Direct catalytic transformation of white phosphorus into arylphosphines and phosphonium salts

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Abstract

Phosphorus compounds are ubiquitous in the chemical sciences, finding applications throughout industry and academia. Of particular interest to synthetic chemists are organophosphorus compounds, which contain P—C bonds. However, state-of-the-art processes for the synthesis of these important materials rely on an inefficient, stepwise methodology involving initial oxidation of white phosphorus (P_4) with hazardous chlorine gas and the subsequent displacement of chloride ions. Catalytic P_4 organofunctionalisation reactions have remained elusive, as they require multiple P—P bond breaking and P—C bond formation events to break down the P_4 core, all of which must occur in a controlled manner. Herein, we describe an efficient transition metal-catalyzed process capable of forming P—C bonds from P_4. Using blue light photocatalysis, this method directly affords valuable triarylphosphines and tetraarylphosphonium salts in a single reaction step.

The academic, industrial and societal importance of phosphorus chemistry is difficult to overstate. Phosphorus is one of the six essential 'biogenic elements' required in large quantities by every living organism, and synthetic phosphorus compounds find myriad industrial and commercial applications due to their diverse array of useful chemical, physical and biological properties.[1] This importance is reflected in the fact that white phosphorus (P_4) is currently produced on an estimated scale of >1 Mt / year.[2] P_4 is by far the most reactive and industrially-relevant form of elemental phosphorus, and acts as the common precursor from which effectively all synthetic phosphorus-containing species are ultimately

prepared.[3] Notable families of industrially-relevant organophosphorus species prepared from P_4 include triarylphosphines (Ar_3P) and salts of the related quaternary phosphonium cations (Ar_4P^+). The former are widely used both in organic chemistry (notably in the classic Wittig reaction)[4,5] and as ligands for metal complexes,[6–11] including the homogeneous catalysts for numerous landmark chemical reactions (e.g. industrial-scale hydroformylation).[12] The latter meanwhile find uses as ion-pair extractants,[13] phase-transfer catalysts,[14–16] aryl-transfer reagents,[17,18] and additives in Heck reactions.[19] Like most organophosphorus species, these compounds are currently prepared using hazardous and wasteful multi-step procedures involving initial oxidation of P_4 to give phosphorus chlorides (PCl_3, PCl_5), followed by displacement of chloride with suitable organometallic nucleophiles (Fig. 1a).[1] Far superior would be efficient catalytic methods to form the desired P–C bonds directly from P_4; however such reactions are all but unknown.[20] Notably, P_4 activation through binding to reactive low-valent transition metal complexes[21] or unsaturated main group species[22] such as carbenes[3,23] has become well established in recent years (albeit with results that are often challenging to predict). However, selective subsequent functionalisation and, in particular, release of the resulting organophosphorus compounds remains highly problematic (the new P_n moieties typically act as strong many-electron donors, with correspondingly low lability). [21,22] Similarly, while direct reactions of P_4 with organic or organometallic nucleophiles are known, these typically proceed with poor yields and selectivities, or only lead to partial breakup of the P_4 tetrahedron.[3]

As a result, even stoichiometric functionalisation reactions that can efficiently convert P_4 into valuable monophosphorus species remain rare. In this context, Barton and coworkers have previously shown that P_4 can act as an excellent trap for carbon centered radicals and have applied this methodology to the synthesis of phosphonic acids;[24,25] however, this method is inefficient with respect to P atom economy. Based on this work, Cossairt and Cummins were also able to develop a direct, stoichiometric method for P_4 activation: in the presence of equimolar amounts of a titanium(III) complex (or, in more recent work, samarium(II) halides)[26,27] halogenated organic compounds undergo halide atom abstraction to yield reactive organoradicals, and subsequent addition to P_4 yielded the corresponding tertiary monophosphines.

Herein, we describe a catalytic method for the preparation of valuable triarylphosphines and tetraarylphosphonium salts directly from P_4 using visible light. These useful organophosphorus compounds are obtained from P_4 and aryl iodides using an iridium photocatalyst and blue light irradiation in the presence of triethylamine. We present the scope of this catalytic system and we propose an outline mechanism based on NMR monitoring and other spectroscopic observations.

Results

Reaction development

We reasoned that an efficient method for the catalytic transformation of P_4 directly into useful organophosphorus compounds could be developed if carboradicals were catalytically generated from a suitable precursor in the presence of P_4; fortunately, recent years have seen dramatic progress in this area through the use of photoredox methods driven by visible or

UV light for the addition of carboradicals to unsaturated organic substrates,[28–31] and we anticipated that photocatalytic functionalisation of white phosphorus could plausibly proceed *via* similar mechanisms. Notably, these methods do not require the use of powerful stoichiometric reagents that might be vulnerable to unproductive, direct reactions with P_4. Thus, as a model system the reduction of halobenzenes was chosen for initial investigation. After screening several established visible-light-driven photoredox catalysts (see Supplementary Table 1 for further details), we were delighted to observe that the catalytic conversion of P_4 into tetraphenylphosphonium iodide is viable using the known photocatalyst $[Ir(dtbbpy)(ppy)_2]PF_6$ ([**1**]PF$_6$; dtbbpy = 4,4′-bis-tertbutyl-2,2′-bipyridine, ppy = 2-(2-pyridyl)phenyl; structure shown in Fig. 1b). Employing [**1**]PF$_6$, blue light irradiation (455 nm) of a solution of P_4, PhI (as a simple model substrate) and Et_3N (as a reductive quencher of the excited state photocatalyst; *vide infra*) in a 3:1 MeCN/PhH (v/v) mixture (chosen to ensure solubility of all components) for 18 h yielded with excellent selectivity the phosphonium salt [Ph$_4$P]I: 76 % conversion to [Ph$_4$P]I was observed by quantitative ^{31}P NMR spectroscopy (Table 1, entry 1). Following oxidation the Et_3N reductant is presumed to undergo formal H atom loss to give the iminium salt $[Et_2NC(H)Me]I$, whose formation also accounts for the fate of the PhI-derived iodide, but this has not been confirmed experimentally. On a preparative scale, the clean salt could be isolated from the reaction mixture by simple crystallisation from H_2O on the open bench, followed by recrystallisation from EtOH (Table 2, entry 1 and Supplementary Method 2).

This represents an effective example both of catalytic P_4 transformation directly into an organophosphorus species, and of successful catalytic functionalisation of P_4 using a transition metal complex.[20] Switching from PhI to less reactive PhBr or PhCl was found to be severely detrimental (Table 1, entries 2 and 3); further variations in solvent, oxidant, catalyst loading, and reaction time (Supplementary Tables 2 and 3) indicate that the reaction parameters given in Table 1 are optimal. Meanwhile, control experiments confirmed that all reaction components (PhI, Et_3N, [**1**]PF$_6$ and blue light) are necessary in order to observe formation of the product (Table 1, entries 4-7). Interestingly, full consumption of white phosphorus was still observed in the absence of PhI (Table 1, entry 4), which suggests the possibility that it can be directly reduced under these reaction conditions (in this case, formation of small amounts of PH_3 was observed by ^{31}P NMR spectroscopy, suggesting possible H atom transfer to P_4 from the oxidised sacrificial donor, $[Et_3N]^{+\cdot}$).

Reaction scope

Having established an optimum procedure for the model substrate PhI, attention was shifted to investigating the scope of this new reaction. Gratifyingly, under identical conditions, a variety of substituted iodobenzene coupling partners could successfully be employed (Tables 2 and 3), including substrates bearing both electron-donating (Me, OMe) and electron withdrawing (COOMe, CF_3) groups. Interestingly – and in contrast to the model substrate PhI – in many cases the expected [PAr$_4$]I salt was accompanied by significant quantities of the tertiary phosphine PAr$_3$ in the product mixture, often with high selectivity for the latter. In particular, the reaction of (*o*-tol)I (*o*-tol = 2-methylphenyl) was found to give exclusively the tertiary phosphine (*o*-tol)3P (Table 2, entry 4), which has found extensive use as a bulky ligand in transition metal coordination chemistry and related catalysis,[6–11] and could be

cleanly isolated from a scaled up reaction mixture by simple sublimation (71% isolated yield, 216 mg; Supplementary Method 5). Other substituted derivatives of [Ph$_4$P]I and (*o*-tol)$_3$P could also be isolated using similar procedures (Table 2, entries 2, 3, 5, 6, Supplementary Methods 3, 4, 6, 7), although in practice this was limited to examples that proceeded with good conversion and high selectivity. The difference in reaction outcome between PhI and (*o*-tol)I is most likely steric in nature, with the additional bulk of the *o*-Me groups limiting the maximum coordination number at P. Indeed, when even bulkier substrates were employed the reaction was observed to stall earlier still: at the secondary (MesI; Mes = mesityl, 2,4,6-trimethylphenyl; Table 3, entry 9) or even primary phosphines (DmpI; Dmp = 2,6-dimesitylphenyl; Table 3, entry 10). In addition, electron-withdrawing groups also seemingly disfavour the quaternary phosphonium salt (for example, compare entry 4 to entries 5 and 6 in Table 3), plausibly due to destabilisation of the requisite positive charge. Finally, a pair of heteroatomic substrates were investigated (Table 3, entries 11 and 12). While the silicon-centered substrate Me3SiI yielded no P—Si bonded products, reaction with PH$_3$SnCl was found to selectively yield the potentially useful "P^{3-}" synthon (PH$_3$Sn)$_3$P with excellent conversion. The observed reactivity is qualitatively consistent with the known ready accessibility of Sn-based radicals, and the much lower stability of Si-centered analogues.[32]

Mechanistic studies

Mechanistic investigations strongly suggest that the functionalisation of P$_4$ proceeds *via* the mechanism summarised in Fig. 2. Radical generation proceeds through a reductive quenching cycle in which the catalyst first oxidises Et$_3$N in its excited state (steps i and ii), before then (as the reduced complex [**1**]) reducing PhI to Ph· (step iii). The aryl radicals thus generated then sequentially functionalise P$_4$ (step iv), producing in sequence PhPH$_2$, Ph$_2$PH, PH$_3$P and finally Ph$_4$P$^+$ (steps v-viii). Other Ph$_x$H$_y$P$_z$ species must presumably be formed *en route* to PhPH$_2$; however, attempts to observe these early intermediates have thus far been unsuccessful and we are therefore unable to propose a specific mechanism for initial break-up of the tetrahedral P$_4$ core. Nevertheless, we note that previous reports (for example, see ref. 26) have demonstrated the formation of stable Ar$_2$P$_4$, Ar$_3$P$_3$, and Ar$_4$P$_4$ compounds through direct reaction of P$_4$ with C-centred radicals. At this point the complexity of this reaction must be acknowledged, however. For each P$_4$ molecule functionalised six P—P and at least 16 C—I bonds are broken; 16 C—P bonds are formed; and least 16 Et$_3$N are oxidized. As such the possibility that other elementary reaction steps may be mechanistically significant cannot be excluded. For example, UV/VIS observations (*vide supra*) and additional *in situ* NMR experiments (see Supplementary Discussions) both suggest that direct activation of P$_4$ by the reduced photocatalyst [**1**] is a plausible side-reaction (either productive or unproductive).

The proposed mechanism is nevertheless in line with both spectroscopic and electrochemical investigations. Measured redox potentials (Supplementary Figs. 42–44) support the plausibility a reductive quenching mechanism, in which the photocatalyst excited state is reduced by Et$_3$N to produce the neutral complex [**1**] (Fig. 2, steps i and ii). Further, conclusive evidence for this proposal was provided by emission quenching experiments, which showed that out of all the reaction components (including intermediate phosphines

PhPH$_2$, Ph$_2$PH, Ph$_3$P), only Et$_3$N effectively quenches the excited state of the [**1**]$^+$catalyst in MeCN/PhH (Supplementary Figs. 45–52). Furthermore, photo-CIDNP effects were detected during *in situ* NMR experiments (*vide infra*), indicative of direct reaction of Et$_3$N with the [**1**]$^+$photoexcited state (Supplementary Fig. 62). An alternative oxidative quenching mechanism, in which the photoexcited state reacts directly with the aryl iodide, is thus highly improbable (Supplementary Fig. 53).

Following reduction by Et$_3$N, complex [**1**] can in turn effect reduction of the PhI substrate (Fig. 2, step iii), thereby forming phenyl radicals Ph•. This was corroborated by UV/VIS spectroscopy (Supplementary Fig. 54). While a solution containing Et$_3$N and [**1**]PF$_6$ in MeCN/PhH showed only a broad absorption band up to 500 nm, two new bands (λ_{max} = 501 nm, 537 nm) were formed after irradiation with 455 nm blue light (a new orange/red coloration was also noticeable by eye), which was taken to indicate the formation of the reduced neutral catalyst [**1**] as discussed above (despite its significance to many reported photocatalytic cycles, to our knowledge neutral [**1**] has not previously been characterised in detail; as such, chemical and electrochemical reduction experiments have been performed to support this assignment, as described in detail in the Supplementary Information (see Supplementary Figs. 55 and 56)). The initial spectrum was quickly regenerated upon addition of excess PhI (within seconds), confirming the ability of the substrate to effect oxidation of [**1**] back to the catalyst resting state [**1**]$^+$ (similar recovery was also observed upon addition of P$_4$ as a solution in PhH). In the absence of PhI and P$_4$ the [**1**]PF$_6$ signal recovered far more slowly (over the course of *ca.* 20 minutes in the absence of blue light irradiation, presumably due to re-oxidation by the previously-generated [Et$_3$N]$^{+•}$ cation or decomposition products thereof).

Having established a feasible mechanism for aryl radical generation, *in situ* NMR monitoring was used to investigate subsequent P$_4$ functionalisation. A slightly altered 1:1 MeCN:PhH solvent mixture was used to ensure homogeneity throughout. This change was not found to significantly alter the final reaction outcome. (see Supplementary Method 9). Time-resolved ^{31}P{^{1}H} NMR spectra showed rapid consumption of the P$_4$ starting material (completely consumed within five hours under *in situ* NMR conditions) with the primary, secondary and tertiary monophosphines (PhPH$_2$, Ph$_2$PH, PH$_3$P) all visible as sequential reaction intermediates (Fig. 3). While practical limitations preclude a quantitative analysis, it is qualitatively clear that the concentrations of these species in the initial stages of the reaction are too low to fully account for the consumption of P$_4$. This suggests the presence of other as-yet-unidentified P-containing intermediates. Traces of the diphosphine Ph$_4$P$_2$ were observed by ^{31}P NMR. The H atoms in the primary and secondary products most likely derive from the Et$_3$N reductant (experiments using deuterated solvents showed no deuterium incorporation), either by deprotonation or H atom abstraction from its oxidation products. The subsequent loss of these hydrogen atoms (as required for conversion to Ph$_4$P$^+$) presumably involves similar steps; for example, ^{1}H NMR shows formation of PhH during the course of the reaction, plausibly through H atom abstraction by a phenyl radical. ^{1}H NMR spectroscopy also suggests formation of Et$_2$NH as a minor side-product, which is also observed in many other photochemical reactions that use Et$_3$N as a reductant.[33]

Given the observation of $PhPH_2$, Ph_2PH and PH_3P as successive reaction intermediates, control experiments were performed using these phosphines as individual starting materials in place of P_4. In all cases conversion to Ph_4P^+ was observed *via* the respective downstream intermediates, with similar or superior conversion to the analogous reaction using P_4, consistent with the above *in situ* observations. Notably, each individual arylation step appears to be photochemically-mediated, with comparable conversions never observed in the absence of light, [**1**]PF_6 or Et_3N. Low, but non-zero conversions were observed for these substrates in the absence of [**1**]PF_6 or Et_3N, suggesting some, much slower background photochemical reaction (see Supplementary Tables 4-6 and Supplementary Figs. 58, 59).

Conclusions

In summary, we have described a direct catalytic formation of P–C bonds from P_4. Synthetically useful triarylphosphines and tetraarylphosphonium salts were formed in up to *ca.* 80% yield. This Cl_2-free process represents an important step towards direct and catalytic approaches for the production of organophosphorus compounds and highlights the ability of modern photoredox techniques to solve pressing challenges in inorganic as well as organic chemistry. Furthermore, the successful catalytic functionalization of P_4 illustrates the promising potential of radical methods for the activation and functionalisation of white phosphorus, and their increasing significance in organosphosphorus chemistry. Ongoing research efforts in our groups are focused on further clarifying the mechanism of this highly elaborate transformation, as well as expanding the range of viable organic radical precursors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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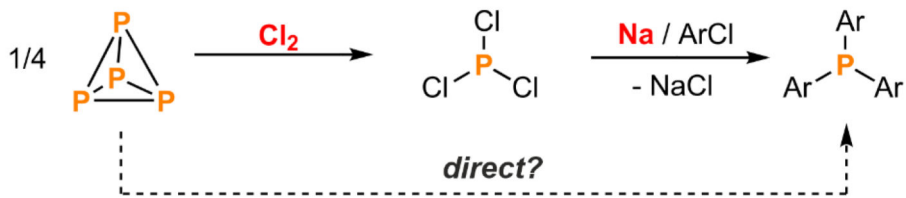
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a) *state-of-the-art: industrial synthesis of triarylphosphines*

■ **indirect**
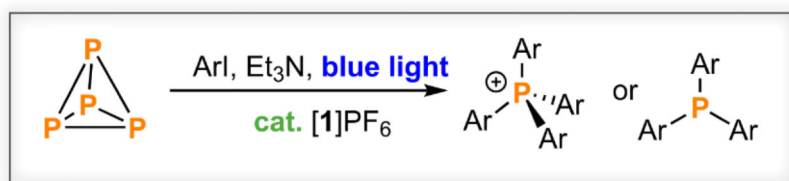■ **hazardous reagents**

white phosphorus:
■ reactive
■ produced on >1 Mt scale
■ direct functionalisation challenging

direct?

■ *Cossairt and Cummins (ref. 26),* **stoichiometric** *in TM*

b) <u>*this work:*</u> *single-step synthesis of tetraarylphosphonium salts and triarylphosphines*

■ **catalytic in TM**   ■ **mild reagents and conditions**
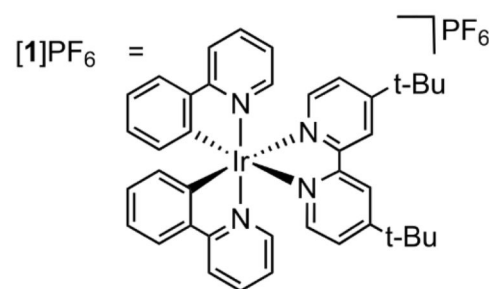
Fig. 1. White phosphorus functionalisation
a) State-of-the-art methods for the industrial synthesis of triarylphosphines. **b)** Direct, catalytic functionalisation of P_4 to give triarylphosphines and tetraarylphosphonium salts, as described in this work. TM = transition metal complex
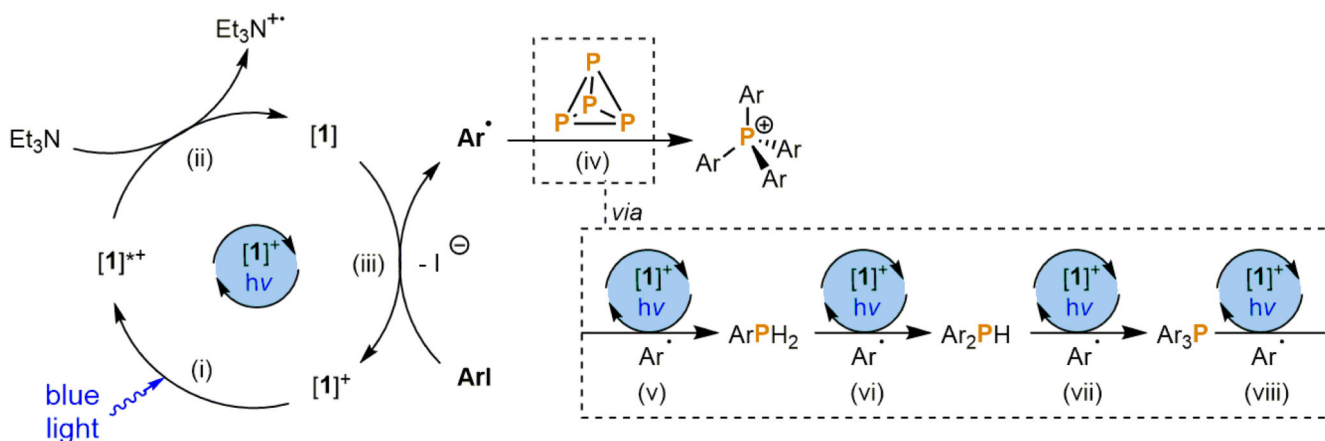
Fig. 2. Catalytic cycle.

Proposed mechanism for the photocatalytic functionalisation of white phosphorus to triarylphosphines and tetraarylphosphonium salts with [1]+ in the presence of aryl halides.
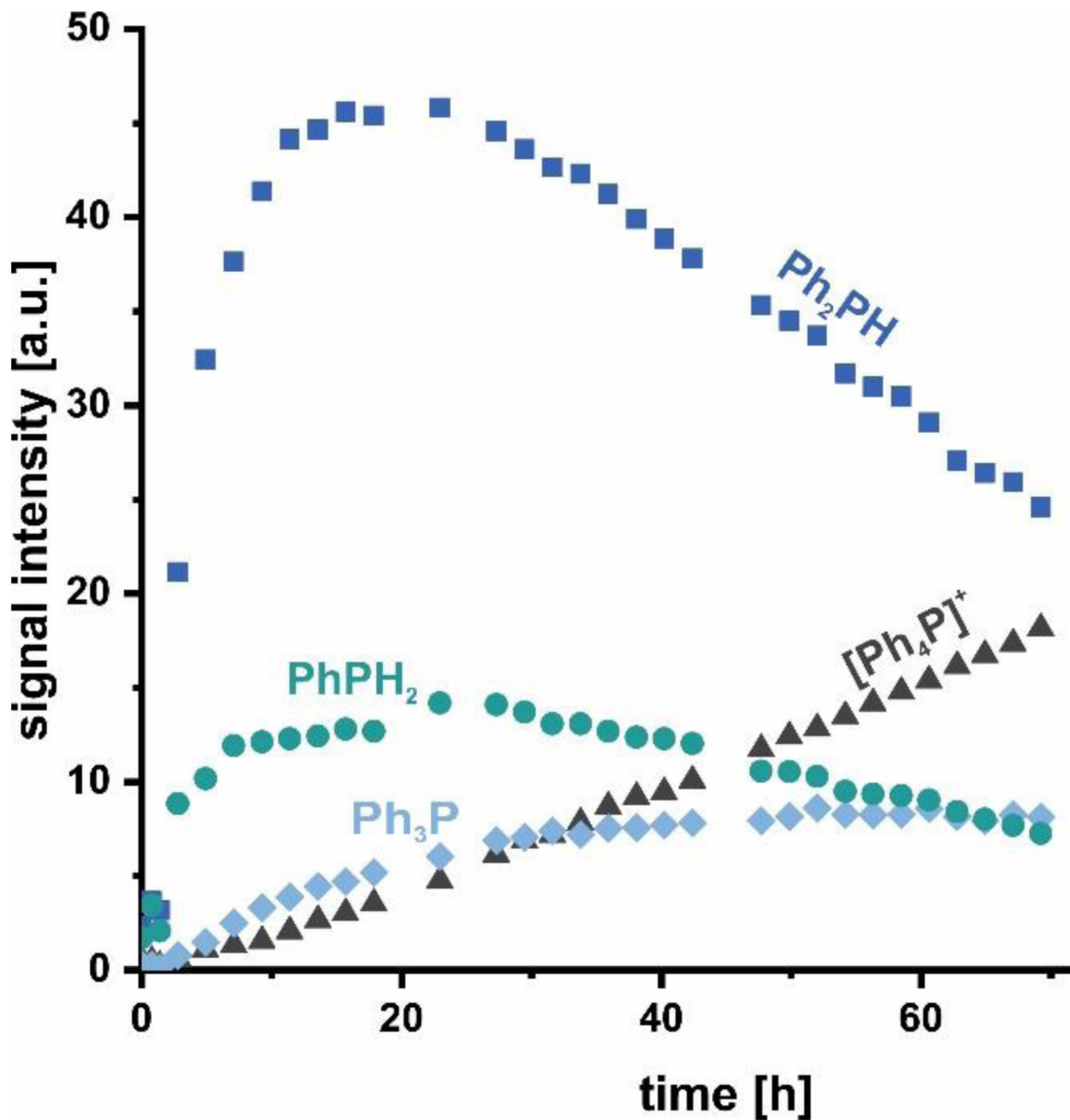
Fig 3. Time-resolved ^{31}P{^{1}H} NMR study.
In situ ^{31}P NMR monitoring of the formation of primary, secondary, and tertiary phosphines and quaternary phosphonium salt during photocatalytic P_4 functionalisation using PhI as substrate (see Supplementary Method 9 for full reaction details). The relatively long reaction time is probably attributed to the reduced irradiation power of the *in situ* light source and non-stirring conditions in the NMR tube.

Table 1

Photocatalytic functionalisation of P_4 to [Ph_4P]I: screening of radical sources and control experiments.

Entry	Conditions	Conv. to [Ph4P]I / %[b]	Full conv. of P_4
1	standard[a]	76	✓
2	PhBr instead of PhI	<1[c]	✓
3	PhCl instead of PhI	0[c]	✓
4	no PhI	0	✓
5	no [1]PF_6	0	X
6	no light	0	X
7	no Et_3N	0	X

[a] All reactions were performed with 123 µL iodobenzene (11 equiv. based on phosphorus atoms, 44 equiv. based on P4), 200 µL Et_3N (14.4 equiv. based on phosphorus atom), 3.1 mg P_4 (0.025 mmol, 1 equiv.), and 2.0 mg [1]PF_6 (2.2 mol% based on phosphorus atom) in 2 mL MeCN/PhH (3:1, v/v) as solvent. The samples were prepared under N_2-atmosphere in a sealed tube and placed in a water-cooled block during irradiation (18 h) with blue LED light (455 nm).

[b] Conversions determined by quantitative ^{31}P NMR experiments with Ph_3PO as internal standard.

[c] A complex mixture of P-containing species was observed by ^{31}P NMR spectroscopy.

Table 2

Substrate scope for photocatalytic P4 functionalisation.

Entry	R	Time / h	Product	Yield / %[a,b]
1	H	18		**34** (76)
2	*p*-Me	30		**41** (54)
3	*m*-OMe	24		**60** (63, 3[c])
4	*o*-Me	18		**71** (79)
5	*o*-OMe	30		**37** (54)
6	*o*-SMe	18		**19** (21)

[a] Isolated yields. Reactions were performed with substrate (11.0 equiv. based on phosphorus atom), 2.0 mL Et$_3$N (14.4 equiv. based on phosphorus atom), 31 mg P$_4$ (0.25 mmol, 1 equiv.), and 20 mg [**1**]PF$_6$ (2.2 mol% based on phosphorus atom) in 20 mL MeCN/PhH (3:1, v/v) as solvent. (Supplementary Methods 2–7). The samples were prepared under N$_2$-atmosphere in a sealed tube and placed in a water-cooled block during irradiation with blue light (455 nm).

[b] Values in parentheses are conversions determined by quantitative ^{31}P NMR experiments with subsequently-added Ph$_3$PO as internal standard, for equivalent reactions on 0.1 mmol scale (Supplementary Method 1).

[c] Conversion to corresponding triarylphosphine.

Table 3

Further substrate scope for photocatalytic P$_4$ functionalisation.[a]

cat. [**1**]PF$_6$, blue LEDs

MeCN/PhH, N$_2$ atmosphere
xs. Et$_3$N, xs. substrate

Product

substrates:

Entry	Time / h	Substrate	Product	Conv. / % [b]
1	18	**2**		63 (5[c])
2	24	**3**		48 (8[c])
3	24	**4**		25 (20[c])
4	18	**5**		37 (5[c])
5	18	**6**		39
6	24	**7**		30
7	24	**8**		11
8	24	**9**		-
9	18	**10**		24 (3[d])

cat. [1]PF$_6$, blue LEDs

$\frac{1}{4}$ P$_4$ ⟶ Product

MeCN/PhH, N$_2$ atmosphere
xs. Et$_3$N, xs. substrate

substrates:

2 (3-iodotoluene)	**3** (methyl 3-iodobenzoate, CO_2Me)	**4** (3-iodo-CF_3)	**5** (4-iodoanisole, OMe)
6 (methyl 4-iodobenzoate, CO_2Me)	**7** (4-iodo-CF_3)	**8** (methyl 2-iodobenzoate, CO_2Me)	**9** (2-iodo-CF_3)
10 = MesI	**11** = DmpI	**12** Me–Si–I (Me$_3$SiI)	**13** Ph–Sn–Cl (Ph$_3$SnCl)
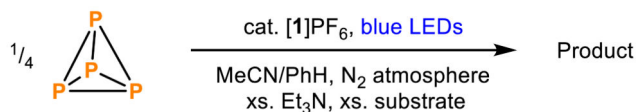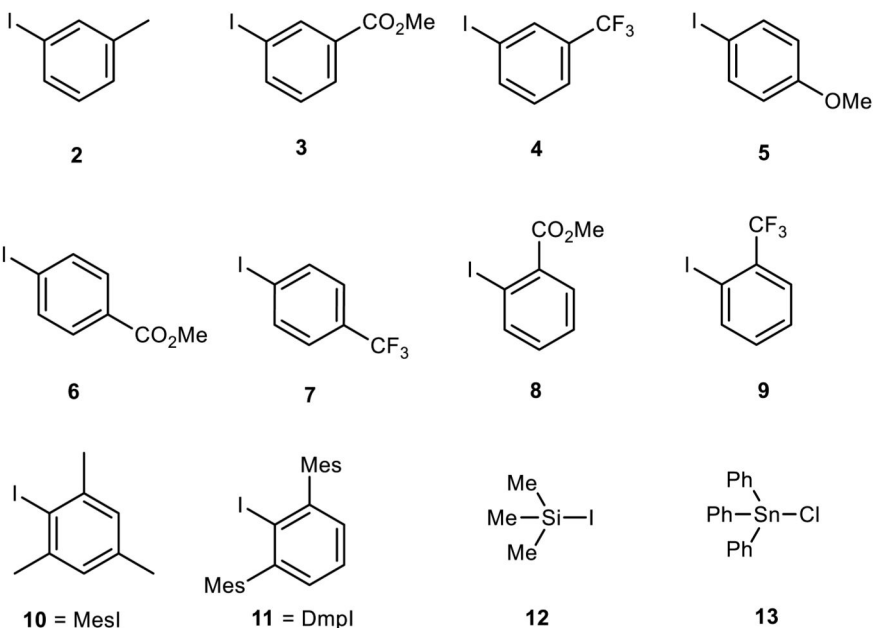
			Product	
10[e]	18	**11**	Dmp–PH$_2$ (Mes, Mes)	12
11	18	**12**	No P—Si bond formation	-
12	18	**13**	Ph$_3$Sn–P(SnPh$_3$)(SnPh$_3$)	77, 14[f]

[a] Refer to Table 1 and Supplementary Method 1 for standard conditions

[b] Conversions determined by quantitative ^{31}P NMR experiments with subsequently-added Ph$_3$PO as internal standard.

[c] Conversion to corresponding triarylphosphine.

[d] Conversion to corresponding monoarylphosphine.

[e] The reaction was performed with 88.1 mg **11** (2.0 equiv. based on phosphorus atom, 8.0 equiv. based on P$_4$), 200 μL Et$_3$N (14.4 equiv. based on phosphorus atom), 3.1 mg P$_4$ (0.025 mmol, 1 equiv.), and 2.0 mg [1]PF$_6$ (2.2 mol%) in 2 mL MeCN/PhH (1:3, v/v) as solvent. The sample was prepared under N$_2$-atmosphere in a sealed tube and placed in a water-cooled block during irradiation with blue light (455 nm).

[f] Second value is isolated yield for equivalent reaction on 1 mmol scale (see Supplementary Method 8).