66 %)

6.9 Experiments on the Formation of Diphenyl Phosphoriodidite

The PI_3 used in these experiments was synthesized by the method described in section 6.7. Diphenyl chlorophosphite was prepared by the method of Gandheker *et al.*¹⁰⁸ Its identity was confirmed by $^{31}\text{P}\{\text{H}\}$ NMR (δ = 158.2 ppm, lit. 158.6 ppm¹⁴⁶)

6.9.1 Attempted Oxidation of PI_3 with and without Catalyst

A solution of phosphorus triiodide (1.30 g, 3.16 mmol) in toluene (5 mL) was prepared in a 25 mL round bottomed Schlenk flask. The solution was heated to 60 °C with stirring and dry air was bubbled through the solution at a rate of 40 mL/min for 3 hours. After this time a sample of the solution was taken and analysed by ^{31}P NMR. Unreacted PI_3 starting material was the only peak observed in this spectrum. Iron(III) acetylacetone (1.12 g, 3.16 mmol) was added to the solution and the reaction was continued for a further 3 hours. At the end of this time the solution was analysed by ^{31}P NMR. Whilst the spectrum was broadened and weak due to the paramagnetic nature of the iron catalyst, however a broad peak centred at about 167 ppm was observed, presumably showing the unreacted PI_3 starting material.

6.9.2 Synthesis and Oxidation of Diphenyl Phosphoriodidite

Diphenyl chlorophosphite (1.25 g, 0.005 mol), sodium iodide (0.75 g, 0.005 mol) and acetone (10ml) were charged to a 25 mL Schlenk flask under nitrogen. The mixture was stirred at RT under nitrogen for 1 hour, then filtered to remove NaCl and analysed by ^{31}P NMR. Though the spectrum obtained was complicated and contained several unidentifiable peaks, the characteristic diphenyl phosphoriodidite singlet was observed at $\delta_{\text{p}} = 201.4$ ppm (lit. 201 ppm¹⁴⁷). Diphenyl phosphoriodidate was also observed in this spectrum, perhaps due to the oxidation of the phosphoriodidite in the NMR tube before the sample was run. Exposing the reaction mass briefly to air caused the complete disappearance of the phosphoriodidite peak in the NMR and the consequent enhancement of the phosphoriodidate peak.

6.9.3 Reaction of Triphenyl Phosphate with Iodine

Triphenyl phosphate (5.00 g, 0.0161 mol) and iodine (4.09 g, 0.0161 mol) were charged to a 25 mL Schlenk under nitrogen. The reaction was stirred at RT for 16 h, at the end of this time the reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3) δ -48.5 ($\text{OP(OPh)}_2\text{I}$, 5 %), -17.1 (OP(OPh)_3 , 2 %), 118.9 (P(OPh)_3 , 91 %), 175.8 (PI_3 , 3 %) 202.6 ($\text{P(OPh)}_2\text{I}$, 2%)

6.9.4 Anaerobic Reaction of PI_3 with Phenol (excess iodine)

A solution of PI_3 (3 g, 7.28 mmol) in toluene (10 mL) was prepared in a 25 mL Schlenk flask. Phenol (1.37 g, 0.0146 mol) and iodine (1.85 g, 7.28 mmol) were added to the

solution and the mixture was stirred for 4 h at 80 °C under nitrogen. The final reaction mass was analysed by ^{31}P NMR.

^{31}P NMR (109.4 MHz, CDCl_3) δ -47.1 ($\text{OP}(\text{OPh})_2\text{I}$, 20 %), -17.4 ($\text{OP}(\text{OPh})_3$, 10 %), 175.0 (PI_3 , 70 %)

6.9.5 Aerobic Reaction of PI_3 with Phenol

See Reaction 6.7.1.

6.10 Kinetic Studies

6.10.1 Reaction with Iron(III) Acetylacetone and Iodine

See Reaction 6.4.1

6.10.2 Reaction with Low Iron(III) Acetylacetone Loading

See Reaction 6.4.2

6.10.3 Reaction with Low Iodine Loading

Iron(III) acetylacetone (1.08 g, 3.02 mmol), phenol (3.40 g, 0.036 mol), iodine (0.12 g, 0.49 mmol) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P_4 (0.37 g, 3.02 mmol) in toluene (20 mL) was added to the reaction at a rate of 6.7 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The reaction had to be abandoned due to the immediate formation of white phosphorus smoke.⁸⁸

6.11 Phosphite Forming Reactions

The PI₃ used in these experiments was synthesized by the method described in section 6.7.

6.11.1 Anaerobic Reaction of PI₃ with Phenol (with 3Å molecular sieves)

A solution of PI₃ (3.32 g, 8.72 mmol) in toluene (20 mL) was prepared in a 100 mL Schlenk flask. Phenol (2.46 g, 0.026 mol) and 3Å molecular sieves (5.0 g) were added to the flask. The reaction was conducted using the same set up and conditions as Reaction 6.7.1. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ 174.0 (PI₃)

6.11.2 Aerobic Reaction of PI₃ with Phenol (with 3Å molecular sieves)

A solution of PI₃ (1.59 g, 3.87 mmol) in toluene (10 mL) was prepared in a 100 mL Schlenk flask. Phenol (1.09 g, 0.012 mol) and 3Å molecular sieves (3.0 g) were added to the flask. The reaction was conducted using the same set up and conditions as Reaction 6.7.1. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -48.1 (O=P(OPh)₂I, 10 %), -16.3 (O=P(OPh)₃, 9 %), 22.4 (unknown compound, 4 %), 124.1 (P(OPh)₃, 67 %), 175.1 (PI₃, 5 %), 203.0 (P(OPh)₂I, 5 %)

6.11.3 White Phosphorus Reaction Using 3Å Molecular Sieves (0.50

mmol/h/mmolFe(acac)₃ addition rate)

Iron(III) acetylacetone (0.48 g, 1.36 mmol), phenol (3.11 g, 0.033 mol), iodine (0.23 g, 0.91 mmol), 3Å molecular sieves (5.0 g) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.34 g, 2.74 mmol) in toluene (20 mL) was added to the reaction at a rate of 5.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -519.9 (P₄, 5%), -16.2 (O=P(OPh)₃, 50 %), 128.9 (P(OPh)₃, 45 %)

6.11.4 White Phosphorus Reaction Using 3Å Molecular Sieves (0.80

mmol/h/mmolFe(acac)₃ addition rate)

Iron(III) acetylacetone (0.34 g, 0.97 mmol), phenol (3.65 g, 0.039 mol), iodine (0.49 g, 1.94 mmol), 3Å molecular sieves (5.0 g) and toluene (10 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.24 g, 1.94 mmol) in toluene (10 mL) was added to the reaction at a rate of 4.0 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -16.6 (O=P(OPh)₃, 40 %), 128.9 (P(OPh)₃, 60 %)

6.11.5 White Phosphorus Reaction Using 3Å Molecular Sieves (1.60

mmol/h/mmolFe(acac)₃ addition rate)

Iron(III) acetylacetone (0.32 g, 0.89 mmol), phenol (2.01 g, 0.021 mol), iodine (0.45 g, 1.78 mmol), 3 \AA molecular sieves (5.0 g) and toluene (5 mL) were charged to a 100 mL 3-neck round bottomed flask under nitrogen. A solution of P₄ (0.22 g, 1.78 mmol) in toluene (10 mL) was added to the reaction at a rate of 5.9 mL/h. The reaction was conducted using the same set up and conditions as Reaction 6.2.4. White phosphorus smoke was observed towards the end of the reaction. The final reaction mass was analysed by ³¹P NMR.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -519.7 (P₄, 34 %), -16.6 (O=P(OPh)₃, 9 %), 129.3 (P(OPh)₃, 57 %)

6.12 Independent Synthesis of Reaction Intermediates

6.12.1 Synthesis of Diphenyl Phosphoriodidate

Diphenyl phosphoriodidate was synthesized from PI₃ (5.68 g, 13.9 mmol) by the method of Reaction 6.7.1. The solvent was removed *in vacuo* to yield O=PI(OPh)₂ (3.8 g, 76 %) as brown oil which solidified on prolonged standing at 5 °C. Further purification using chromatography was not possible due to rapid hydrolysis on silica.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -47.0 (s).

¹H NMR (270.2 MHz, CDCl₃): δ 6.80-7.51 (m).

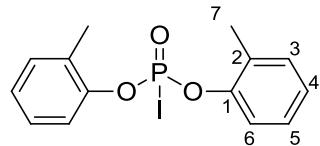
¹³C{¹H} NMR (67.9 MHz, CDCl₃): δ 122.7 (s, *p*-C), 127.1 (s, *m*-C), 131.8 (s, *o*-C), 150.3 (s, *i*-C)

IR (KBr disc) ν/cm^{-1} = 3044 (s, Ar-H), 1593 (s, Ar-C=C), 1487 (vs, Ar-C=C), 1365 (m), 1263 (s, P=O), 1226 (s), 1179 (s, P-O-Ar), 1158 (vs), 1071 (m), 1024 (s), 1011 (s), 960 (vs), 782 (s, Ar-H), 510 (s).

MS (EI+) (m/z): 359.9 (100%, $[M]^+$), 126.9 (60 %, $[I]^+$), 233.0 (45 %, $[M-I]^+$),

MS (Exact mass, EI+): $C_{12}H_{10}O_3PI$ requires 359.9412, found 359.9421, error of 2.4 ppm).

6.12.2 Synthesis of Ditolyl Phosphoriodidate



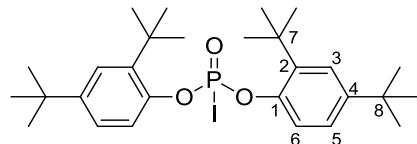
Ditolyl phosphoriodidate was synthesized from PI_3 (0.56 g, 1.45 mmol) by the method of Reaction 6.7.1.

$^{31}P\{^1H\}$ NMR (109.4 MHz, $CDCl_3$): δ -51.8 (s).

1H NMR (270.2 MHz, $CDCl_3$): δ 2.28 (s, 3H, CH_3), 7.04-7.49 (complex multiplet, 4H, Ar-H)

$^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ 17.2 (s, 7- CH_3), 120.8 (d, 3.1 Hz, 2-C_q), 126.7 (d, $^3J(PC) = 1.9$ Hz, 3-CH), 127.6 (d, $^4J(CP) = 2.0$ Hz, 5-CH), 129.9 (d, $^3J(CP) = 7.3$ Hz, 6-CH), 132.2 (s, 4-CH), 148.7 (d, $^2J(CP) = 10.4$ Hz, 1-C_q)

6.12.3 Synthesis Bis(2,4-di-tert-butyl phenyl) Phosphoriodidate



Phosphorus triiodide (2.30 g, 5.6 mmol), 2,4-di-tert-butyl phenol (2.31 g, 11.2 mmol) and toluene (10 mL) were heated to 60 °C with vigorous stirring, whilst dry air was bubbled through the reaction mass at a rate of 40 mL/min. After 24 hours the air flow was stopped and the reaction was allowed to cool to room temperature. The solvent was removed *in*

vacuo to leave crude O=PI(2,4-*t*Bu₂C₆H₃)₂ as a dark oil. This was purified by column chromatography on silica gel (eluent hexane:ether 3:1) to yield O=PI(2,4-*t*BuC₆H₃)₂ (0.36 g, 13 %) as white powder.

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -60.0 (s).

¹H NMR (270.2 MHz, CDCl₃): δ 1.31 (s, 18H, 8-*t*Bu), 1.44 (s, 18H, 7-*t*Bu), 7.21 (d of d, ³J(HH) = 8.9 and ⁴J(HH) = 2.1 Hz, 2H, 5-CH), 7.41 (≈t, J = 2.4 Hz, 2H, 3-CH), 7.66 (d of d, ³J(HH) = 8.9 and ⁵J(HH) = 2.1 Hz, 2H, 6-CH)

¹³C{¹H} NMR (67.9 MHz, CDCl₃): δ 30.4 (s, 7-CH₃), 31.5 (s, 8-CH₃), 34.7 (s, 2-C_q), 34.9 (s, 4-C_q), 119.4 (d, ³J(PC) = 4.0 Hz, 6-CH), 124.3 (s, 5-CH), 125.0 (s, 3-CH), 139.3 (d, ²J(CP) = 9.4 Hz, 1-C_q), 147.2 (d, ³J(CP) = 7.7 Hz, 2-C_q), 148.1 (s, 4-C_q)

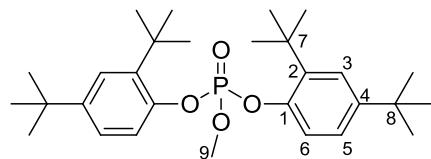
IR (KBr disc) v/cm⁻¹ = 2954 (vs, CH), 1494 (s, Ar-C=C), 1273 (m, P=O), 1182 (s, P-O-Ar), 1104 (m), 1079 (m), 991 (s), 960 (vs), 552 (vs), 495 (vs).

MS (ES+, solution in methanol) (m/z): 489.2 (100 %, [M-I+MeO+H⁺]), 999.4 (65 %, [2(M-I+MeO)+Na]), 977.4 (60 %, [2(M-I+MeO)+H]), 433.2 (60 %, [M-I+MeO-*t*Bu+H]⁺), 511.2 (50 %, [M-I+MeO+Na]⁺), 377.2 (20 %, [M-I-2*t*Bu+MeO+H]⁺)

6.13 Synthesis of Mixed Phosphates

The bis(2,4-di-tert-butyl phenyl) phosphoriodidate used in these experiments was prepared by the method described in Reaction 6.12.3. The alcohols used were dried by distillation over calcium hydride and deoxygenated by nitrogen bubbling. Microanalysis was performed on these compounds however due to their physical nature (viscous oils) satisfactory results were not obtained.

6.13.1 Synthesis of Bis(2,4-di-tert-butylphenyl)methyl Phosphate



Bis(2,4-di-tert-butyl phenyl) phosphoriodidate (0.16 g, 0.27 mmol) and methanol (10 mL) were charged to a 25 mL Schlenk flask under nitrogen. The solution formed was stirred at RT for 1 hour, after which time only product was observed in a ^{31}P NMR of the solution. The excess methanol was removed *in vacuo* to yield crude bis(2,4-di-tert-butylphenyl)methyl phosphate as a white oil (0.13 g, 0.27 mmol). This was purified by column chromatography (eluents DCM, 200 mL then MeOH) to give pure bis(2,4-di-tert-butylphenyl)methyl phosphate as a colourless oil (0.07 g, 0.14 mmol, 52 %).

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -11.4

^{31}P NMR (109.4 MHz, CDCl_3): δ -11.5 (q, $^3\text{J}(\text{PH}) = 12.1$ Hz)

^1H NMR (270.2 MHz, CDCl_3): δ 1.29 (s, 18H, tBu), 1.39 (s, 18H, tBu), 3.93 (d, $^3\text{J}(\text{HP}) = 11.9$ Hz, 3H, 9-Me), 7.16 (d of d, $^3\text{J}(\text{HH}) = 8.7$ and $^4\text{J}(\text{HH}) = 2.7$ Hz, 2H, 5-CH), 7.36 (~t, $J = 1.9$ Hz, 2H, 3-CH), 7.43 (d of d, $^3\text{J}(\text{HH}) = 8.7$ and $^5\text{J}(\text{HH}) = 0.8$ Hz, 2H, 6-CH)

$^{13}\text{C}\{\text{H}\}$ NMR (67.9 MHz, CDCl_3): δ =30.2 (s, tBu- CH_3), 31.5 (s, tBu- CH_3), 34.6 (s, tBu- C_q), 35.0 (s, tBu- C_q), 55.3 (d, $^2\text{J}(\text{CP}) = 6.2$ Hz, 9-Me), 118.8 (s, 6-CH), 124.1 (s, 5-CH), 124.6 (s, 3-CH), 138.6 (d, $^2\text{J}(\text{CP}) = 8.3$ Hz, 1- C_q), 147.1 (s, 4- C_q), 147.6 (d, $^3\text{J}(\text{CP}) = 7.3$ Hz 2- C_q)

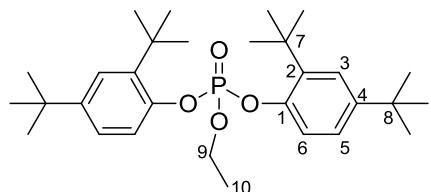
IR (KBr disc) ν/cm^{-1} = 2962 (vs, CH), 2872 (s, CH), 1496 (s, Ar-C=C), 1364 (m), 1280 (m, P=O), 1210 (m), 1191 (s, P-O-Ar), 1084 (s), 1009 (s), 958 (vs), 893 (m), 492 (m)

MS (ES+) (m/z): 511.3 (100%, $[\text{M}+\text{Na}]^+$), 999.6 (85%, $[\text{2M}+\text{Na}]^+$)

MS (ES-) (m/z): 473.2 $[\text{M}-\text{Me}]^-$

MS (Exact mass, ES+): C₂₉H₄₅O₄PNa requires 511.2953, found 511.2953 (error -2.1 ppm)

6.13.2 Synthesis of Bis(2,4-di-tert-butylphenyl)ethyl Phosphate



Bis(2,4-di-tert-butyl phenyl) phosphoriodidate (0.30 g, 0.51 mmol) and ethanol (10 mL) were charged to a 25 mL Schlenk flask under nitrogen. The solution formed was stirred at RT for 1 hour, after which time only product was observed in a ³¹P NMR of the solution. The excess ethanol was removed *in vacuo* to yield crude bis(2,4-di-tert-butylphenyl)ethyl phosphate as a light yellow oil (0.16 g, 0.32mmol). This was purified by column chromatography (eluents DCM (200 mL) then MeOH) to give pure bis(2,4-di-tert-butylphenyl)ethyl phosphate as a colourless oil (0.11 g, 0.22 mmol, 43 %).

³¹P{¹H} NMR (109.4 MHz, CDCl₃): δ -12.4 (s)

³¹P NMR (109.4 MHz, CDCl₃): δ -12.4 (t, ³J(PH) = 7.4 Hz)

¹H NMR (270.2 MHz, CDCl₃): δ 1.28 (s, 18H, tBu), 1.32 (m, 3H, 10-CH₃), 1.38 (s, 18H, tBu), 3.93 (m, 2H, 9-CH₂), 7.15 (d of d, ³J(HH) = 8.5 and ⁴J(HH) = 2.5 Hz, 2H, 5-CH), 7.35 (~t, J = 1.9 Hz, 2H, 3-CH), 7.43 (d, ³J(HH) = 8.5 Hz, 2H, 6-CH)

¹³C{¹H} NMR (67.9 MHz, CDCl₃): δ 30.2 (s, tBu-CH₃), 30.5 (s, CH₂), 31.6 (s, tBu-CH₃), 34.6 (s, tBu-C_q), 35.0 (s, tBu-C_q), 62.3 (d, ²J(CP) = 6.2 Hz, 9-CH₂), 118.9 (s, 6-CH), 124.1 (s, 5-CH), 124.5 (s, 3-CH), 138.6 (d, ²J(CP) = 8.3 Hz, 1-C_q), 147.0 (s, 4-C_q), 147.7 (d, ³J(CP) = 7.3 Hz 2-C_q)

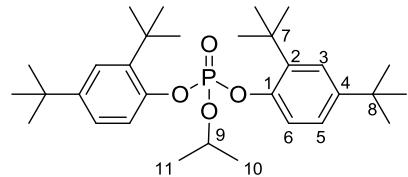
IR (KBr disc) ν/cm^{-1} = 2963 (vs, CH), 2871 (s, CH), 1496 (s, Ar-C=C), 1399 (m), 1364 (m), 1279 (m, P=O), 1191 (s, P-O-Ar), 1084 (s), 1010 (s), 959 (vs), 893 (m), 493 (m)

MS (ES+) (m/z): 1027.3 (100 %, $[2\text{M}+\text{Na}]^+$), 525.2 (40 %, $[\text{M}+\text{Na}]^+$), 503.2 (30 %, $[\text{M}+\text{H}]^+$)

MS (ES-) (m/z): 473.2 $[\text{M}-\text{Et}]^-$

MS (Exact mass, ES+): $\text{C}_{30}\text{H}_{47}\text{O}_4\text{PNa}$ requires 525.3116, found 525.3110 (error 1.2 ppm)

6.13.3 Synthesis of Bis(2,4-di-tert-butylphenyl)*i*-propyl Phosphate



Bis(2,4-di-tert-butyl phenyl) phosphoriodidate (0.22 g, 0.37 mmol) and 2-propanol (10 mL) were charged to a 25 mL Schlenk flask under nitrogen. The solution formed was refluxed for 1 hour, after which time only product was observed in a ^{31}P NMR of the solution. The excess 2-propanol was removed *in vacuo* to yield crude Bis(2,4-di-tert-butylphenyl)*i*-propyl phosphate as a white oil. This was purified by column chromatography (eluents DCM (200 mL) then MeOH) to give pure bis(2,4-di-tert-butylphenyl)*i*-propyl phosphate as a colourless oil (0.11 g, 0.21 mmol, 57 %)

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -13.5 (s)

^{31}P NMR (109.4 MHz, CDCl_3): δ -13.3 (d, $^3\text{J}(\text{PH})$ = 8.0 Hz)

^1H NMR (270.2 MHz, CDCl_3): δ 1.28 (s, 18H, tBu), 1.31 (d, $^4\text{J}(\text{HP})$ = 0.6 Hz, 6H, 10-CH₃), 1.36 (s, 18H, tBu), 4.91 (m, 1H, 9-CH), 7.14 (d of d, $^3\text{J}(\text{HH})$ = 8.5 and $^4\text{J}(\text{HH})$ = 2.5 Hz, 2H, 5-CH), 7.34 (~t, J = 2.2 Hz, 2H, 3-CH), 7.47 (d of d, $^3\text{J}(\text{HH})$ = 8.5 Hz and $^5\text{J}(\text{HH})$ = 0.8 Hz, 2H, 6-CH)

$^{13}\text{C}\{\text{H}\}$ NMR (67.9 MHz, CDCl_3): δ 23.7 ($\sim\text{d}$, $J = 12$ Hz, *10&11-CH₃*), 30.2 (s, tBu-CH₃), 31.6 (s, tBu-CH₃), 34.6 (s, tBu-C_q), 34.9 (s, tBu-C_q), 74.5 (d, $^2\text{J}(\text{CP}) = 6.2$ Hz, 9-CH), 119.0 (s, 6-CH), 123.9 (s, 5-CH), 124.4 (s, 3-CH), 138.6 (d, $^2\text{J}(\text{CP}) = 9.3$ Hz, 1-C_q), 146.8 (s, 4-C_q), 147.7 (d, $^3\text{J}(\text{CP}) = 6.2$ Hz 2-C_q)

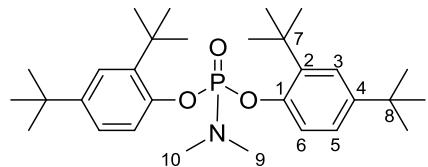
IR (KBr disc) ν/cm^{-1} = 2961 (vs, CH), 2871 (s, CH), 1496 (s, Ar-C=C), 1306 (m), 1280 (m, P=O), 1209 (m), 1190 (s, P-O-Ar), 1083 (s), 1047 (s), 959 (vs), 892 (m), 491 (m)

MS (ES+) (m/z): 539.2 [M+Na]⁺

MS (ES-) (m/z): 473.3 [M-*i*Pr]⁻

MS (Exact mass, ES+): $\text{C}_{31}\text{H}_{49}\text{O}_4\text{PNa}$ requires 539.3264, found 539.3266 (error -0.5 ppm)

6.13.4 Synthesis of Bis(2,4-di-tert-butylphenyl)dimethyl Phosphoroamidate



Bis(2,4-di-tert-butyl phenyl) phosphoriodidate (0.13 g, 0.22 mmol) and dimethylamine (10 mL) were charged to a 25 mL Schlenk flask under nitrogen. The solution formed was stirred at 0 °C for 1 hour after which time the excess dimethylamine was removed *in vacuo* to yield crude bis(2,4-di-tert-butyl phenyl)dimethyl phosphoroamidate as a white oil. This was extracted into dichloromethane (10 mL) and washed with water (2 x 10 mL). The organic layer was separated and dried over magnesium sulfate and the solvent was removed *in vacuo*. Bis(2,4-di-tert-butyl phenyl)dimethyl phosphoroamidate was obtained as a white solid (0.08 g, 0.16 mmol, 71 %)

$^{31}\text{P}\{\text{H}\}$ NMR (109.4 MHz, CDCl_3): δ -0.4 (s)

³¹P NMR (109.4 MHz, CDCl₃): δ -0.4 (sep, ³J(PH) = 10.0 Hz)

¹H NMR (270.2 MHz, CDCl₃): δ 1.29 (s, 18H, tBu), 1.40 (s, 18H, tBu), 2.84 (d, ³J(HP) = 10.2 Hz, 6H, 9+10-CH₃), 7.15 (d of d, ³J(HH) = 8.5 and ⁴J(HH) = 2.5 Hz, 2H, 5-CH), 7.32-7.37 (m, 4H, 6+3-CH)

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 30.1 (s, tBu-CH₃), 31.5 (s, tBu-CH₃), 34.5 (s, tBu-C_q), 35.0 (s, tBu-C_q), 36.8 (~d, J = 4.6 Hz, 9&10 CH₃), 118.2 (d, ³J(PC) = 2.9 Hz, 6-CH), 123.9 (s, 5-CH), 124.3 (s, 3-CH), 138.1 (d, ²J(CP) = 9.2 Hz, 1-C_q), 146.1 (s, 4-C_q), 147.8 (d, ³J(CP) = 5.3 Hz 2-C_q).

IR (KBr disc) ν/cm⁻¹ = 2962 (vs, CH), 2871 (s, CH), 1496 (s, Ar-C=C), 1363 (m), 1270 (m, P=O), 1211 (m), 1191 (s, P-O-Ar), 1084 (s), 1003 (s), 930 (vs), 889 (s), 820 (m), 492 (m)

MS (ES+) (m/z): 524.1 [M+Na]⁺

MS (Exact mass, ES+): C₃₀H₄₈O₃NPNa requires 524.3267, found 524.3270 (error -0.6 ppm)

Conclusion and Further Work

This study has demonstrated the synthesis of triaryl phosphates directly from white phosphorus with high selectivity and in high yields. The process uses sub-stoichiometric amounts of PI_3 as an intermediate as opposed to stoichiometric amounts of PCl_3 . The choice of phosphorus triiodide, rather than phosphorus trichloride, has two main advantages. Firstly, it is critical for the design of the catalytic cycle, since the reoxidation of $\text{HI} \rightarrow \text{I}_2$ can be achieved by air. Secondly, we have demonstrated that water produced in such a catalytic cycle does not pose a significant problem (with respect to hydrolysis), whilst use of any other phosphorus halide is likely to result in formation of significant amounts of side products via hydrolysis.

Many other phosphorus products are synthesized via phosphorus trichloride. In longer term, investigations of direct catalytic routes to phosphites, phosphines and similar phosphorus chemicals are desirable. It is hoped the work on the catalytic synthesis of triaryl phosphites will be continued. A reaction producing triphenyl phosphite in high selectivity and good isolated yield is highly desirable. It would also be interesting to investigate the phosphite forming reaction with a range of substrates.

It has been shown that bis(2,4-di-tert-butyl phenyl) phosphoroiidate can be reacted with alcohols and amines to synthesise a range of new mixed phosphates and phosphoramidates. This series of compounds should be extended with the goal of

creating new high molecular weight phosphate molecules, for screening as flame retardants.

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Publication

Some of the work appearing in Chapters 2, 3, 4 and 5 of this thesis has appeared in the publication –

Catalytic Synthesis of Triaryl Phosphates from White Phosphorus, Armstrong, K. M.; Kilian, P. *European Journal of Inorganic Chemistry*, **2011**, in press

References

- ¹ D. E. C. Corbridge in Phosphorus World, 2005, ch. 1, pp 2-3.
- ² Maxwell, L. R.; Hendrichs, S. B. Mosley, V. *J. Chem. Phys.* **1935**, *3*, 699
- ³ EH40/2005 Workplace exposure limits.
- ⁴ Sparling, D. W.; Day, D.; Klein, P. *Arch. Environ. Contam. Toxicol.*, **1999**, *36*, 316-322.
- ⁵ Mallinckrodt Baker Inc., Material safety data sheet no. P5708, **2009**.
- ⁶ Davis, K. G. *Military medicine*, **2002**, *167*, acute management of white phosphorus burns.
- ⁷ M. A. Armour in Hazardous Laboratory Chemicals Disposal Guide, **2003**, CRC Press.
- ⁸ Ben-Hur, N.; Giladi, A.; Applebaum, J. *Br. J. Plast. Surg.*, **1972**, *25*, 149-157.
- ⁹ Emergency war surgery NATO handbook : Part 1, ch. 3. Burn injury: Chemical burns and White Phosphorus injury.
- ¹⁰ M. M. Rauhut in Topics in Phosphorus Chemistry, ed. M. Grayson and E. J. Griffith, Wiley, **1964**, vol. 1, ch. 1, pp. 1-2.
- ¹¹ Dumas, J. B. *Ann Chim Phys.*, **1859**, *55*, 129-210.
- ¹² Ginsberg, A.P.; Lindsell, W. E. *J. Am. Chem. Soc.*, **1971**, , 2082-2084.
- ¹³ Peruzzini, M.; Gonsalvi, L.; Romerosa, A. *Chem. Soc. Rev.*, **2005**, *34*, 1038-1047.

¹⁴ Di Vaira, M.; Stoppioni, P. *Polyhedron*, **1987**, *6*, 351-382.

¹⁵ Caporali, M.; Gonsalvi, L.; Rossin, A.; Peruzzini, M. *Chem. Rev.* **2010**, *110*, 4178-4235.

¹⁶ Cossairt, B. M.; Piro, N. A.; Cummins, C. C. *Chem. Rev.* **2010**, *110*, 4164-4177.

¹⁷ Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.*, **1980**, *19*, 301-306.

¹⁸ Capozzi, L. Chiti, M. Di Vaira, M. Peruzzini, P. Stoppioni, *Chem Commun.*, **1986**, 1799-1986.

¹⁹ Alvarez, M. A.; Garcia, M. E.; Garcia-Vivo, D.; Ramos, A.; Ruiz, M. A. *Inorg. Chem.* **2011**, 2064-2066.

²⁰ Scherer, O. J. Bruck, T. *Angew. Chem. Int. Ed.*, **1987**, *26*, 59.

²¹ Scherer, O. J.; Hilt, T.; Wolmershauser. *Organometallics*, **1998**, *17*, 4110-4112.

²² Scherer, O. J.; Hilt, T.; Wolmershauser, G. *Angew. Chem. Int. Ed.*, **2000**, *39*, 1425-1427 (*Angew. Chem.* **2000**, *112*, 1483-1485).

²³ Scherer, O. J.; Regitz, M.; Meiers, J.; Hofmann, M. A.; Karaghiosoff, K.; Wolmerhauser, G. *ZAAC*, **2001**, *627*, 1532-1536.

²⁴ Scheer, M.; Becker, E.; Matern, E. *Chem. Ber.*, **1996**, *129*, 721.

²⁵ Barbaro, P.; Ienco, A.; Mealli, C.; Peruzzini, M.; Scherer, O. J.; Schmitt, G.; Vizza, F.; Wolmershauser, G. *Chem. Eur. J.* **2003**, *9*, 5195-5210.

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- ²⁶ Figueroa, J. S.; Cummins, C. C.; *Dalton Trans.*, **2006**, 2161-2168.
- ²⁷ Peruzzini, M.; Abdreimova, R.R.; Budnikova, Yu.; Romerosa, A.; Scherer, O.J.; Sitzmann, H. *J. Organomet. Chem.* **2004**, 689, 4319-4331.
- ²⁸ Di Vaira, M.; Frediani, O.; Costantini, S. S; Peruzzini, M.; Stoppioni, P. *Dalton Trans.*, **2005**, 2234-2236.
- ²⁹ Barbaro, P.; Di Vaira, M.; Peruzzini, M.; Costantini, S. S.; Stoppioni, P. *Chem. Eur. J.* **2007**, 13, 6682-6690.
- ³⁰ Barbaro, P.; Di Vaira, M.; Peruzzini, M.; Costantini, S. S.; Stoppioni, P. *Inorg. Chem.* **2009**, 48, 1091-1096.
- ³¹ J. Heise, E. Sall and M McGrath, *int. pat.*, WO 99/43612, **1999**.
- ³² Scheer, M.; Balazs, G.; Seitz, A. *Chem. Rev.* **2010**, 110, 4236-4256.
- ³³ Rauhut, M. M.; Semsel, A. M. *J. Org. Chem.*, **1962**, 28, 471-473.
- ³⁴ Fritz, G.; Häger, J. *ZAAC*, **1983**, 504, 23-37.
- ³⁵ Baudler, M.; Faber, W. *Chem. Ber.*, **1980**, 113, 3394-3395.
- ³⁶ Buss, D. H.; Schaumberg, G.; Glemser, O. *Angew. Chem. Int. Ed.* **1985**, 24, 1057-1058.
- ³⁷ Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Gusarova, N. K.; *Russ. Chem. Bull.* **1997**, 46, 849-850.
- ³⁸ Kudryavtseva, L. I. *Zh. Obshch. Khim.*, **1990**, 60, 74-79.

³⁹ Walling, C.; Stacey, F. R.; Jamison, S. E.; Huyser, E. S. *J. Am. Chem. Soc.*, **1958**, *80*, 4543-4546.

⁴⁰ Walling, C.; Stacey, F. R.; Jamison, S. E.; Huyser, E. S. *J. Am. Chem. Soc.*, **1958**, *80*, 4546-4549.

⁴¹ Tofan, D.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2010**, *49*, 7516-7518.

⁴² Schmidpeter, A.; Burget, G.; Zwaschka, F.; Sheldrick, W. S. *Z. Z. annorg. allg. Chem.* **1985**, *527*, 20.

⁴³ Power, M. B.; Barron, A. R. *Angew. Chem. Int. Ed.* **1991**, *30*, 1353.

⁴⁴ Fox, A. R.; Wright, R. J.; Rivard, E.; Power, P. P. *Angew. Chem. Int. Ed.* **2005**, *44*, 7729-7733.

⁴⁵ Deacon, G. B.; Parrott, J. C. *J. Organomett. Chem.* **1970**, *22*, 287-295.

⁴⁶ Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.*, **2007**, *46*, 7052-7055.

⁴⁷ Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180-14181.

⁴⁸ Holscumacher, D.; Bannenberg, T.; Ibrom, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, Matthias. *J. Chem. Soc. Dalton. Trans.* **2010**, *39*, 10590-10592.

⁴⁹ Becker, G.; Holderich, W. *Chem. Ber.* **1975**, *108*, 2484

⁵⁰ Askham, F. R.; Stanley, G. G.; Marques, E. C. *J. Am. Chem. Soc.* **1985**, *107*, 7423-7431

⁵¹ Falius, H.; Krause, K.; Sheldrick, W. S. *Angew. Chem. Int. Ed.* **1981**, *20*, 103-104.

-
- ⁵² Rotter, C.; Schuster, M.; Karaghiosoff, K.; *Inorg. Chem.* **2009**, *48*, 7531-7533.
- ⁵³ Bennett, F. W.; Emeléus, H. J.; Haszeldine, R. N. *J. Chem. Soc.*, **1953**, 1565-1571.
- ⁵⁴ Burg, A. B.; Mahler, W.; Bilbo, A. J.; Haber, C. P.; Herring, D. L. *J. Am. Chem. Soc.*, **1957**, *79*, 247.
- ⁵⁵ Chan, W. T. K.; Garcia, F.; Hopkins, A. D.; Martin, L. C.; McPartlin, M.; Wright, D. S. *Angew. Chem. Int. Ed.* **2007**, *46*, 3084-3086.
- ⁵⁶ Xiong, Y.; Yao, S.; Brym, M.; Driess, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4511-4513.
- ⁵⁷ Schoeller, W. W. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5273-5280.
- ⁵⁸ Lynam, J. M.; *Angew. Chem. Int. Ed.* **2008**, *47*, 831-833.
- ⁵⁹ Gächter, R.; Müller, H. *Plastics Additives, 2nd Ed.*; Hanser Publishers, **1984**.
- ⁶⁰ Van Wazer, J. R. *Phosphorus and its Compounds*, Interscience, **1961**, vol 2.
- ⁶¹ UK Health and Safety Executive, *The dangers of cellulose nitrate film*, **2010**.
- ⁶² Official Journal of the European Union, L396, Regulation (EC) No 1907/2006.
- ⁶³ Costa, L.; Rossi Di Montelera, L.; Camino, G.; Weil, E. D.; Pearce, E. M. *J. Appl. Polym. Sci.*, **1997**, *68*, 1067-1076.
- ⁶⁴ Ji, Y.; Kim, J.; Bae, J. *J. Appl. Polym. Sci.*, **2006**, *102*, 721-728.
- ⁶⁵ Solbu, K.; Thorud, S.; Hersson, M.; Øvrebo, S.; Ellingsen, D. G.; Lundanes, E.; Molander, P. *Journal of Chromatography A*, **2007**, *1161*, 275-283.
- ⁶⁶ Pringle, P. G.; Baker, M. J.; *Chem. Comm.* **1991**, 1292-1293.

-
- ⁶⁷ Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* **1986**, *119*, 3089-3101.
- ⁶⁸ Wang, Y.; Marrocco, M. L.; Trimmer, M. S. *EU. Pat.* WO9639455, **1996**.
- ⁶⁹ Moon, J.; Lee, S. *J. Organomett. Chem.* **2009**, *694*, 473-477.
- ⁷⁰ Peruzzini, M. *Speciality Chemicals Magazine*, **2003**, *23*, 32-35.
- ⁷¹ Segall, J.; Shorr, L. M. *US Pat.* 5097056, 1992.
- ⁷² Becker, P. *Phosphates and Phosphoric Acid: raw materials, technology and economics of the wet process*, 2nd Ed.; Marcell Dekker, **1989**.
- ⁷³ Ilia, G.; Iliescu, S.; Popa, A. *Green Chemistry*, **2005**, *7*, 217-218.
- ⁷⁴ Perich, J. W.; Johns, R. B. *Synthesis*, **1988**, 142-144.
- ⁷⁵ Brown, C.; Hudson, R. F.; Wartew, G. A.; Coates, H. *Phosphorus Sulfur*, **1978**, *5*, 121-122.
- ⁷⁶ Brown, C.; Hudson, R. F.; Wartew, G. A.; Coates, H. *J.C.S. Chem. Comm.*, **1978**, *7*.
- ⁷⁷ Sterzel, H.; Brand, A. *int. pat.*, WO 01/51416, **2001**.
- ⁷⁸ Akbayeva, D.; Faisova, F. Kh.; Abdreimova, R.; Peruzzini, M. *J. mol. Cat. A.*, **2007**, *267*, 181-193.
- ⁷⁹ Budnikova, Yu.; Kargin, Yu.; Martyov, B.; Turygin, V.; Tomilov, A. *J. Electroanal. Chem.*, **2001** *507*, 157-169.
- ⁸⁰ Budnikova, Yu.; Yakhvarov, D.; Sinyashin, O. *J. Organomet. Chem.*, **2005**, *690*, 2416-2425.

⁸¹ Budnikova, Yu.; Tazeev, D.; Gryaznova, T.; Sinyashin, O. *Russ. J. Electrochem* **2006**, *42*, 1127-1133.

⁸² Budnikova, Yu.; Kafiyatullina, A.; Sinyashin, O.; Abdreimova, R. *Russ. Chem. Bull.*, **52**, 929-938.

⁸³ Dorfman, Ya.; Aleshkova, M.; Polimbetova, G.; Levina, L.; Petrova, T.; Abdreimova, R.; Doroshkevich, D. *Russ. Chem Rev.*, **1993**, *62*, 877-896.

⁸⁴ Dorfman, Ya.; Abdreimova, R.; Akbaeva, D. *Kinetics and Catalysis*, **1993**, *36*, 103-111.

⁸⁵ Abdreimova, R.; Faizova, F.Kh.; Akbayeva, D.; Polimbetova, G.; Aibasova, S.; Borangazieva, A.; Aliev, M. *Eurasian ChemTech Journal*, **2002**, *4*, 11-17.

⁸⁶ Abdreimova, R.; Akbayeva, D.; Polimbetova, G.; Caminade, A.; Majoral, J. *Phosphorus Sulfur*, **2000**, *156*, 239-254.

⁸⁷ Whilst FeCl₃, CuCl₂ are in reality catalysts in the reaction the term co-oxidant is accurate when referring to NaBrO₃, NaNO₂ and benzoquinone.

⁸⁸ Formation of smoke indicates white phosphorus is reacting directly with air to form a mist of phosphorus oxides and phosphorus oxoacids.

⁸⁹ Cariati, E.; Roberto, D.; Ugo, R.; Ford, P. C.; Galli, S.; Sironi, A. *Inorg. Chem.*, **2005**, *44*, 4077-4085.

⁹⁰ Yiu, S.; Wu, Z.; Mak, C.; Lau, T. *J. Am. Chem. Soc.*, **2004**, *126*, 14921-14929.

⁹¹ Legros, J.; Bolm, C. *Angew. Chem. Int. Ed.* **2004**, *43*, 4225-4228.

-
- ⁹² Soria-Sanchez, M.; Maroto-Valiente, A.; Alvarez-Rodriguez, J.; Rodriguez-Ramos, I.; Guerrero-Ruiz, A. *Carbon*, **2009**, *47*, 2095-2102.
- ⁹³ Hu, X.; Mao, J.; Sun, Y.; Chen, H.; Li, H. *Catal. Comm.* **2009**, *10*, 1908-1912.
- ⁹⁴ Schultz, M. J.; Sigman, M. S. *tetrahedron*, **2006**, *62*, 8227-8241.
- ⁹⁵ Shultz, J.; Tarbutton, G.; Jones, T.; Deming, M.; Smith, C.; Cantelou, M *Ind. Eng. Chem.*, **1950**, *42*, 1608-1615.
- ⁹⁶ Landon, P.; Collier, P.; Papworth, A.; Kiely, C.; Hutchings, G. *Chem. Commun.*, **2002**, 2058-2059.
- ⁹⁷ Enache, D.; Knight, D.; Hutchings, G. *Catal. Lett.*, **2005**, *103*, 43-52.
- ⁹⁸ Enache, D.; Barker, D.; Edwards, J.; Taylor, S.; Knight, D.; Carley, A.; Hutchings, G. *Catal. Today.*, **2007**, *122*, 407-411.
- ⁹⁹ Zhou, K.; Wang, R.; Xu, B.; Li, Y. *Nanotechnology*, **2006**, *17*, 3939-3943.
- ¹⁰⁰ Jiang, Y.; Liu, M.; Wang, Y.; Song, H.; Gao, J.; Meng, G. *J. Phys. Chem. A*, **2006**, *110*, 13479-13486.
- ¹⁰¹ Hakkarainen, M. *Advances in Polymer Science*, **2008**, *211*, 159-185.
- ¹⁰² Budnikova, Yu.; Kargin, Ju.; Sinyashin, O.; Romakhin, A. *Rus. Pat.*, 2199545, **2003**.
- ¹⁰³ Akbarali, P. M. *et al. US. Pat.*, 20030100787.

-
- ¹⁰⁴ Chemtura, Technical Data Sheet, Reofos RDP.
- ¹⁰⁵ Santry, D.; Segal, G. *J. Chem. Phys.*, **1967**, *47*, 153-174.
- ¹⁰⁶ Tamuliene, J.; Balevicius, M. L.; Tamulis, A. *Lithuanian Journal of Physics*, **2002**, *42*, 5-10.
- ¹⁰⁷ E. DiBella, *US Pat.*, US 4469644, **1982**.
- ¹⁰⁸ Conant, J. B.; Wallingford, V. H.; Gandheker, S. S. *J. Am. Chem. Soc.* **1922**, *45*, 762-768.
- ¹⁰⁹ Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd. Ed.; Butterworth Heinmann, **1997**.
- ¹¹⁰ Richert, S. A.; Tsang, P. K. S.; Sawyer, D. T. *Inorg. Chem.* **1989**, *28*, 2471-2475.
- ¹¹¹ Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley & Sons, **1988**.
- ¹¹² Albouy, D.; Etemad-Moghadam, G.; Vinatoru, M.; Koenig, M. *J. Organomett. Chem.* **1997**, *529*, 295-299.
- ¹¹³ Nilsson, J.; Kraszewski, A.; Stawinski, J. J. *Chem. Soc., Perkin Trans. 2*, **2001**, 2263-2266.
- ¹¹⁴ Goubeau, Von J.; Schulz, P. *Z. anorg. allg. Chem.* **1958**, *294*, 224-232.
- ¹¹⁵ Allaf, A. W. *Spectrochim. Acta A*, **1998**, *54*, 921-926.
- ¹¹⁶ Lopex, X.; Dejaegere, A.; Karplus, M. *J. Am. Chem. Soc.* **2001**, *123*, 11755-11763.

-
- ¹¹⁷ Thilo, V. E.; Heinz, D. Z. *Anorg. Allg. Chemie*. **1955**, 281, 303-321.
- ¹¹⁸ Grunze, H.; Z. *Anorg. Allg. Chemie*. **1961**, 313, 323-337.
- ¹¹⁹ McNaught, A. D.; Wilkinson, A. *IUPAC. Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Blackwell Scientific Publications, Oxford, **1997**.
- ¹²⁰ Sorensen-Stowell, K.; Hengge, A. C. *J. Org. Chem.* **2005**, 70, 4805-4809.
- ¹²¹ Jacobsen, G. *Chem. Ber.* **1875**, 8, 1519-1523.
- ¹²² Acharya, J.; Gupta, A. K.; Shakya, P. D.; Kaushik, M. P. *Tet. Lett.* **2005**, 46, 5293-5295.
- ¹²³ Saindane, M. T. *Int. Pat. WO 99/05200*, **1999**.
- ¹²⁴ Audrieth, L. F.; Toy, A. D. F. *J. Am. Chem. Soc.* **1942**, 1337-1339.
- ¹²⁵ Foster, A. B.; Overend, W. G.; Stacey, M. *J. Chem. Soc.* **1951**, 980-987.
- ¹²⁶ Necas, M.; Foreman, M. R. St. J.; Marek, J.; Woollins, J. D.; Novosad, J.; *New J. Chem.* **2001**, 25, 1256-1263.
- ¹²⁷ Tamura, K. *EU Pat. EP 1403272 A1*, **2004**.
- ¹²⁸ Kannan, P.; Kishore, K. *European Polymer Journal*, **1991**, 27, 1017-1021.
- ¹²⁹ Fontain, G.; Bourbigot, S.; Duquesne, S.; Delobel, R. *Advances in Flame Retardency of Polymeric Materials*, **2007**, 18, 104-110.
- ¹³⁰ Durairaj, R. B.; Jesionowski, G. A. Conference proceedings – *Conference on Recent Advances in Flame Retardancy of Polymeric Materials*, **2005**, 16, 93-103.
- ¹³¹ Yu, B.; Lu, L.; He, Y.; Tang, K. *Zhongguo Suliau*, **2008**, 22, 72-75.
- ¹³² Moy, P. *Journal of Vinyl & Additive Technology*, **2004**, 10, 187-192.

-
- ¹³³ Bright, D. A.; Aaronson, A. M. *US Pat* 5041596, **1991**.
- ¹³⁴ Corby, N. S.; Kenner, G. W.; Todd, A. R. *J. Chem. Soc.* **1951**, 1234-1242.
- ¹³⁵ Fujisawa, T.; Tajima, K.; Sato, T. *Bull. Chem. Soc. Jpn.* **1983**, 56, 3529-3530.
- ¹³⁶ Arnold, M. B.; Ornstein, P. L.; Zarrinmayeh, H.; Zimmerman, D. M. *US Pat.* 6521605, **2003**.
- ¹³⁷ Muller, P. C. Lauterbur, J. Goldenson, *J. Am. Chem. Soc.* **1956**, 78, 3557-3561.
- ¹³⁸ Mori, M. Abe, M. Nojima, *J. Org. Chem.* **2001**, 66, 3548-3553.
- ¹³⁹ P. J. Garegg, T. Regberg, J. Stawinski, R. Stromberg, *Tetrahedron letters*, **1986**, 27, 2665-2666.
- ¹⁴⁰ Mukhopadhyay, M. K.; Sanyal, M. K.; Datta, A.; Webster, J.; Penfold, J. *Chem. Phys. Lett.* **2005**, 407, 276-282.
- ¹⁴¹ Sobkowiak, A.; Naróg, D.; Sawyar, D. T. *J. mol. Catal. A: Chem.*, **2000**, 159, 247-256.
- ¹⁴² Infrared spectral data from Coblenz Society was obtained from the National Institute of Standards and Technology. © 2008 by the U.S. Secretary of Commerce on behalf of the United States of America.
- ¹⁴³ Besbyatov, M. A.; Naumov, V. N. *Thermochim. Acta.* **2007**, 463, 90-92.
- ¹⁴⁴ Infrared spectral data from the Bio-Rad/Sadtler IR Data Collection was obtained from Bio-Rad Laboratories, Philadelphia, PA (US).
- ¹⁴⁵ Germann, F. E. E.; Traxler, R. N.; *J. Am. Chem. Soc.* **1927**, 49, 307-312.
- ¹⁴⁶ Wada, T.; Hotoda, H.; Sekine, M.; Hata, T. *Tet. Lett.* **1988**, 29, 4143-4146.

¹⁴⁷ Chojnowski, J.; Cypryk, M.; Michalski, J. *J. Organomet. Chem.* **1981**, *215*, 315-365.