Synthesis of Monophosphines Directly from White Phosphorus

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Abstract

Monophosphorus compounds are of enormous industrial importance due to the crucial roles they play in applications including pharmaceuticals, photoinitiators, and ligands for catalysis, among many others. White phosphorus (P_4) is the key starting material for the preparation of all such chemicals. However, current production depends upon indirect and inefficient, multi-step procedures. Here, we report a simple, effective 'one pot' synthesis of a wide range of organic and inorganic monophosphorus species directly from P_4. Reduction of P_4 using tri-*n*-butyltin hydride and subsequent treatment with various electrophiles affords compounds that are of key importance for the chemical industry, and requires only mild conditions and inexpensive, easily handled reagents. Crucially, we also demonstrate facile and efficient recycling and ultimately even catalytic use of the tributyltin reagent, thereby avoiding the formation of significant Sn-containing waste. Accessible, industrially relevant products include the fumigant PH_3, the reducing agent hypophosphorous acid, and the flame-retardant precursor tetrakis(hydroxymethyl)phosphonium chloride.

Main Text

White phosphorus (P_4) is one of the most important synthetic feedstocks for the modern chemical industry,[1] and is produced on a scale of > 1 Mt per year. The pyrophoric nature of P_4 and its hazardous and energy-intensive synthesis from phosphate ores have prompted recent academic efforts to bypass this compound and instead use phosphate materials directly as synthetic precursors.[2-4] Other researchers have emphasized the need to develop more sustainable routes for the recycling and reuse of P-containing materials, which are otherwise

lost as environmentally-hazardous wastes.[2,5,6] However, despite these efforts, P_4 remains the only industrially-viable precursor from which to prepare the vast majority of monophosphorus compounds, which find applications ranging from pharmaceuticals to chemical catalysts.[7-9] Unfortunately, state-of-the-art industrial methods for the synthesis of these useful P_1 species rely on indirect and correspondingly inefficient multi-step processes. The most common route (Fig. 1a) involves oxidation of P_4 by toxic Cl_2 gas to generate extremely corrosive PCl_3.[10] Treatment with suitable nucleophiles then provides the desired products *via* substitution of chloride, with concomitant generation of chloride-containing waste. Alternatively, some P_1 products can be generated by hydrophosphination of unsaturated organic compounds using PH_3 gas. However, industrial-scale preparation of PH_3 involves acid-catalysed or alkali-mediated disproportionation of P_4, which demands harsh reactions conditions and produces phosphorus oxyacid derivatives as stoichiometric byproducts (Figure 1).[10]

Recognition of the deficiencies of current routes for generating P_1 products has prompted a strong desire to discover reactions that are capable of transforming P_4 into these useful compounds directly, bypassing the need for isolation and manipulation of potentially hazardous intermediates.[11-13] Unfortunately, such reactions are highly challenging, as they demand the complete and controlled cleavage of all six P–P bonds of the P_4 tetrahedron, alongside similarly orderly formation of up to 16 new P–E bonds. As a result, methods for the direct functionalisation of P_4 remain exceedingly rare.[14-24] The few known examples typically require highly forcing conditions and/or undesirable reagents (such as alkali metal reductants or elaborate transition metal – even precious metal – complexes) to ensure that the reactions are driven to completion, severely limiting their scope and practicality.

We describe herein a simple, efficient, 'one-pot' synthesis of various valuable and industrially relevant monophosphorus species from P_4 using only commonly available reagents (Fig. 1b). The ubiquitous reducing agent tri-*n*-butyltin hydride (Bu_3SnH) provides clean access to stannyl-substituted monophosphines in a process that is both very mild and highly versatile, being compatible with either photoinitiation or common chemical radical initiators.[25-27] The product

phosphines can be treated with organic and inorganic electrophiles to directly furnish commercially relevant P_1 products. Furthermore, we show that the key Bu_3Sn moiety can be readily recycled, and even employed catalytically, thereby mitigating any problems that might arise from formation of stoichiometric Sn-containing waste. Accessible products include PH_3 (used as a fumigant, a reagent in the microelectronics industry, and a precursor to other organophosphorus compounds),[10] hypophosphorous acid (used industrially as a reducing agent and synthetic intermediate),[9,10,28] the tetrabenzylphosphonium salt $[Bn_4P]Br$ (a Wittig chemistry precursor),[29] and the phosphonium salt tetrakis(hydroxymethyl)phosphonium chloride (THPC, an important precursor to flame-retardant materials).[9,30]

Results and Discussion

Hydrostannylation of P_4

The reactivity of P_4 towards radical reagents potentially provides a viable route for the preparation of P_1 products. However, in the few examples that have been reported to date, the elaborate strategies required to selectively access the necessary radical intermediates have severely limited their practicality and scope.[17-22] We reasoned that the inexpensive, commercially available radical source Bu_3SnH could serve as a convenient reagent for breaking apart the P_4 molecule, since Bu_3SnH readily generates formal H· and Bu_3Sn· radicals upon photolysis or thermolysis in the presence of a radical initiator.[31-34]

In an initial experiment, Bu_3SnH and P_4 were combined in a 6:1 molar ratio in PhMe at room temperature. Gratifyingly, $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the mixture showed clear consumption of P_4 over the course of several days, with concomitant appearance of new upfield resonances at −288.7 and −324.9 ppm (major), and −242.0 and −346.4 ppm (trace), which collectively correspond to the products $(Bu_3Sn)_nPH_{3-n}$ (n = 0-3, *vide infra*). Control experiments showed negligible reactivity when the reaction was repeated in the dark, suggesting a light-driven reaction. Indeed, when the reaction was performed under blue LED irradiation complete consumption of P_4 was observed within 18 h (Figure 2 and Extended Data Figs. 1-4). Nearly identical product distributions were observed in various other common

organic solvents (*n*-hexane, PhH, Et_2O, THF, DME; Extended Data Fig. 5) and an analogous outcome was also observed for the equivalent reaction of P_4 with Ph_3SnH (see Supplementary Method 2 for full details).[35]

The signal observed at −242.0 ppm is consistent with the formation of minor PH_3 (**1**),[3] while the remaining resonances are assigned to the formation of new products Bu_3SnPH_2 (**2**; −288.7 ppm),[36] $(Bu_3Sn)_2PH$ (**3**; −324.9 ppm) and $(Bu_3Sn)_3P$ (**4**; −346.4 ppm).[19] The observed upfield chemical shifts agree with previously-reported stannyl phosphines,[37] and the presence of P–Sn and P–H bonds is confirmed by observation of $^{117/119}$Sn satellites and of multiplicity in the proton-coupled ^{31}P spectra, respectively (see Methods section and Extended Data Figs. 2 and 3).[16,38,39] The products obtained are consistent with complete, stoichiometric hydrostannylation of all six P–P bonds of P_4, as shown in Fig. 2a. The observed preference for Bu_3SnPH_2 and $(Bu_3Sn)_2PH$ over PH_3 and $(Bu_3Sn)_3P$ is likely kinetic in origin (Supplementary Method 3) and may be attributable to steric factors that would disfavor installation of multiple Bu_3Sn moieties on a single P atom. The major products can be separated by distillation under high vacuum (105 °C, 10^{-2} mbar, see Supplementary Method 3) to give Bu_3SnPH_2 (**2**; 31%) and $(Bu_3Sn)_2PH$ (**3**; 45%, typically containing *ca*. 10% Bu_3SnPH_2/$(Bu_3Sn)_3P$) as colourless oils. Both are indefinitely stable when stored at −35 °C but undergo noticeable scrambling of their H and Bu_3Sn ligands within a few days at room temperature, or more rapidly at elevated temperature (hence the minor impurities observed in samples of $(Bu_3Sn)_2PH$ isolated by distillation). Notably, however, all three of the stannylated phosphines are highly stable in the presence of hydroxylic species such as H_2O or alcohols. They are even moderately stable in the presence of O_2 and can be exposed to air overnight at ambient temperature without significant decomposition (see Supplementary Method 4). This stands in stark contrast to other common "P^{3-}" synthons such as $P(SiMe_3)_3$ and represents a considerable practical advantage.[15]

The precise mechanism of the P_4 hydrostannylation reaction remains under investigation. Nevertheless, the use of light as an initiator clearly suggests a radical process, as radical chain

reactions mediated by Bu_3SnH are well established.[31-34] A plausible mechanism is therefore outlined in Fig. 2b, in which each P–P bond is cleaved through initial attack of a $Bu_3Sn\cdot$ radical (for example, generated by photoelectron catalysis; Supplementary Method 1),[40-42] followed by abstraction of H· by the resulting P-centred radical from another equivalent of Bu_3SnH, to regenerate $Bu_3Sn\cdot$ and continue the radical chain. Based on the proposed mechanism, it should also be possible to initiate hydrostannylation through use of a chemical (rather than photochemical) radical source. And, indeed, addition of 2.5 mol% per P atom of the thermally activated radical initiator azo*bis*(isobutyronitrile) (AIBN) was found to induce similarly efficient $(Bu_3Sn)_xPH_{3-x}$ formation over a comparable timeframe in the dark, upon only very gentle heating (shorter reaction times could be used at higher temperatures; Supplementary Method 5).[43] Comparable results were observed at more elevated temperatures using the related radical initiator 1,1'-azo*bis*(cyclohexanecarbonitrile) (ACN; Supplementary Method 6).[44] Similarly, addition of the stable radical 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) also led to slow hydrostannylation in the dark at room temperature (Supplementary Method 7; see also Supplementary Methods 8-11 for discussion of reactions involving excess TEMPO).[45] $^{31}P\{^1H\}$ NMR spectroscopic analysis of reaction mixtures at partial conversion revealed no resonances attributable to intermediate structures (see Supplementary Method 1, for example). However, we note that other P–P bonded species such as P_2Ph_4 and cyclo-P_5Ph_5 were also efficiently hydrostannylated under identical conditions (Supplementary Methods 12 and 13),[46] suggesting that analogous H/Bu_3Sn-substituted oligophosphorus structures are plausible.

Functionalisation of $(Bu_3Sn)_xPH_{3-x}$

As with other phosphines, the P_4 hydrostannylation products $(Bu_3Sn)_xPH_{3-x}$ (x = 1-3) were expected to display nucleophilic character at P. To confirm this, the reactions of the major isolated products Bu_3SnPH_2 (**2**) and $(Bu_3Sn)_2PH$ (**3**) with pivaloyl chloride (*t*BuC(O)Cl) were investigated. It was anticipated that these could provide access to acyl-phosphorus linkages, which are a key structural motif in many industrially employed photoinitiators.[47] While both the

P–Sn and P–H bonds of the starting phosphines are potentially reactive, in this case the reactions were seen to lead to mild cleavage of the P–Sn bonds only. Thus, the reaction of Bu_3SnPH_2 (**2**) with 1 equiv. *t*BuC(O)Cl was observed by $^{31}P\{^1H\}$ NMR spectroscopy to lead to the formation of a single major species, which was identified as the primary acyl phosphine *t*BuC(O)PH_2 (**5**; Fig. 3(iii) and Supplementary Method 14) and could be isolated as a spectroscopically clean solution by simple trap-to-trap distillation.[48] Similarly, reactions with $(Bu_3Sn)_2PH$ (**3**) sequentially gave the *mono*- and *bis*-acyl phosphines *t*BuC(O)P(H)$SnBu_3$ and [*t*BuC(O)]$_2$PH as the major products (**6** and **7**, respectively; Fig. 3(iv),(v) and Supplementary Method 15).[49]

P–Sn bond cleavage could also be accomplished through addition of a Brønsted acid (Supplementary Method 16), leading to formation of PH_3, which is employed industrially as a fumigant, in the synthesis of semiconductors, and as a precursor to many other P_1 chemicals.[10] Since in this case the same product was produced from both starting materials it was possible to combine P_4 hydrostannylation and subsequent acidification into a simple one pot procedure, producing PH_3 (**1**) directly and with high efficiency (Fig. 3(vi)).

Transformation of only the P–H bonds of the hydrostannylation products could also be achieved. Reacting Bu_3SnPH_2 (**2**) or $(Bu_3Sn)_2PH$ (**3**) with Bu_3SnOMe led to selective formation of the fully stannylated phosphine $(Bu_3Sn)_3P$ (**4**), thereby completing the set of isolable phosphines $(Bu_3Sn)_xPH_{3-x}$ (x = 1-3). The same product is again produced from both starting materials, and it was possible to combine P_4 hydrostannylation and subsequent functionalisation into a simple one pot procedure in which **4** was isolated in excellent yield (85%) without the need for isolation of any intermediates (Fig. 3(vii) and Supplementary Method 17).

In the above reactions Bu_3SnPH_2 and $(Bu_3Sn)_2PH$ behave as formal sources of "$[H_2P]^-$", "$[HP]^{2-}$", "$[Bu_3SnP]^{2-}$" and "$[(Bu_3Sn)_2P]^-$". Also of great interest, however, are reactions in which these phosphines react as simple "P^{3-}" synthons. Thus, repeating their acylation using *t*BuC(O)Cl (*vide supra*) in the presence of a suitable base led to successful cleavage of both

P–Sn and P–H bonds, and clean formation of the tertiary product $P(C(O)tBu)_3$ (**8**).[50] Again, because the same compound is produced regardless of the starting phosphine, it was possible to access this species in an efficient, one pot manner directly from P_4, and this reaction could be easily generalised to a variety of other acid chlorides substrates (RC(O)Cl, R = Ph, *i*Pr, Cy, Bu, Me; **9**-**13**; Fig. 3(viii) and Supplementary Methods 18-23).[51]

Alternatively, *in-situ* treatment of the hydrostannylation products with benzyl bromide (BnBr) under gentle heating led to selective formation of the corresponding fully alkylated phosphonium salt, $[Bn_4P]Br$ (**14**), which is a precursor for useful Wittig chemistry (Fig. 4(ii) and Supplementary Method 24).[29] As for the previous acylation reactions, in the absence of base the formation of **14** is proposed to proceed through functionalisation of P–Sn bonds only,[52] with P–H bonds ultimately sequestered in the form of PH_3 (Extended Data Fig. 6). In the presence of base, productive functionalisation of the P–H bonds could also be achieved, leading to very efficient incorporation of P (Fig. 4(iii)). An analogous reaction using EtBr could also be used to obtain the ethyl-substituted salt $[Et_4P]Br$ (**15**; Fig. 4(iv) and Supplementary Method 25; for further reactions with organic halide substrates see Supplementary Methods 26-28).

Formaldehyde is also a suitable *C*-centred electrophile for reaction with the crude hydrostannylation product mixture.[53] Such reactions result in hydroxymethyl-substituted phosphines which possess specific industrial importance. Most notably, salts of the *tetrakis*(hydroxymethyl)phosphonium cation, $[(HOCH_2)_4P]X$ (THPC, X = Cl; THPS, X = ½SO_4) are used to prepare flame retardant materials through the PROBAN® process (THPC).[9] They are also employed as microbicides for water treatment (THPS), and as precursors to other valuable P_1 chemicals *via* extrusion of CH_2O.[30] Treatment of the *in situ*-generated $(Bu_3Sn)_xPH_{3-x}$ mixture with paraformaldehyde in EtOH provided good conversion to the parent phosphine $(HOCH_2)_3P$ (THP, **16**), which is conventionally produced by dealkylation of THPC,[9] and is also used as a synthetic P_1 precursor, as well as a water-soluble ligand for transition metals.[54] This could be isolated directly (Fig. 4(v) and Supplementary Method 29), or quenched with HCl to furnish THPC (**17**) in one pot and good yield following a simple workup (Fig. 4(vi)

and Supplementary Method 30). Notably, excellent yields of THPC were also obtained when the initial hydrostannylation step was already performed in EtOH in the presence of paraformaldehyde, or when hydrostannylation was achieved using AIBN instead of light (82% and 87% yield, respectively; Supplementary Methods 31 and 32). The latter procedure could conveniently be used to prepare THPC on over gram scale (3.3 g, 87%; Supplementary Method 33). Alternatively, quenching THP through exposure to air provided direct access to the corresponding phosphine oxide $(HOCH_2P)_3PO$ (THPO, **18**), also in good isolated yield (Fig. 4(vii) and Supplementary Method 34). Like THPC, THPO has been used for the preparation of flame-retardant materials.[55]

Oxidation of the $(Bu_3Sn)_xPH_{3-x}$ mixture in the absence of paraformaldehyde was also investigated, and treatment with H_2O_2 was found to selectively furnish partially oxidised hypophosphorous acid ($H_2P(O)OH$, HPA, **19**) after workup (Fig. 4(viii) and Supplementary Method 35), alongside minor amounts (<10 %) of the known HPA oxidation product $HP(O)(OH)_2$. In comparison, direct oxidation of P_4 using peroxide reagents is known to be much less selective.[56] HPA is another important P_1 precursor, used to prepare phosphinic acid derivatives (e.g. Cyanex®, used in metal separation processes),[9] and is also employed industrially as a reductant (e.g. for electroless Nickel plating).[28]

Bu_3Sn regeneration and recycling

Having established the ability of Bu_3SnH to efficiently mediate the direct transformation of P_4 into various useful and industrially relevant monophosphorus species, we became interested in the possibility of recovering and/or recycling the key Bu_3Sn moiety.[57] Such recycling would bypass any net formation of Sn-containing waste and could also provide a first step towards the development of catalytic reactions, which are all but unknown for P_4 (*vide infra*).[21-24] Fortunately, the Bu_3Sn moiety is relatively robust, and in the above reactions is ultimately incorporated into a byproduct of the type Bu_3SnX (X = OR or halide, R = Bu_3Sn or alkyl) that is easily separated from the target product. For example, Bu_3SnCl (**20**) could be recovered in high yield and with minimal effort from the syntheses of THPC and HPA by a simple extraction

procedure after the reaction mixture was quenched with HCl (Fig. 5a). Transformation of Bu_3SnCl into Bu_3SnH is well established and can be achieved by various means (either directly or *via* facile hydrolysis or alcoholysis to Bu_3SnOR), commonly with near-quantitative conversions and excellent isolated yields (up to 95%).[58] Combination of any of these methods with the above reactions thus provides a simple and efficient synthetic cycle that does not produce any stoichiometric Sn-containing byproducts (Fig. 5b).

Although any known method could be employed for the regeneration of Bu_3SnH, especially attractive is the reaction of Bu_3SnOR under mild conditions with polymethylhydrosiloxane (PMHS), a benign, stable and inexpensive polymeric reductant (Fig. 5c).[59,60] In particular, it was anticipated that use of such a gentle method might allow generation of Bu_3SnH to be combined with subsequent P_4 functionalisation in a single reaction step (in a similar manner to Bu_3SnH-mediated reduction of some organic substrates),[61] further simplifying the synthetic cycle. And, indeed, hydrostannylation of P_4 could be successfully achieved upon replacement of Bu_3SnH with a mixture of Bu_3SnOMe or $(Bu_3Sn)_2O$ and PMHS (Supplementary Methods 36–38). These tandem reactions could be fed directly into subsequent steps, as illustrated by the synthesis of THPC, which was isolated in one pot and excellent yields starting from both Bu_3SnOMe and $(Bu_3Sn)_2O$ (Fig. 6a,b and Supplementary Methods 39-40). The Bu_3SnCl by-product of the latter reaction could again be separated from the target product by simple extraction, alongside PMHS-derived by-products. In fact, it was found that this 'crude' Bu_3SnCl could be employed directly as a Bu_3Sn source for further P_4 functionalisation, without the need for separation of the pure compound. Thus, after simple stirring over aqueous Na_2CO_3 (to convert back to $(Bu_3Sn)_2O$) this unpurified material was added to a fresh reaction mixture, ultimately yielding a new batch of THPC in good yield (albeit reduced somewhat relative to the first 'cycle'; Fig. 6c).

Catalytic use of Bu_3Sn

Having established the viability of a synthetic cycle that is closed in Bu_3Sn, attention was finally turned to the development of a catalytic process.[61] Such reactions represent a longstanding

but almost entirely unmet goal in the field of P_4 activation.[21-24] Reducing the amount of the Bu_3SnX reagent employed should also further minimize any risks associated with its use. Gratifyingly, the formation of THP *en route* to THPC could be achieved using only a catalytic quantity (8.25 mol% per P atom) of Bu_3SnOMe, with turnover numbers (TONs) greater than ten achievable after only minor modification of the stoichiometric procedures (Fig. 7 and Supplementary Method 41; see Extended Data Fig. 7 for an outline catalytic cycle). Only one other example of catalytic P–C bond formation from P_4 is known, which is strictly limited to P–C(aryl) bonds.[21,22]

Conclusions

We have developed a practical, versatile method for the direct transformation of P_4 into useful monophosphorus species, mediated by the readily-available triorganotin(IV) moiety Bu_3Sn. This method can be used to prepare diverse monophosphorus compounds which are of clear industrial relevance in areas such as flame retardants, photoinitiators and fumigants. Both organic and inorganic phosphorus products are accessible in a 'one pot' manner without the need for wasteful or time-consuming isolation of intermediates, and the reactions require only inexpensive, commercially available reagents. Importantly, facile recovery and recycling of the Bu_3Sn moiety has been achieved, which prevents the formation of significant Sn-containing waste. Indeed, the Bu_3Sn moiety may even be employed in a truly catalytic fashion, as illustrated for the synthesis of the important industrial precursor THPC. This catalytic use of the tri-*n*-butyltin reagent further minimises any risks associated with the use of organotin compounds. The use of a p-block element catalyst to produce a highly useful organophosphorus compound was previously unknown, and our results thus suggest that the conspicuous shortage of catalytic methods of the transformation of P_4 can be overcome. While our research has so far focused on commercially available butyl-substituted tin derivatives, the practical and conceptual simplicity of the approach described herein promises ready extension to a much wider range of radical sources, potentially even including those based on other

p-block elements. We therefore anticipate that the reported method will have a major impact on the future synthesis of monophosphorus compounds in laboratory and industrial settings.

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Author contributions

D.J.S. developed the hydrostannylation procedures, developed initial procedures for formation of final products, and performed mechanistic studies. D.J.S. and J.C. optimised the synthesis, isolation and purifications of products at increased scale, and the recovery and recycling of Bu_3Sn-based byproducts. D.J.S. and M.S. developed the catalytic synthesis of THPC. D.J.S. and R.W. conceived, oversaw and directed the project. D.J.S. prepared the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

A patent covering all of the results described herein has been filed (as of 13/02/2020) by the University of Regensburg (EP 20 157 197.3; D.J.S., R.W. inventors). The authors declare no other conflicts of interest.

Figures

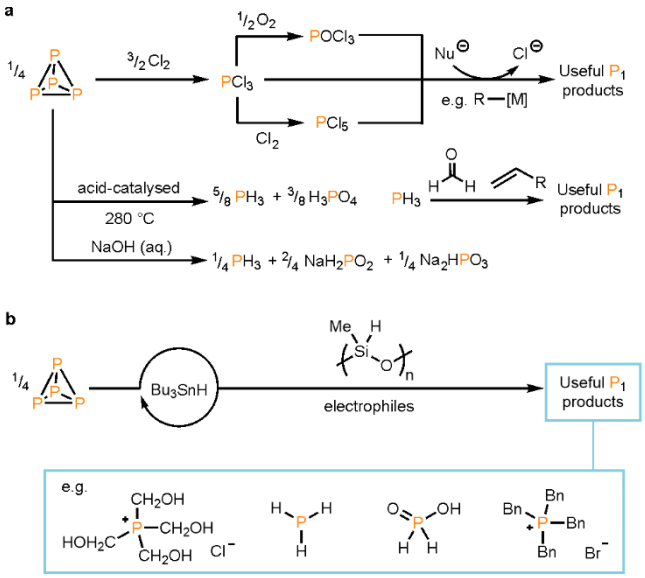

Figure 1. Strategies for the transformation of P_4 into monophosphorus products. a, Current state-of-the-art methods, which involve either: oxidation with Cl_2 (to generate PCl_3, which may be oxidized further to PCl_5 or $POCl_3$) and subsequent reaction with nucleophiles; or base-induced or acid-catalysed disproportionation to form PH_3, which is then used for hydrophosphination of unsaturated substrates. **b**, The strategy reported herein, in which hydrostannylation of P_4 using Bu_3SnH is followed by reaction with electrophiles in a 'one pot' fashion. The Bu_3SnH-derived byproducts can be recovered and used to regenerate Bu_3SnH in a closed synthetic loop, using polymethylhydrosiloxane as a cheap and benign terminal reductant.

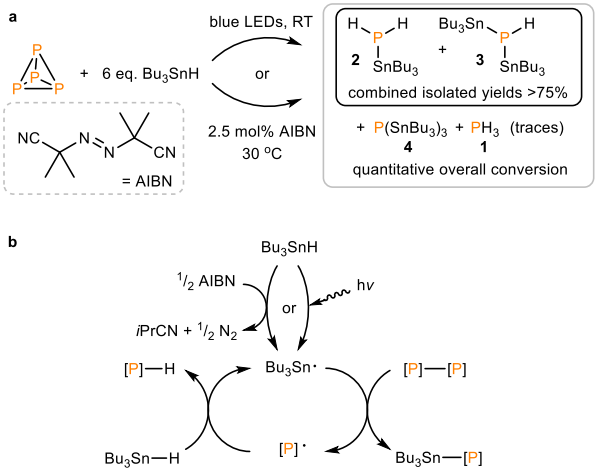

Figure 2. Hydrostannylation of P_4. a, Stoichiometric reaction of P_4 with Bu_3SnH to give products $(Bu_3Sn)_xPH_{3-x}$ (x = 0-3), initiated by either light or a chemical radical initiator. **b**, A plausible radical chain

mechanism for P_4 hydrostannylation, where [P]–[P] represents a generic P–P bond. AIBN loading (mol%) is defined per P atom.

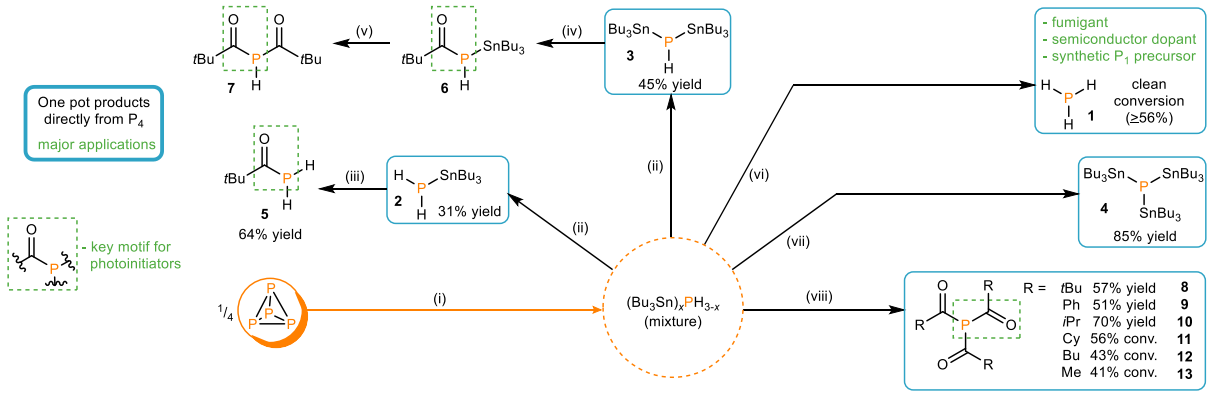

Figure 3. Functionalisation of phosphines $(Bu_3Sn)_xPH_{3-x}$ and direct, 'one pot' functionalisation of P_4. Equivalents, equiv., are here defined per P atom. (i) Hydrostannylation of P_4 using Bu_3SnH (from P_4: 1.56 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h). (ii) Preparative separation of Bu_3SnPH_2 (**2**) and $(Bu_3Sn)_2PH$ (**3**) (from crude $(Bu_3Sn)_xPH_{3-x}$: distillation, ca. 70 °C, 10^{-5} mbar). (iii) Monoacylation of Bu_3SnPH_2 (**2**) using *t*BuC(O)Cl (from Bu_3SnPH_2: 0.95 equiv. tBuC(O)Cl, PhMe, dark, RT, 16 h). (iv) Monoacylation of $(Bu_3Sn)_2PH$ (**3**) using *t*BuC(O)Cl (from $(Bu_3Sn)_2PH$: 1 equiv. *t*BuC(O)Cl, C_6D_6, RT). (v) Double acylation of $(Bu_3Sn)_2PH$ (**3**) using *t*BuC(O)Cl (from $(Bu_3Sn)_2PH$: 2 equiv. *t*BuC(O)Cl, C_6D_6, RT). (vi) One pot, selective transformation of P_4 into PH_3 (**1**) (from crude $(Bu_3Sn)_xPH_{3-x}$: 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 1 h). (vii) One pot synthesis of $(Bu_3Sn)_3P$ (**4**) (from P_4: 1.5 equiv. Bu_3SnH, 1.5 equiv. Bu_3SnOMe, PhMe, 455 nm LEDs, RT, 16 h, then –PhMe, 100 °C, 16 h). (viii) One pot synthesis of triacylphosphines $P(C(O)tBu)_3$ (**8-13**) (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 4 equiv. RC(O)Cl, 1.5 equiv. KHMDS (R = *t*Bu, Ph) or NEt_3 (R = *i*Pr, Cy, Bu, Me), PhMe, dark, RT, 16 h).

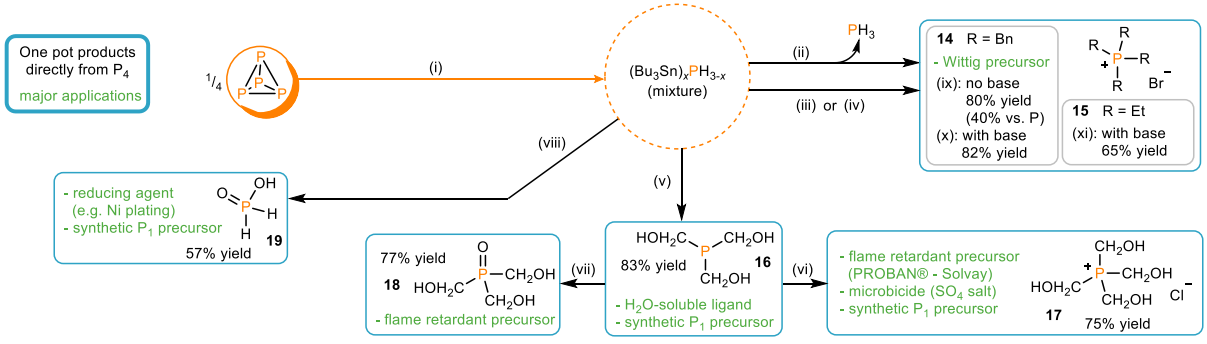

Figure 4. Further, direct, 'one pot' functionalisation of P_4. Equivalents, equiv., are here defined per P atom. (i) Hydrostannylation of P_4 using Bu_3SnH (from P_4: 1.56 equiv. Bu_3SnH, PhMe, 455 nm LEDs,

RT, 16 h). (ii) One pot synthesis of [Bn_4P]Br (**14**), without base (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 10 equiv. BnBr, 60 °C, 3 d). (iii) One pot synthesis of [Bn_4P]Br (**14**), with base (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 10 equiv. BnBr, 1 equiv. KHMDS, 60 °C, 3 d). (iv) One pot synthesis of [Et_4P]Br (**15**), with base (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 5 equiv. EtBr, 2 equiv. KHMDS, 100 °C, 3 d). (v) One pot synthesis of $(HOCH_2)_3P$ (THP, **16**) (from P_4: 1.6 equiv. Bu_3SnH, 3 equiv. paraformaldehyde, EtOH, 455 nm LEDs, RT, 16 h). (vi) One pot synthesis of [$(HOCH_2)_4P$]Cl (THPC, **17**) (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then –PhMe, EtOH, 12.5 equiv. paraformaldehyde, RT, 16 h, then 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 2 h). (vii) One pot synthesis of $(HOCH_2)_3PO$ (THPO, **18**) (from crude THP: PhMe/H_2O, air, 90 °C, 16 h). (viii) One pot synthesis of $H_2P(O)OH$ (HPA, **19**) (from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 10 equiv. H_2O_2 (35% aq.), RT, 30 min, then H_2O, 2.5 equiv. HCl (4.0 M in 1,4-dioxane)).

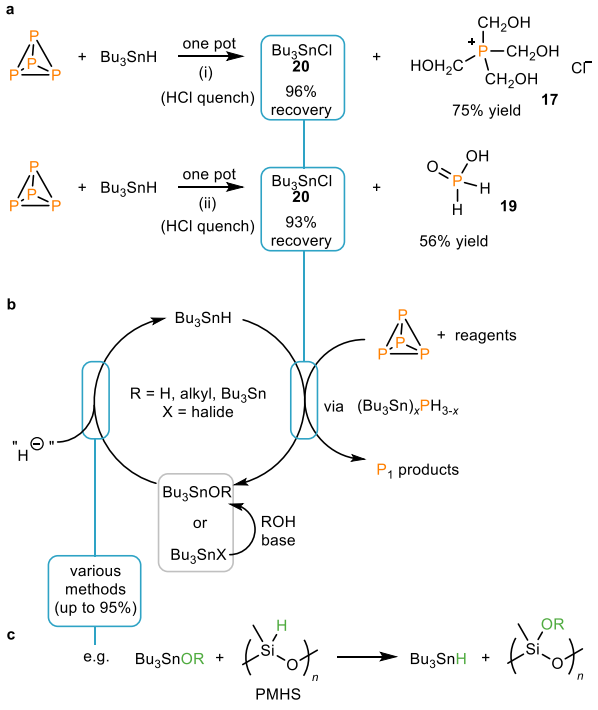

Figure 5. Recycling of the Bu_3Sn moiety. a, Recovery of Bu_3SnCl from the syntheses of THPC and HPA. **b**, An outline 'Bu_3Sn-neutral' synthetic cycle for transformation of P_4 into monophosphorus species, through reduction of recovered Bu_3Sn derivatives with hydride sources (see ref. 58). **c**, A specific example of regeneration of Bu_3SnH using PMHS as hydride source. Conditions (equivalents, equiv., are here defined per P atom): (i) from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then –PhMe, EtOH, 12.5 equiv. paraformaldehyde, RT, 16 h, then 10 equiv. HCl (4.0 M in 1,4-dioxane),

RT, 2 h; (ii) from P_4: 1.6 equiv. Bu_3SnH, PhMe, 455 nm LEDs, RT, 16 h, then 10 equiv. H_2O_2 (35% aq.), RT, 30 min, then H_2O, 2.5 equiv. HCl (4.0 M in 1,4-dioxane).

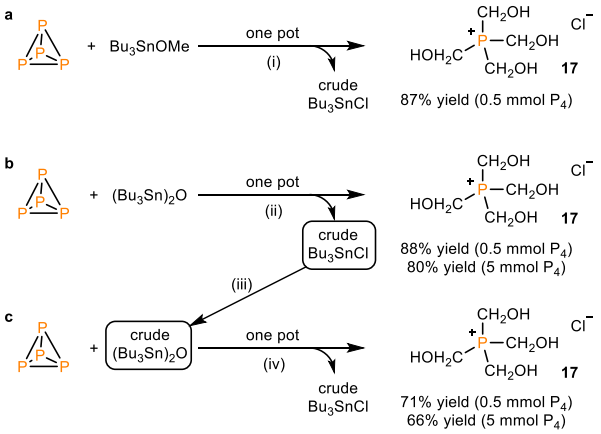

Figure 6. Synthesis of THPC (17) *via in situ* generation of Bu_3SnH. One pot synthesis of THPC starting directly from P_4 and **a**, Bu_3SnOMe or **b**, $(Bu_3Sn)_2O$. **c**, Direct recycling of the Bu_3Sn moiety without re-isolation of any intermediate Bu_3SnX. Conditions (equivalents, equiv., are here defined per P atom): (i) from P_4: 2 equiv. Bu_3SnOMe, 2 equiv. PMHS, PhMe, 455 nm LEDs, RT, 16 h, then –PhMe, EtOH, 12.5 equiv. paraformaldehyde, RT, 16 h, then 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 2 h; (ii) from P_4: 1 equiv. $(Bu_3Sn)_2O$, 5 mol% ACN, 2 equiv. PMHS, PhMe, dark, 80 °C, 3 d, then –PhMe, EtOH, 12.5 equiv. paraformaldehyde, RT, 16 h, then 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 2 h; (iii) from crude Bu_3SnCl: sat. Na_2CO_3 (aq.), RT, 16 h; (iv) from P_4: 1 equiv. crude $(Bu_3Sn)_2O$, 5 mol% ACN, 2 equiv. PMHS, PhMe, dark, 80 °C, 3 d, then –PhMe, EtOH, 12.5 equiv. paraformaldehyde, RT, 16 h, then 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 2 h.

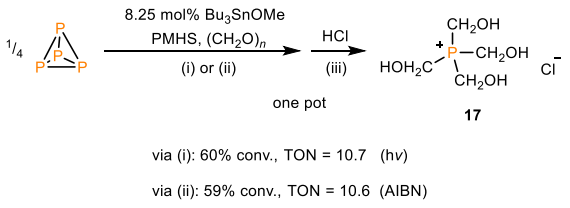

Figure 7. Synthesis of THPC (17) *via* catalytic transformation of P_4 into THP (16). Turnover numbers (TON) are calculated from the measured conversion (conv.) to THPC and factor in the 1:6 stoichiometry of the P_4 hydrostannylation reaction, as described in Supplementary Methods 30 and 31. Conv. and TON values are based upon an average of two runs. Catalyst/initiator loadings (mol%) and molar equivalents (equiv.) are defined per P atom. Conditions: (i) 8.3 mol% Bu_3SnOMe, 4 equiv. PMHS, 8.3 equiv. paraformaldehyde, EtOH/PhH (2:1), 365 nm LEDs, RT, 65 h; (ii) 8.3 mol% Bu_3SnOMe, 8

equiv. PMHS, 8.3 equiv. paraformaldehyde, 8.3 mol% AIBN, EtOH/PhH (2:1), 60 °C, 65 h; (iii) 3.3 equiv. HCl (4.0 M in 1,4-dioxane), RT, 1 h.

Methods

Herein can be found general experimental information, and representative experimental procedures for key reactions. Those procedures not described below can instead be found in the Supplementary Information, alongside relevant characterisation data.

Note: P_4 is toxic and highly pyrophoric and should be handled, manipulated and quenched with corresponding caution.

General information

Unless stated otherwise, all reactions and manipulations were performed under an N_2 atmosphere (< 0.1 ppm O_2, H_2O) through use of MBraun Unilab and GS MEGA Line gloveboxes, and standard Schlenk line techniques. All glassware was oven-dried (160 °C) overnight prior to use. PhH and DME were distilled from Na/benzophenone and stored over molecular sieves (3 Å). MeCN was distilled from CaH_2 and stored over molecular sieves (3 Å). *n*-Pentane was distilled from Na and stored over K. *n*-Hexane was purified using an MBraun SPS-800 system and stored over K. PhMe, Et_2O and THF were purified using an MBraun SPS-800 system and stored over molecular sieves (3 Å). EtOH was degassed and dried by standing over at least three sequential batches of molecular sieves (3 Å). C_6D_6 was distilled from K and stored over molecular sieves (3 Å). CD_3CN, CD_3OD and D_2O were used without purification. All reagents and starting materials were purchased from major suppliers. Liquids were degassed (if not supplied under inert atmosphere) but were otherwise used as supplied, unless stated otherwise. Bu_3SnH was supplied containing 0.05% BHT as stabilizer and was used as received. Bu_3SnOMe and PMHS were degassed and stored over molecular sieves (3 Å). PhBr was distilled and degassed. $(Bu_3Sn)_2O$, NEt_3 and BnBr were distilled, degassed, and stored over molecular sieves (3 Å). H_2O_2 (ca. 35%) was used as supplied. Solids were dried under vacuum (with the exception of paraformaldehyde and Na_2CO_3) but otherwise used as supplied,

unless stated otherwise. P_4 was sublimed prior to use. P_5Ph_5 was prepared in accordance with the literature.[62]

NMR spectra were recorded at room temperature on Bruker Avance 400 (400 MHz) spectrometers and were processed using Topspin 3.2. Chemical shifts, δ, are reported in parts per million (ppm); ^{1}H NMR and ^{13}C NMR shifts are reported relative to $SiMe_4$ and were referenced internally to residual solvent peaks, while ^{31}P and ^{119}Sn NMR shifts were referenced externally to 85 % H_3PO_4 (aq.) and $SnMe_4$ (90% in C_6D_6), respectively. Except where stated otherwise, integrals for $^{31}P\{^{1}H\}$ and ^{31}P spectra are provided for the purposes of qualitative comparison only, and should not be considered quantitatively accurate. The abbreviations s, d, t, q, m are used to indicate singlets, doublets, triplets, quartets and multiplets, respectively.

Mass spectrometry was performed by the analytical department of the University of Regensburg using Jeol AccuTOF GCX and Agilent Q-TOF 6540 UHD spectrometers.

Reactions driven by light were performed using apparatus that has been illustrated in a previous publication,[21] in which reaction vessels are illuminated from beneath by LEDs while placed in a metal block through which cooling water is constantly circulated to maintain near-ambient temperature.

Hydrostannylation of P_4 using Bu_3SnH under blue LED irradiation (0.01 mmol scale)

To a 10 mL, flat-bottomed, stoppered tube were added PhMe (500 µL), P_4 (0.01 mmol, as a stock solution in 79.6 µL PhH) and Bu_3SnH (16.1 µL, 0.06 mmol). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (±15 nm), 3.2 V, 700 mA, Osram OSLON SSL 80) for 18 h. The resulting mixture was analysed by ^{1}H, $^{31}P\{^{1}H\}$, ^{31}P and $^{119}Sn\{^{1}H\}$ NMR spectroscopy, as shown in Extended Data Figs. 1-4.

Of the four product resonances observed in the $^{31}P\{^{1}H\}$ spectrum, the most downfield is readily identified as belonging to PH_3 (**1**) on the basis of both chemical shift (–242.0 ppm) and the characteristic quartet splitting (with large $^{1}J(^{31}P\text{-}^{1}H)$ = 186.5 Hz) of the corresponding signal in

the proton-coupled ^{31}P spectrum.[3] The remaining signals are consistent with the products $(Bu_3Sn)_xPH_{3-x}$ (x = 1-3; **2**-**4**, respectively), with larger x leading to increasingly upfield resonances. These assignments are consistent with the upfield chemical shifts reported for similar triorganotin-substituted phosphines,[37] with the multiplicities observed in the corresponding proton-coupled ^{31}P spectrum (as well as the magnitude of the $^{1}J(^{31}P\text{-}^{1}H)$ coupling constants), with the presence and relative intensities of observed $^{117/119}Sn$ satellites (as well as the magnitude of the corresponding coupling constants), and with the absence of any observable $^{31}P\text{-}^{31}P$ couplings.

Spectra for analogous reactions performed using *n*-hexane, PhH, Et_2O, THF or DME in place of PhMe gave very similar NMR spectra. For illustration, the $^{31}P\{^{1}H\}$ spectra are shown in Extended Data Fig. 5.

Synthesis and isolation of P(C(O)*t*Bu)$_3$ (8)

To a 50 mL flat-bottomed Schlenk were added P_4 (62.0 mg, 0.5 mmol) and PhMe (25 mL). After stirring to obtain a homogeneous solution Bu_3SnH was added (847 µL, 3.15 mmol). The resulting colorless solution was stirred under irradiation with blue LED light (7X Osram OSLON SSL80, 455 nm (±15 nm), 20.3 V 1000mA) for 22 h, during which time the Schlenk tube was placed in a block cooled by circulating water to maintain near-ambient temperature. *t*BuC(O)Cl (979 µL, 8.0 mmol) and KHMDS (599 mg, 3.0 mmol) were added, the Schlenk tube was immediately and thoroughly wrapped in Al foil to exclude any ambient light, and the reaction mixture was stirred at room temperature for 16 h. The resulting light yellow suspension was filtered, and volatiles were removed under vacuum. The remaining white residue was recrystallized from n-hexane at –35 °C, to afford the desired product as colourless needles (325 mg, 57%). For characterisation data, see Supplementary Method 18.

Synthesis and isolation of [Bn$_4$P]Br (14) (with KHMDS)

To a 50 mL flat-bottomed Schlenk were added P_4 (62.0 mg, 0.5 mmol), PhMe (25 mL), and Bu_3SnH (847 µL, 3.15 mmol). The resulting homogeneous, colorless solution was stirred under

irradiation with blue LED light (7X Osram OSLON SSL80, 455 nm (±15 nm), 20.3 V 1000mA) for 22 h, during which time the Schlenk tube was placed in a block cooled by circulating water to maintain near-ambient temperature. Benzyl bromide (2.4 mL, 20 mmol) and KHMDS (399 mg, 2.0 mmol) were added and the reaction mixture heated to 60 °C with stirring for 3 days. After cooling to room temperature the pale yellow suspension was evaporated to dryness, and the resulting solid was washed with pentane (2 x 20 mL) and extracted with acetone (4 x 15 mL; undried, 'bench' acetone was used). Removal of volatiles under vacuum yielded the target product as a white solid (775 mg, 82%). For characterisation data, see Supplementary Method 24.

Synthesis and isolation of THPC (17) via hydrostannylation under blue LEDs in PhMe, with recovery of Bu_3SnCl (20)

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and PhMe (25 mL). After stirring to obtain a homogeneous solution, Bu_3SnH (847 µL, 3.15 mmol) was added. The resulting colourless, homogeneous mixture was stirred under irradiation with blue LED light (7X Osram OSLON SSL80, 455 nm (±15 nm), 20.3 V 1000mA) for 16 h, during which time the Schlenk tube was placed in a block cooled by circulating water to maintain near-ambient temperature. Following removal of volatiles under vacuum, EtOH (25 mL) and paraformaldehyde (750 mg, 25 mmol) were added, and the resulting suspension was stirred at room temperature for 16 h. The mixture was frozen in a liquid nitrogen bath and HCl (4.0 M in 1,4-dioxane, 5 mL, 20 mmol) was added. After thawing, the reaction mixture was stirred at room temperature for 2 h. The yellowish suspension was filtered, and volatiles were removed under vacuum. The remaining oily solid residue was triturated with Et_2O (20 mL) overnight, filtered and washed with further Et_2O (20 mL) to afford the desired product as a white solid (281 mg, 75%) after drying under vacuum.

The combined Et_2O washes from the above reaction were dried under vacuum to afford Bu_3SnCl (**20**) as a pale yellow oil (987 mg, 96%). For characterisation data of both isolated products, see Supplementary Method 30.

Synthesis and isolation of HPA (19), with recovery of Bu_3SnCl (20)

To a 50 mL flat-bottom Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and PhMe (25 mL). After stirring to obtain a homogeneous solution, Bu_3SnH (847 µL, 3.15 mmol) was added. The resulting colourless, homogeneous mixture was stirred under irradiation with blue LED light (7X Osram OSLON SSL80, 455 nm (±15 nm), 20.3 V 1000mA) for 16 h, during which time the Schlenk tube was placed in a block cooled by circulating water to maintain near-ambient temperature. The resulting solution was frozen in a liquid nitrogen bath and H_2O_2 (35% aq., 0.43 mL, 5.0 mmol) was added. After thawing, the reaction mixture was stirred at room temperature for 30 minutes. Subsequent work-up was performed under air. H_2O (20 mL) was added and, after mixing thoroughly, the organic phase was separated and washed with further H_2O (3 x 15 mL). Volatiles were removed under vacuum, and *n*-hexane (20 mL) and MeCN (20 mL) were added. HCl was added dropwise to the stirred biphasic mixture (4.0 M in 1,4-dioxane, 1.25 mL, 5 mmol), and after stirring for 1 h the MeCN layer was separated and volatiles were removed under vacuum. The resulting colourless oil was washed with further n-hexane (20 mL) and dried thoroughly under vacuum to yield the desired product as a colourless oil (127 mg, 57%). The material obtained in this manner typically contains *ca.* 10% $HP(O)(OH)_2$ (as judged by $^{31}P\{^1H\}$ NMR spectroscopy), which is a known oxidation product of $H_2P(O)OH$.[56]

In order to ascertain the H_2O content, quantitative $^{31}P\{^1H\}$ NMR spectroscopic analysis (D1 = 14 s) was performed on a CD_3CN solution containing precisely known quantities of both this product (6.5 mg) and Ph_3PO (23.0 mg), with the latter acting as an internal standard for integration. In this manner the precise amount of HPA (and $HP(O)(OH)_2$) in the sample could be calculated, with the remaining mass being attributed to H_2O. The overall composition was thus determined to be $HPA{\cdot}(HP(O)(OH)_2)_{0.14}{\cdot}(H_2O)_{1.92}$, and this composition was used to calculate the isolated yield.

The combined *n*-hexane washes from the above reaction were dried under vacuum to afford Bu_3SnCl (**20**) as a pale yellow oil (953 mg, 93%). For characterisation data of both isolated products, see Supplementary Method 35.

Synthesis and isolation of THPC (17) *via* hydrostannylation starting from $(Bu_3Sn)_2O$, with recycling of Bu_3SnCl (20) (5 mmol scale)

To a 500 mL round-bottomed Schlenk flask were added P_4 (620 mg, 5 mmol) and PhMe (250 mL). After stirring to obtain a homogeneous solution, $(Bu_3Sn)_2O$ (10.2 mL, 20 mmol), PMHS (2.3 mL, 40 mmol) and ACN (244 mg, 1 mmol) were added. The Schlenk flask was immediately and thoroughly wrapped in Al foil to exclude any ambient light, and the stirred reaction mixture was then heated to 80 °C for 3 days. Following removal of volatiles under vacuum, EtOH (250 mL) and paraformaldehyde (7.51 g, 250 mmol) were added, and the resulting suspension was stirred at room temperature for 16 h. The mixture was frozen in a liquid nitrogen bath and HCl (4.0 M in 1,4-dioxane, 50 mL, 200 mmol) was added. After thawing, the reaction mixture was stirred at room temperature for 4 h. The pale yellow suspension was filtered through a bed of Celite in a glass frit (P4) column, and volatiles were removed under vacuum. The remaining oily solid residue was triturated with Et_2O (200 mL) overnight, filtered and washed with further Et_2O (2 x 25 mL). The resulting white solid was then again extracted into EtOH (2 x 100 mL). Following filtration and removal of volatiles under vacuum, the desired product was obtained as a white solid (3.05 g, 80%).

NMR data are identical to those reported in Supplementary Method 30.

To the combined Et_2O washes from the above reaction was added a saturated aqueous solution of Na_2CO_3 (150 mL). The resulting biphasic mixture was stirred under open bench conditions for 24 h, and the organic phase was separated and washed with H_2O (4 x 100 mL). The organic phase was transferred into a 500 mL Schlenk flask and volatiles were removed under vacuum. The remaining procedure was performed under an inert atmosphere. A solution of P_4 (620 mg, 5 mmol) pre-dissolved in PhMe (250 mL) was added, followed by PMHS (2.3 mL, 40 mmol) and ACN (244 mg, 1 mmol). The Schlenk tube was immediately and thoroughly wrapped in Al foil to exclude any ambient light, and the stirred reaction mixture was then heated to 80 °C for 3 days. Following removal of volatiles under vacuum, EtOH (250 mL) and paraformaldehyde (7.51 g, 250 mmol) were added, and the resulting suspension was

stirred at room temperature for 16 h. The mixture was frozen in a liquid nitrogen bath and HCl (4.0 M in 1,4-dioxane, 50 mL, 200 mmol) was added. After thawing, the reaction mixture was stirred at room temperature for 4 h. The yellowish suspension was filtered through a bed of Celite in a glass frit (P4) column, and volatiles were removed under vacuum. The remaining oily solid residue was triturated with Et_2O (200 mL) overnight, filtered and washed with further Et2O (2 x 25 mL). The resulting white solid was then again extracted into EtOH (2 x 100 mL). Following filtration and removal of volatiles under vacuum, the desired product was obtained as a white solid (2.52 g, 66%).

NMR data are identical to those reported in Supplementary Method 30.

Catalytic hydrostannylation of P_4 using Bu_3SnOMe and PMHS under near UV irradiation

To a 10 mL, flat-bottomed, stoppered Schlenk tube were added EtOH (500 µL), P_4 (0.03 mmol, as a stock solution in 232 µL PhH), Bu_3SnOMe (2.9 µL, 0.01 mmol), PMHS (28.7 µL, 0.48 mmol) and paraformaldehyde (30 mg, 1.0 mmol). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with near UV (365 nm) LEDs for 65 h. The mixture was then frozen in a liquid nitrogen bath and HCl (4.0 M in 1,4-dioxane, 0.1 mL, 0.4 mmol) was added. After thawing, the reaction mixture was stirred at room temperature for 1 h. Following addition of Ph_3PO (0.04 mmol, as a stock solution in 506 µL MeCN) as an internal standard, the resulting mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy, as shown in Supplementary Fig. 136. The chemical shift observed for THPC (**17**) in these spectra is *ca.* 1 ppm downfield of that observed in spectra of isolated samples, which is attributed to solvent effects and the presence of excess HCl. That these peaks correspond to THPC was unambiguously confirmed by subsequent addition of an authentic sample to one representative reaction, which clearly increased the intensity of this peak.

Accurate conversion to THPC was measured by integration of a single-scan, inverse-gated $^{31}P\{^1H\}$ NMR spectrum (Supplementary Fig. 137), in line with our previously-described methodology.[21] For two independent runs, conversions of 57% and 62% were determined.

Turnover numbers (TONS; 10.2 and 11.2, respectively, for an average of 10.7) were calculated from these conversions by factoring in the 1:6 stoichiometry of the reaction between P_4 and Bu_3SnH. Because of this stoichiometry, full consumption of 1 eq. of P_4 relative to Bu_3SnOMe requires six turnovers of the catalyst (i.e. it must be used to regenerate Bu_3SnH six times). Equivalently, formation of 1 eq. of THPC (from 0.25 eq. P4) requires 1.5 turnovers of the catalyst. The TON is therefore calculated as 1.5 times the molar ratio between the THPC formed and the Bu_3SnOMe catalyst employed.

References (methods)

62. Barnard, J. H., Brown, P. A., Shuford, K. L. & Martin, C. D. 1,2-Phosphaborines: hybrid inorganic/organic P-B analogues of benzene. *Angew. Chem. Int. Ed*. **54**, 12083-12086 (2015).

Data availability

The authors declare that the data supporting the findings of this study are available within the paper (and its Supplementary Information files).