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Catalytic Synthesis of Triaryl Phosphates from White Phosphorus

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Triaryl phosphates were synthesized from white phosphorus and phenols under aerobic conditions and in the presence of iron catalysts and iodine. Full conversion to phosphates was achieved without the use of chlorine, 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 high selectivities. Various iron(III) diketonates were used to catalyze the conversion. Mechanistic studies showed that the reaction proceeds by formation of PI_3, then $O{=}PI(OPh)_2$ before the final formation of the phosphate. The nucleophilic substitution of $O{=}PI(OPh)_2$ with phenol to form $O{=}P(OPh)_3$ was found to be the rate-limiting step.

Introduction

Triorganophosphates are added to polymers to act as plasticizers and/or flame retardants. Triphenyl phosphate and tritolyl phosphate are often used for cellulose-based polymers such as cellulose acetate. 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 market for plasticizers is largely dominated by phthalates; however, triaryl phosphates still maintain a small but significant share of the market. In some particular applications, phosphates are preferred over phthalate plasticizers because of their light stability, better rheological properties at low temperatures and flame retardant properties.[1]

Tritolyl phosphate is also used as an additive in leaded petrol. It serves as a lead scavenger, preventing the formation of lead metal deposits on vital engine components. This is still a major application for aviation fuel, to which tetraethyl lead is still added as an antiknock agent. Tritolyl phosphate is also used as an additive for high-pressure lubricants to decrease wear on metal parts.[2] 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.

Flame retardants are added to almost all commercially available plastics. Halogen-containing flame retardants 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 January 1st 2007.[3] This opens up new opportunities in the market for non-halogenated flame retardants like triaryl phosphates. Both triphenyl phosphate and tritolyl phosphate are sold commercially as flame retardants. Among these, tritolyl phosphate is the one that is most commonly used, because of its compatibility with PVC.[4]

The bulk production of triorganophosphates uses white phosphorus (P_4) as precursor and proceeds in three steps [Equations (1), (2) and (3)].[5]

$$P_4 + 6Cl_2 \rightarrow 4PCl_3 \quad (1)$$

$$PCl_3 + \tfrac{1}{2}O_2 \rightarrow O{=}PCl_3 \quad (2)$$

$$O{=}PCl_3 + 3ROH \rightarrow O{=}P(OR)_3 + 3HCl \quad (3)$$

Many aliphatic and aromatic homoleptic phosphates are produced in this way. This process is atom- and energy-inefficient; 1.5 mol chlorine gas are consumed for every mol of product formed and three mol HCl waste are also produced. Significant environmental risks are involved in the production and transport of chlorine gas as well as phosphorus trichloride.

Chlorination is used in this process to moderate the reactivity of phosphorus, and chlorine is used in a stoichiometric manner. Because of environmental concerns, its replacement with a catalyst, acting in a substoichiometric manner, is highly desirable. Abdreimova et al. have been developing catalyst/phosphorus/alcohol systems with some very interesting results.[6–9] It was shown that copper(II) complexes catalyze the formation of P–O bonds and that the nature of the ligands controls the product distribution. Copper halides were found to enhance the formation of phosphates, whereas copper sulfate and copper acetates were found to enhance the formation of phosphites. No changes in the reaction conditions other than changing the catalyst are reported to be necessary to cause this remarkable change in selectivity. The best selectivity towards phosphite was ob-

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served for tri-isopropyl phosphite, which was obtained in 87.3% yield by using a copper stearate catalyst.[7] The highest selectivity towards phosphate was 87.9% in the case of tributyl phosphate, with copper chloride as the catalyst.[8]

These catalytic systems did not work well with phenols, and neither triphenyl phosphite nor triphenyl phosphate could be successfully formed by using copper catalysts. With another catalytic system based on iron(III) chloride and iodine, formation of triphenyl phosphate in low yield (28%) was reported.[9]

In a series of studies by Budnikova et al., the possibility of synthesizing organophosphorus compounds from white phosphorus by electrochemical means was examined.[10–13] Aliphatic alcohols were treated with white phosphorus in the presence of Et_4NI electrolyte and Cu^{II} or Ni^{II} catalysts. Under electrolytic conditions at 20–60 °C, trialkyl phosphates were formed in yields of up to 70%. These electrochemical systems were also shown to be capable of forming triphenyl phosphate in 82% yield.[10]

There has been much recent work on the activation of the P_4 tetrahedron by using transition metal complexes. Examples of metals that have been found to activate P_4 include cobalt, rhodium and iridium.[5,14] Complexes formed from white phosphorus and iron compounds, such as pentaphosphaferrocene, have also been known for some time.[15]

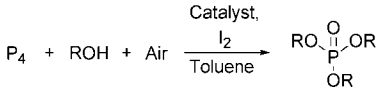
In addition to metal activation of P_4, new allotropes of phosphorus stabilized by base (carbene) are investigated intensely as possible sources of unusual reactivity.[16] Whilst many of these species have been shown to modify the reactivity of phosphorus, the catalytic conversion of white phosphorus to useful products remains elusive.[5]

In this study, we have developed new catalytic routes to triaryl phosphates directly from white phosphorus. After catalyst trials, the most successful system was optimized, and the mechanism of the reaction was elucidated.

Results and Discussion

Catalytic Reactions of Phenol with White Phosphorus

The catalytic aerobic reaction of phenol with white phosphorus was tested under varying reaction conditions, with the aim of optimizing the reaction towards selective formation of triaryl phosphates (Scheme 1). Typically, a solution of P_4 in toluene was added slowly to a stirred mixture of phenol, catalyst and iodine in toluene (heated to 80 °C), whilst air was bubbled into the reaction mixture.



Scheme 1. Desired catalytic reaction of white phosphorus with phenols in the presence of air.

A wide variety of catalysts were tried for this system, including $CuSO_4$, $CuCl_2$, $Cu(CH_3CO_2)_2$, $FeCl_3$, $FeBr_2$, $Fe(C_{17}H_{35}CO_2)_2$, $Fe(bipy)_3Cl_2$ (bipy: 2,2′-bipyridine), ferrocene, $[CpFe(CO)_2]_2$, $MoCl_5$, $Co^{II}Pc$ (Pc: phthalocyanine, $C_{32}H_{16}N_8$), $VO(acac)_3$ (acac: acetylacetonate), $Ni(Cl_2Py_2)$, $Mn(acac)_3$, nanodisperse Au/Pd on TiO_2 and CuO(s). In all cases, the inclusion of a small quantity of iodine was necessary to facilitate the conversion of P_4 to products. Whilst many of these catalysts showed at least some activity, the selectivity was often poor, and complex mixtures were produced. Iron(III) catalysts with diketonate ligands were found to be the most effective catalysts, and further study concentrated on these compounds. The successful reactions were conducted at 70–80 °C in toluene in the presence of less than stoichiometric amounts of iodine. Lowering the reaction temperature always caused a significant decrease in reaction rate.

Iron is a desirable metal for the catalysis of industrial processes due to its low toxicity, low cost and ready availability. Indeed, iron(III) acetylacetonate $[Fe(acac)_3]$ has been used as a catalyst in a variety of oxidation reactions previously. The wide range of oxidizing agents (and substrates) used in conjunction with it include H_2O_2 (used in stereospecific oxidations of sulfides),[17] high-pressure oxygen (oxidation of phenol)[18] and air (aerobic oxidation of the ethylene bond in β-isophorone).[19]

In our application of iron(III) acetylacetonate as a catalyst (using the conditions mentioned above), a complete conversion of P_4 to triphenyl phosphate (with 100% selectivity as assessed by ^{31}P NMR spectroscopy) was achieved. A loading of 25 mol-% $Fe(acac)_3$ with respect to P was required to achieve this selectivity. When the catalyst load was decreased to 12.5 mol-%, only 66% selectivity towards the phosphate was achieved; the remainder of phosphorus was converted to diphenyl phosphate $[O=P(OPh)_2OH]$. Comparable results were achieved with *o*-cresol as substrate, 100% selectivity towards tri-*o*-tolyl phosphate was achieved with 25 mol-% $Fe(acac)_3$ loading, whilst reducing the loading to 12.5 mol-% gave a mixture of tritolyl phosphate (88%) and tetra-*o*-tolyl pyrophosphate, $(o\text{-}CH_3C_6H_4)_2OP–O–PO(O\ o\text{-}CH_3C_6H_4)_2$, 12%.

Derivatives of Iron Acetylacetonate as Catalysts

Whilst triphenyl phosphate was formed with 100% selectivity by using $Fe(acac)_3$ as catalyst, the separation of the mixtures after reaction proved difficult. Partial thermal decomposition of the catalyst was found to occur at the high temperatures needed for the distillation of the triphenyl phosphate (b.p. 160 °C at 0.4 mbar). Recovery of the catalyst by extraction with organic solvents was not possible either, because the solubility of $Fe(acac)_3$ matches closely that of triphenyl phosphate.[19] Because of the difficulties with $Fe(acac)_3$ catalyst recovery, a series of iron(III) catalysts with modified diketonate ligands were tested as catalysts in the reactions of phenols with white phosphorus. It was hoped that catalytic efficacy would not be diminished (and could be improved) by modification of the ligand, while the modified solubility characteristics would allow the catalyst to be separated from the phosphate product by sol-

vent 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-1,4-butanedione (**3**) were tested. (Figure 1).

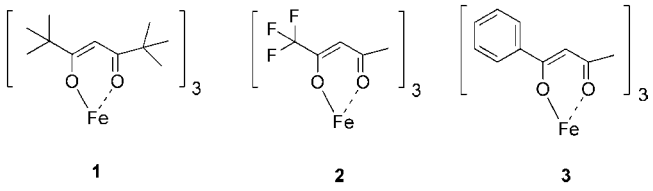


Figure 1. Diketonate catalysts tested for activity.

All three catalysts (**1–3**) showed some degree of catalytic activity in the aerobic reactions of white phosphorus with phenol. By gradually decreasing the ratio of catalyst to phosphorus (whilst keeping the P_4 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 was increased, the preferential formation of side products was observed. The major side product was identified as $O{=}P(OPh)_2OH$ by ^{31}P NMR spectroscopy. If the P_4/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 direct oxidation of white phosphorus by air, observed as the formation of white smoke above the reaction mixture.[20] As direct oxidation by air is unsafe (danger of explosion), 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 1. The order, from most effective to least effective, is $Fe(acac)_3 \approx$ **1**, **2**, **3**. Further experiments showed that this order is the same irrespective of which phenol is used.

Table 1. Comparison of catalytic activity in the aerobic reaction of P_4 with phenol for various Fe^{III} complexes. All reactions were conducted at 80 °C in toluene. See Experimental Section for details.

	Minimum catalyst loading to achieve 100% selectivity (mol-% with respect to P)	Notes
$Fe(acac)_3$	25	12% catalyst loading gives 66% conversion to $OP(OPh)_3$.
1	25	12% catalyst loading gives 88% conversion to $OP(OPh)_3$.
2	33	Reaction starts smoking if less than 33 mol-% of catalyst is used.
3	50	–

Of the alternative catalysts, only **1** was as effective as iron(III) acetylacetonate. Isolation of the phosphate product and catalyst recovery was achieved from the mixture after the reaction with **1** as catalyst. The volatiles (mainly toluene) were removed in vacuo at room temp., and a 50:50 mixture of toluene and hexane was added to the residue. Addition of a small volume of water resulted in the formation of two distinct liquid layers and a solid. The organic layer was found to contain catalyst **1**, which, after evaporation of the solvents, appeared to be pure as observed by IR spectroscopy and had a melting point of 158–160 °C (literature values: 162–164).[21] The dry weight of catalyst recovered was 92% of the starting mass, and it was successfully used in a further reaction. The light brown solid[22] was filtered off and identified as triphenyl phosphate by IR and NMR spectroscopy (isolated yield 82%).

Reaction 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.[23] 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.[24] To address this gap, we chose 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. It was hoped that further insight into the mechanism of the catalytic transformations might be provided by using this substrate.

Initially, the reactions were performed with iron(III) acetylacetonate 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 P_4 addition, a significant decrease in selectivity towards triaryl phosphate was observed (Table 2). ^{31}P NMR spectroscopy showed that the resulting reaction mixture contained only 30% 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.[25] The remaining 70% was accounted for by tetrakis(2,4-di-*tert*-butylphenyl) pyrophosphate, $(2,4\text{-}t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_2(\mathrm{O}{=})\mathrm{P}\text{–}\mathrm{O}\text{–}\mathrm{P}(=\mathrm{O})(\mathrm{O}2,4\text{-}t\mathrm{Bu}_2\text{-}\mathrm{C}_6\mathrm{H}_3)_2$. Increasing the reaction temperature to 110 °C (at reflux in the presence of toluene) resulted in the production of pyrophosphate only (100% conversion). Decreasing the reaction temperature to 60 °C slowed down the reaction rate and led to the formation of bis(2,4-di-*tert*-butylphenyl)-phosphoroiodidate, $O{=}PI(2,4\text{-}t\mathrm{BuC}_6\mathrm{H}_3)_2$, as a side product. This product was synthesized separately and was fully characterized by ^{31}P, ^{1}H, ^{13}C NMR and IR spectroscopy and mass spectrometry (see Experimental Section for details).

Catalysts **1**, **2** and **3** were also tested with 2,4-di-*tert*-butylphenol as substrate (Table 2), and the product mixtures were analyzed by ^{31}P NMR spectroscopy. Catalyst **2**

Table 2. Catalytic reactions with 2,4-di-*tert*-butylphenol. In all cases, the ratio P/catalyst/I_2/2,4-*t*BuC_6H_3OH was 2:1:0.6:12. All reactions were conducted in toluene over approximately 7 h. See Experimental Section for details.

Catalyst	Rate of P_4 addition [mmol/h]	Reaction temp. [°C]	Composition of product mixture (analyzed by ^{31}P NMR spectroscopy)
$Fe(acac)_3$	0.70	80	70% (2,4-*t*$Bu_2C_6H_3O)_2OP$–O–$PO(O$–2,4-*t*$Bu_2C_6H_3)_2$ 30% $OP(O$–2,4-*t*$Bu_2C_6H_3)_3$
$Fe(acac)_3$	0.53	110	100% (2,4-*t*$Bu_2C_6H_3O)_2OP$–O–$PO(O$–2,4-*t*$Bu_2C_6H_3)_2$
$Fe(acac)_3$	0.34	60	50% O=$PI(O$–2,4-*t*$Bu_2C_6H_3)_2$ 24% (2,4-*t*$Bu_2C_6H_3O)_2OP$–O–$PO(O$–2,4-*t*$Bu_2C_6H_3)_2$ 18% $OP(O$–2,4-*t*$Bu_2C_6H_3)_3$ 8% unknown minor products
1	0.53	80	100% $OP(O$–2,4-*t*$Bu_2C_6H_3)_3$
2	0.78	80	smoke
3	0.67	80	100% (2,4-*t*$Bu_2C_6H_3O)_2OP$–O–$PO($*O*-2,4-*t*$Bu_2C_6H_3)_2$

does not catalyze the reaction at a sufficient rate; white smoke[20] 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. With catalyst **1**, however, the reaction afforded solely the desired tris(2,4-di-*tert*-butylphenyl) phosphate. As expected, to achieve the desired selectivity towards triorganophosphate, 2,4-di-*tert*-butylphenol requires a more effective catalytic system than phenol.

Reactions with *o*-Cresol

The phosphate of cresol is a useful industrial chemical (see above). The tritolyl phosphate 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 a methyl group *ortho* to the oxygen atom. *O*-cresol was reacted aerobically with white phosphorus with iron(III) acetylacetonate and **1** as the catalyst (Table 3). Complete conversion to tritolyl phosphate was achieved with each catalyst as determined by ^{31}P NMR spectroscopy.

In the reactions with 2,4-di-*tert*-butylphenol, the pyrophosphate was formed when the catalyst loadings were insufficient. The analogous process was also observed with cresol as substrate. When the ratio of P to catalyst was increased to 4:1, some tetra-*o*-tolyl pyrophosphate was formed (row 2 in Table 3).

Mechanistic Studies

The combination of iron(III) acetylacetonate and iodine has been shown to be effective in catalyzing the aerobic reaction of white phosphorus with phenol to form triphenyl phosphate. Since understanding the mechanism of the transformation is critical for its further optimization, we paid close attention to elucidating the mechanism and finding the rate-limiting steps in it.

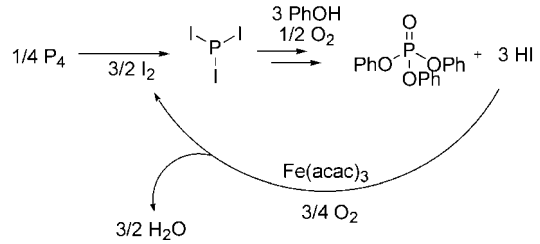
Initial Steps of the Catalytic Cycle

In order to identify the initial step of the transformation, solutions of white phosphorus in toluene were treated with iron acetylacetonate and iodine under *anaerobic* conditions. The reaction was followed by ^{31}P NMR spectroscopy. It was shown that iron(III) acetylacetonate does not react with white phosphorus even at 80 °C. Iodine, however, does react with P_4 instantly to form a mixture of P_2I_4 and PI_3 even at room temperature.

Attempts to react white phosphorus and phenol in the presence of air by using iodine alone resulted in the rapid formation of smoke after a stoichiometric amount of P_4 to form PI_3 was added.[20] 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,[26] which, after phenolysis and further oxidation, afford the triaryl phosphate. Iron(III) acetylacetonate and air chiefly function to reoxidize the HI byproduct (formed at the latter stages of the reaction) back to I_2, thus forming a catalytic cycle (see Scheme 2). However, additional experiments showed that the iron catalyst also plays an important role in the latter stages of the reaction (see below).

Table 3. Aerobic catalytic reactions of P_4 with *o*-cresol. All reactions were conducted at 80 °C in toluene over approximately 7 h. See Experimental Section for details.

Catalyst	Ratio P/catalyst/I_2/*o*-cresol	Rate of P_4 addition [mmol/h]	Composition of product mixture (analyzed by ^{31}P NMR spectroscopy)
$Fe(acac)_3$	2:1:0.6:24	0.34	100% O=$P(OC_6H_4$*o*-$Me)_3$
$Fe(acac)_3$	2:0.5:0.6:24	0.71	88% O=$P(OC_6H_4$*o*-$Me)_3$ 12% (*o*-$MeC_6H_4O)_2OP$–O–$PO(O$–*o*-$MeC_6H_4)_2$
1	2:1:0.6:24	0.34	100% O=$P(OC_6H_4$*o*-$Me)_3$



Scheme 2. Catalytic role of iodine.

Oxidation of HI(aq) with oxygen to I_2 is thermodynamically feasible; however, the uncatalyzed reaction is very slow on kinetic grounds.[27] To investigate the effect of iron acetylacetonate on the rate of this reaction, air was bubbled through an aqueous solution of HI (6 M) 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 five hours. When this experiment was repeated with a 0.5 M solution of HI, the initial concentration of I_2 was measured as 0.020 M (4.2%). After five hours of oxidation under 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 oxidation (HI → I_2) 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.[28]

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) acetylacetonate. Air was bubbled through a 0.2 M solution of HI in methanol at 65 °C.[29] 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 endpoint was determined by monitoring the titration with a pH meter. When a 0.2 M concentration of iron(III) acetylacetonate was used, 94% of the initial amount of HI was found to remain after four hours (indicating a 6% conversion to I_2). When the concentration of iron(III) acetylacetonate was 1.2 M, only 77% of the HI was found to remain after four hours (23% conversion to I_2). This higher ratio of the 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 that iron(III) acetylacetonate significantly increases the rate of the reoxidation of HI in phosphate-forming reaction systems.

It is unlikely that the rate of HI oxidation is affected by the presence of other compounds in the reaction system, since, apart from the Fe^{III} catalyst, none of the known reaction system components have distinct oxidizing properties.

Reactions of Phosphorus Iodides with Phenol

To gain further insight into the mechanism of the phosphate-producing reactions, solutions of PI_3/P_2I_4 in toluene were treated with phenol under various reaction conditions, with and without iron catalyst. The results are summarized in Table 4; the reactions were monitored by ^{31}P NMR spectroscopy.

Table 4. Reactions of PI_3 with phenol. All reactions were performed with a 1:3 stoichiometric ratio of PI_3 to PhOH; the reaction temperature was 80 °C.

Entry	Reaction time	Air flow [mL/min]	$Fe(acac)_3$ catalyst loading	Product
1	5 h	40	None	$O=PI(OPh)_2$
2	3 h	40	$Fe(acac)_3$ (100 mol-%)	$O=P(OPh)_3$
3	5 h	None	None	100% PI_3 recovered
4	5 h	None	$Fe(acac)_3$ (100 mol-%)	Unknown

In the aerobic reaction of PI_3 with PhOH with no catalyst added (entry 1 in Table 4), diphenyl phosphoroiodidate [$O=PI(OPh)_2$] was formed in quantitative yield. Diphenyl phosphoroiodidate has previously been reported in the literature;[30] its identity was confirmed by ^{31}P, ^{1}H, ^{13}C NMR and IR spectroscopy and EI-MS (including exact mass determination). Further proof of its identity was provided via its hydrolysis reaction. On being stirred with water at room temp. for 24 hours, the compound hydrolyzed to a sole phosphorus-containing product, which was identified as $O=P(OPh)_2OH$ by ^{31}P NMR spectroscopy. 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 4). No reaction took place between PI_3 and phenol under anaerobic conditions (entry 3 in Table 4). It proved difficult to monitor the anaerobic reaction of PI_3 with phenol in the presence of catalyst (entry 4 in Table 4). Treatment with sodium sulfite is required to reduce the paramagnetic Fe^{III} before NMR spectroscopic measurements can be taken. Unfortunately, treatment with sulfite decomposes any PI_3 present, making it impossible to tell whether the starting PI_3 was consumed in the reaction.

Since entry 1 in Table 4 showed the formation of the intermediate $O=PI(OPh)_2$ to be essentially stoichiometric, we speculated that it is also formed as a transient intermediate in the catalyzed phosphorus and phenol reactions. The formation of $O=PI(OPh)_2$ does not require the presence of iron(III) catalyst (see entry 1, Table 4). However, in the presence of the catalyst, it is quickly consumed in the reaction that affords triaryl phosphate as an endproduct (entry 2, Table 4). Thus, the iron(III) catalyst appears to play a dual role in the phosphate-forming reaction system, that is, it catalyzes the oxidation of HI back to I_2 (as described above), as well as increasing the rate of the nucleophilic substitution reaction $O=PI(OPh)_2 \rightarrow O=P(OPh)_3$. To verify this hypothesis, independently prepared $O=PI(OPh)_2$ was

Table 5. Reactions of $O=PI(OPh)_2$ with phenol in toluene at 80 °C under anaerobic conditions.

Conc. of $O=PI(OPh)_2$ and phenol	$Fe(acac)_3$ catalyst loading	Reaction time till all $O=PI(OPh)_2$ was consumed	Phosphorus-containing products
0.34 M (molar ratio: 1:1)	None	20 h	66% $O=P(OPh)_2OH$, 4% $O=P(OPh)_3$ 30% $(PhO)_2(O)P–O–P(O)(OPh)_2$
0.32 M (molar ratio: 1:1)	25 mol-%	3 h	$O=P(OPh)_3$

treated 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 $O=PI(OPh)_2$ by the moisture in air; however, a small amount of water may have been present in the phenol used. The results of these experiments are shown in Table 5, the product mixtures were analyzed by ^{31}P NMR spectroscopy.

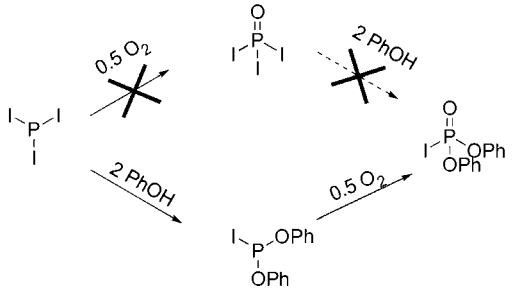
Without catalyst, only a small amount of $O=P(OPh)_3$ (ca. 4%) was produced after twenty hours (row 2 in Table 5). The rest of the starting material hydrolyzed to form pyrophosphate $(PhO)_2(O)P–O–P(O)(OPh)_2$ and $O=P(OPh)_2OH$. In a separate reaction, pyrophosphate was found to form when equal amounts of $O=P(OPh)_2I$ and $O=P(OPh)_2OH$ were heated at reflux in dry toluene for several hours. Presumably this reaction becomes significant when all available water in the reaction has been consumed. The formation of tetraphenyl pyrophosphate from diphenyl phosphoroiodidate has been reported previously in the literature.[30] Notably, related pyrophosphates were formed as side products in our reactions using 2,4-di-*tert*-butylphenol and cresol with low catalyst loadings (see Tables 2 and 3 above).

In the presence of iron(III) acetylacetonate, quantitative conversion to triphenyl phosphate was achieved anaerobically within three hours (row 4 in Table 5). Clearly, the catalyst vastly increases the rate and selectivity in the formation of $O=P(OPh)_3$ from the $O=PI(OPh)_2$ intermediate.

In the next step, we have focused on the mechanism of $O=PI(OPh)_2$ formation in the PI_3/phenol/air system. One of the possible pathways towards $O=PI(OPh)_2$ (with or without catalyst) involves formation of $O=PI_3$ from PI_3 and air. Similar oxidation of phosphorus chloride to $O=PCl_3$ is known to proceed readily.[31] On the other hand, the difficulty of synthesizing $O=PI_3$ in comparison to $O=PCl_3$ has been reported in the literature.[32] To verify this under conditions used in our experiments, a solution of PI_3 in toluene was heated to 80 °C, while air was bubbled through this solution for 3 h. After this, no conversion to $O=PI_3$ was observed, and PI_3 was recovered completely. This reaction was repeated in the presence of iron acetylacetonate (at a 1:1 molar ratio of iron/phosphorus). Once again no conversion to $O=PI_3$ was observed. It is therefore very unlikely that the $O=PI(OPh)_2$ intermediate is formed via $O=PI_3$.

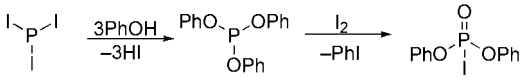
Instead, it is possible that PI_3 undergoes nucleophilic substitution with one or two equivalents of phenol before it is oxidized to P^V; only the reaction with two equivalents of phenol is shown in Scheme 3.

PI_3 was found not to react with phenol under anaerobic conditions without catalyst (entry 3, Table 4), whilst rapid reaction took place under aerobic conditions, giving $O=PI(OPh)_2$ (entry 1, Table 4). Presumably, under aerobic conditions, rapid removal of initially formed $PI(OPh)_2$ or $PI_2(OPh)$ by oxidation to $O=PI(OPh)_2$ or $O=PI_2(OPh)$ drives the otherwise slow P–I → P–OPh substitution reaction. To investigate this, we attempted to synthesize $P(OPh)_2I$ from $P(OPh)_2Cl$ and sodium iodide to determine its stability. Only partial conversion to $P(OPh)_2I$ was observed; however, the $P(OPh)_2I$ produced was found to oxidize to $O=P(OPh)_2I$ very rapidly when exposed to air. This indicates that the involvement of $P(OPh)_2I$ 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 spectroscopy.



Scheme 3. Reaction of PI_3 with oxygen and phenol.

Another possible route for the formation of $O=P(OPh)_2I$ is via the reaction of triphenyl phosphite with iodine, followed by an Arbuzov rearrangement to the product (Scheme 4).



Scheme 4. Alternative mechanism for the formation of $O=P(OPh)_2I$.

To test the feasibility of such a mechanism, a toluene solution of triphenyl phosphite was treated with iodine. After stirring for 16 h under nitrogen at room temp., a 4.5% conversion to $O=P(OPh)_2I$ was observed by ^{31}P NMR spectroscopy. This indicates that the reactions shown in Scheme 4 are a possible but unlikely route to $O=P(OPh)_2I$. To investigate the significance of this route further, the reaction mixture from the aerobic reaction of PI_3 with phenol (entry 1, Table 4) was analyzed by GC. No iodobenzene was observed in the final reaction mixture, indicating that the Arbuzov route had not contributed significantly.

To confirm that the mechanism via $P(OPh)_2I$ (see Scheme 3) is more likely to account for the formation of $O=P(OPh)_2I$, two further experiments were set up. In the

first, PI_3 was treated with three equivalents of phenol in the presence of iodine but not air. In the second PI_3 was treated with phenol in the presence of air but not iodine.

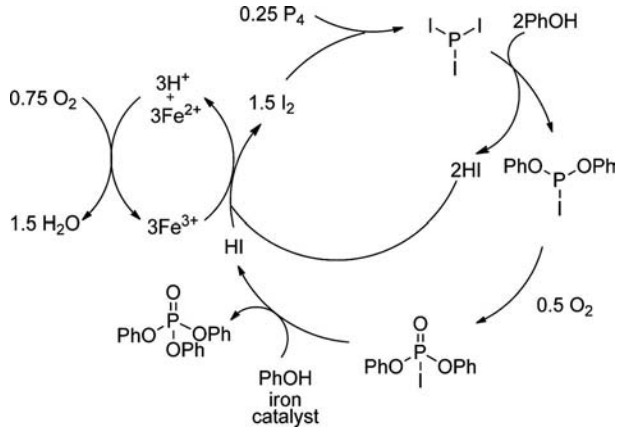
The aerobic reaction with no extra iodine (row 4 in Table 6) rapidly and selectively produced the phosphoroiodidate product, all of the starting phosphorus triiodide was converted to product within the four-hour reaction time. In the anaerobic reaction with extra iodine, only 20% of the PI_3 was converted to the phosphoroiodidate. The reaction mixture was heated to 80 °C for a further four hours; however, no further conversion of PI_3 was observed. These results indicate that it is unlikely that the Arbuzov route (Scheme 4) is responsible for the formation of $O{=}P(OPh)_2I$ in our reactions. The pathway including rapid oxidation of phosphoroiodidate intermediates (Scheme 3) is the more likely mechanism.

Table 6. Studies of the formation of $O{=}P(OPh)_2I$. Both reactions were performed in toluene at 80 °C, and the reaction time was 4 h.

Reaction mixture comp.	Equivalents of I_2	Air flow	Product
PI_3 + 3PhOH	1	None	70% unreacted PI_3 20% $O{=}P(OPh)_2I$ 10% $O{=}P(OPh)_3$
PI_3 + 2PhOH	0	40 mL/min	$O{=}P(OPh)_2I$

Proposed Reaction Scheme

An overall reaction mechanism of phosphate formation shown in Scheme 5 was deduced from the reactions detailed above.



Scheme 5. Overall scheme of catalyzed aerobic reaction of white phosphorus with phenol.

Iodine is believed to be entirely responsible for the initial oxidation of P_4 to PI_3. Phosphorus triiodide reacts with two equivalents of phenol and half an equivalent of O_2 to form $O{=}PI(OPh)_2$. This stage of the reaction is believed to proceed via rapid oxidation of $P(OPh)_2I$ or $P(OPh)I_2$. 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 extent of the hydrolysis is unlikely to be affected by drying the starting phenols better prior to the reaction, since water is generated in the reaction (as HI is reoxidized to I_2 and water). Alkaline hydrolysis of triorganophosphates is well known; however, hydrolysis with water alone is less well documented.[33] The aqueous hydrolysis of phosphorus–halogen bonds, on the other hand, is well documented.[34,35] It is likely that the good iodine leaving group and elevated reaction temperature help facilitate the hydrolysis. The pyrophosphate forming reaction appears only to proceed slowly at 80 °C (see Table 5); however, it becomes an issue if insufficient catalyst loads are used.

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 $Fe(acac)_3$ at 80 °C (see entry 1 in Table 7). At this rate of addition, 100% conversion to triphenyl phosphate is observed. If the addition rate per mmol of catalyst is increased, $O{=}P(OPh)_2OH$ is observed in the final reaction mixture. For example, at a white phosphorus addition rate of 0.30 mmol/h, per mmol of catalyst, the reaction produces approximately 33% $O{=}P(OPh)_2OH$ (entry 2 in Table 7). In this case, the conversion of $O{=}PI(OPh)_2$ to triphenyl phosphate is the rate-limiting step of the reaction. If the amount of iodine present is drastically reduced, the rate-limiting step is altered (entry 3 in Table 7). With these low iodine concentrations, the rate at which the iron catalyst reoxidizes HI back to I_2 is too slow. Therefore, the reaction mixture becomes iodine-deficient, and the formation of smoke is observed, indicating the direct reaction of P_4 with air.[20]

The work outlined above has shown that 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 $O{=}PI(OPh)_2$, favouring this reaction over hydrolysis. Secondly, it increases the rate of reoxidation of HI to form iodine. Meanwhile, the iodine serves to oxidize white phosphorus to phosphorus(III) (in the form of phosphorus triiodide).

Table 7. Conversion of white phosphorus with varying amounts of catalyst and iodine.

Entry	Rate of P_4 addition [mmol/h]	Amount of $Fe(acac)_3$ [mmol]	Rate of P_4 addition per mmol of $Fe(acac)_3$ [mmol/h]	Amount of I_2 [mmol]	Rate of P_4 addition per mmol of I_2 [mmol/h]	Phosphorus-containing products (by ^{31}P NMR spectroscopy)
1	0.79	4.52	0.17	1.59	0.49	100% $O{=}P(OPh)_3$
2	0.75	2.44	0.30	1.67	0.44	67% $O{=}P(OPh)_3$ 33% $O{=}P(OPh)_2OH$
3	1.04	3.02	0.34	0.49	2.10	Reaction smoked[20]

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.

Conclusions

We have demonstrated that triaryl phosphates can be synthesized directly from white phosphorus with high selectivity, without the need to use phosphorus trichloride as an intermediate. Although of little preparative use in their present form, the results presented here are to be considered as a proof of concept. We have shown that substoichiometric amounts of PI_3 can be used in lieu of a stoichiometric amount of PCl_3 in the selective production of triaryl phosphates. The reoxidation $I^- \rightarrow I_2$ can be achieved by air, and water produced in such a catalytic cycle does not pose a significant problem (with respect to hydrolysis) when sufficient amounts of catalyst are used.

Many other phosphorus products are synthesized via phosphorus trichloride. In longer term, investigations of direct catalytic routes to phosphites, phosphanes and similar phosphorus chemicals are desirable. Specifically, more catalysts may be screened with phenols and white phosphorus systems, with the aim of developing a process towards triaryl *phosphites*. Phosphites are unlikely to be synthesized by using iron/iodine catalyst systems, as these have been shown to oxidize phosphites to phosphates efficiently.[38]

Experimental Section

The compounds used in the experiments were supplied by Sigma Aldrich, Alfa Aesar or Acros Organics and were used without further drying or purification unless stated otherwise. Iron complexes **1** and **2** were reported in the literature previously; however, we used a new preparative method, reacting $FeCl_3$ with the respective diketonates (supplied from Sigma Aldrich). Iron complex **3** was purchased from Sigma Aldrich and used as received. All the catalysts were used in their anhydrous form. White phosphorus was supplied by Thermphos International and was used as received without further purification. NMR spectroscopic measurements were performed at 25 °C unless otherwise indicated; 85% H_3PO_4 was used as external standard in ^{31}P NMR spectroscopy; ^1H and ^{13}C NMR shifts are relative to TMS (internal standard). NMR spectroscopic shifts of compounds in this study are presented in Table 8. Expected isotopic patterns were observed in all mass spectra.

Table 8. ^{31} P NMR spectroscopic shifts of compounds in this study (in $CDCl_3$).

	R: phenol	R: *o*-cresol	R: 2,4-di-*tert*-butylphenol
$O=P(OR)_3$	–17.4[36]	–16.1[36]	–19.9
$O=P(OH)(OR)_2$	–9.1[37]	–	–
$O=P(OR)_2I$	–47.0[30]	–	–60.0
$(RO)_2(O)P–O–P(O)(OR)_2$	–24.9[39]	–24.0	–27.1

General Procedure for Reactions of White Phosphorus with Phenol

The results are shown in Tables 1, 2, 3 and 7. The reactions of white phosphorus with phenol were performed in a 250 mL three-necked, round-bottomed flask. The flask was fitted with a reflux condenser with an aqueous copper sulfate bubbler outlet to trap any escaping vapours of P_4. The catalyst (typically ca. 0.3 g, 1.5–3.0 mmol), phenol (typically ca. 3.0 g, 20–40 mmol), iodine (typically ca. 0.2 g, 0.5–1.0 mmol I_2) and toluene (5 mL) were placed into this flask. The mixture was stirred intensely with a magnetic stirrer and heated in a water bath to 80 °C (unless stated otherwise). Solutions of white phosphorus in toluene (typically 20 mL of ca. 2% solution, ca. 0.4 g, 3.0 mmol P_4) were added to the reaction at a rate of 0.34–0.78 mmol P_4/h, with a syringe pump. Air was bubbled through the reaction mixtures at a rate of 30–45 mL/min. The air and white phosphorus solutions 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 came from a compressed air cylinder and was regulated by a needle valve and a flow meter. The water bath temperature and constant flow of air into the mixture were maintained for at least an hour after all the white phosphorus solution was added, to ensure that all remaining white phosphorus was consumed.

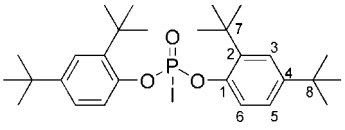
The composition of the dark mixtures after the reaction was analyzed by ^{31}P NMR spectroscopy. The samples were typically prepared by transferring an aliquot (typically 1 mL) of the mixture after reaction to another flask, shaking it with solid sodium sulfite (0.2 g) and filtering the mixture through a sinter. A small amount of $CDCl_3$ was added (for locking purposes), and ^{31}P spectra were measured at 109.4 MHz. Analysis of the mixtures after the reaction by HPLC-MS and GC–MS techniques did not result in a better understanding of the composition of the mixtures.

Separation of phosphorus-containing products was attempted in several cases by using short-path vacuum distillation as well as extraction techniques. Details of the other separating procedures are given in the Results section.

General Procedure for Reactions of Phenol with PI_3: The results are shown in Table 4). The reactions of phenol with PI_3 were performed in a 250 mL three-necked, round-bottomed flask. PI_3 solution was formed in situ by the addition of a solution of P_4 in toluene (typically 20 mL of ca. 2% solution, ca. 0.4 g, 3 mmol P_4) to a solution of iodine in toluene (typically 20 mL of ca. 15% solution, ca. 3.5 g, 18 mmol I_2). The addition was performed at room temperature under nitrogen over the course of two hours. Three equivalents of phenol were added to the resulting PI_3 solution, where appropriate $Fe(acac)_3$ catalyst was also added at this stage (0.25 molar equivalents). A condenser and oil bubbler outlet were added to the flask. The solution was heated to 80 °C and stirred intensely for a period of 3–5 h. Dry air was bubbled through the reaction mixture where appropriate, at the rate of 30–45 mL/min. The composition of the resulting reaction mixture was analyzed by ^{31}P NMR spectroscopy.

$O=PI(O\text{-}2,4\text{-}t\text{Bu}_2C_6H_3)_2$: Phosphorus triiodide (2.30 g, 5.6 mmol), 2,4-di-*tert*-butylphenol (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 mixture at a rate of 40 mL/min. After 24 h the air flow was stopped, and the reaction mixture was allowed to cool to room temperature. The solvent was removed in vacuo to leave crude $O=PI(O\text{-}2,4\text{-}t\text{Bu}_2C_6H_3)_2$ as a dark oil. This was purified by column chromatography on silica gel (eluent hexane/ether 3:1) to yield $O=PI(O\text{-}2,4\text{-}t\text{BuC}_6H_3)_2$ (0.36 g, 13%) as a white powder. Partial hydrolysis on the column during purification accounts for the low yield of the product, swift elution is required. For the NMR

spectroscopic numbering scheme, see Scheme 6. $^{31}P\{^{1}H\}$ NMR (109.4 MHz, $CDCl_3$): δ = –60.0 (s) ppm. ^{1}H NMR (270.2 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, *8*-*t*Bu), 1.44 (s, 9 H, *7*-*t*Bu), 7.21 (dd, *J* = 8.9 and 2.1 Hz, 1 H, *5*-H), 7.41 (≈t, *J* = 2.4 Hz, 1 H, *3*-H), 7.66 (dd, *J* = 8.9 and 2.1 Hz, 1 H, *6*-H) ppm. $^{13}C\{^{1}H\}$ NMR (67.9 MHz, $CDCl_3$): δ = 30.4 (s, *7*-CH_3), 31.5 (s, *8*-CH_3), 34.7 (s, *7*-C_q), 34.9 (s, *8*-C_q), 119.4 [d, ^{3}J(C,P) = 4.0 Hz, *6*-CH], 124.3 (s, *5*-CH), 125.0 (s, *3*-CH), 139.3 [d, ^{2}J(C,P) = 9.4 Hz, *1*-C_q], 147.2 [d, ^{3}J(C,P) = 7.7 Hz, *2*-C_q], 148.1 (s, *4*-C_q) ppm. IR (KBr disc): $\tilde{\nu}$ = 2954 (vs, νCH), 1494 (s), 1273 (m, νP=O), 1182 (s), 1104 (m), 1079 (m), 991 (s), 960 (vs), 552 (vs), 495 (vs) cm^{-1}. MS (ES+, solution in methanol): *m*/*z* = 1488.1 $[(M – I + MeO)_3 + Na]^+$, 999.5 $[(M – I + MeO)_2 + Na]^+$, 977.4 $[(M – I + MeO)_2 + H]^+$, 511.2 $[M – I + MeO + Na]^+$, 489.3 $[M – I + MeO + H]^+$, 433.2 [M – I – *t*Bu + MeO + 2H]$^+$, 377.2 [M – I – 2*t*Bu + MeO + 3H]$^+$, 321.1 [M – I – 3*t*Bu + MeO + 4H]$^+$.



Scheme 6. NMR spectroscopic numbering scheme for O=PI(O-2,4-tBu$_2$C$_6$H$_3$)$_2$.

O=PI(OPh)$_2$: This is a modified version of entry 1 in Table 4. Phosphorus triiodide (5.68 g, 13.9 mmol), phenol (2.60 g, 27.6 mmol) and toluene (20 mL) were heated to 80 °C with vigorous stirring, and dry air was bubbled through the reaction mixture at a rate of 40 mL/min. After 5 h the air flow was stopped, and the reaction mixture was allowed to cool to room temperature. The solvent was removed in vacuo to yield O=PI(OPh)$_2$ (3.8 g, 76%) as a brown oil, which solidified on prolonged standing at 5 °C. Further purification by chromatography was not possible because of rapid hydrolysis on silica. $^{31}P\{^{1}H\}$ NMR (109.4 MHz, $CDCl_3$): δ = –47.0 (s) ppm. ^{1}H NMR (270.2 MHz, $CDCl_3$): δ = 6.80–7.51 (complex multiplet) ppm. $^{13}C\{^{1}H\}$ NMR (67.9 MHz, $CDCl_3$): δ = 122.7 (*p*-C), 127.1 (*m*-C), 131.8 (*o*-C), 150.3 (*i*-C) ppm. IR (KBr disc): $\tilde{\nu}$ = 3044 (s, νCH), 1593 (s), 1487 (vs), 1365 (m), 1263 (s, νP=O), 1226 (s), 1179 (s), 1158 (vs), 1071 (m), 1024 (s), 1011 (s), 960 (vs), 782 (s), 510 (s) cm^{-1}. MS (EI+): *m*/*z* = 359.9 $[M]^+$, 233.0 $[M – I]^+$, 126.9 $[I]^+$. HRMS (EI+): calcd. for $C_{12}H_{10}O_3PI$ 359.9412; found 359.9421; error 2.4 ppm.

(PhO)$_2$(O)P–O–P(O)(OPh)$_2$: Diphenyl phosphoroiodidate O=PI(OPh)$_2$ (0.5 g, 0.0014 mol) and diphenyl phosphate O=POH(OPh)$_2$ (0.35 g, 0.0014 mol) were heated at reflux in toluene (10 mL) for 2 h. By ^{31}P NMR spectroscopy, the resulting solution was shown to contain 86% of (PhO)$_2$(O)P–O–P(O)(OPh)$_2$, along with some unreacted starting materials. The identity of the compound was confirmed by comparing its ^{31}P NMR shift with the literature value[39] and by mass spectrometry. MS (ES+): *m*/*z* = 504.6 $[M + Na]^+$.

General Procedure for Reactions of O=PI(OPh)$_2$ with Phenol: The results are shown in Table 5. The reactions were performed in a 100 mL round-bottomed Schlenk flask under nitrogen. PhOH (typically ca. 1.2 g, 13 mmol), O=PI(OPh)$_2$ (typically ca. 4.7 g, 13 mmol) and toluene (typically 10 mL) were added into the flask, iron acetylacetonate (0.25 molar equivalents) was also added to the flask where appropriate. The reaction mixtures were heated to 80 °C with vigorous stirring. The progress of the reactions was monitored by ^{31}P NMR spectroscopy, and the reactions were continued until all the starting material was consumed.

Independent Synthesis of 2,4-Di-*tert*-butylphenyl Phosphate: 2,4-di-*tert*-butylphenyl phosphite (5.00 g, 0.0078 mol, synthesized according to the method of Akbarali.[25]), 30% hydrogen peroxide solution (5.8 mL, 0.051 mol) and water (20 mL) were added to a round-bottomed flask and stirred for 48 h at room temperature. The resulting mixture after evaporation of volatiles was found to contain 2,4-di-*tert*-butylphenyl phosphate by $^{31}P\{^{1}H\}$ NMR spectroscopy (109.4 MHz, $CDCl_3$): δ = –19.9 (s) ppm.

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 a 50:50 ethanol/water mixture (50 mL). The solution was heated to 60 °C for 1 h with stirring. An orange precipitate formed on cooling with an ice bath. The solid was collected by filtration and washed with water (25 mL). Drying the solid in vacuo yielded **1** (10.34 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 those in the literature.[40,21]

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 a 50:50 ethanol/water mixture (50 mL). The solution was heated to 60 °C for 1 h with stirring. A red precipitate formed on cooling with an ice bath. The solid was collected by filtration and washed with water (25 mL). Drying the solid in vacuo yielded **2** (10.90 g, 43.9%) as a red powder. The IR spectrum was found to be in excellent agreement with that in the literature.[41] M.p. 110–114 °C.

Acknowledgments

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