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Hydrosilylation and hydrogermylation of white phosphorus†

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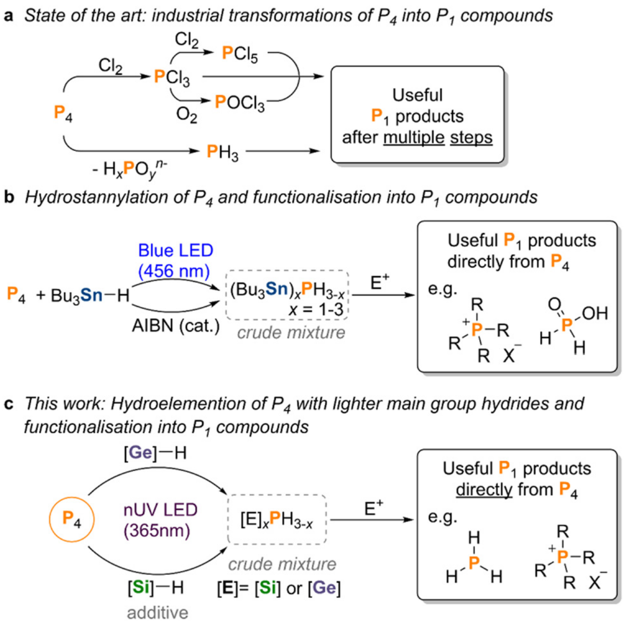
The development of efficient, direct strategies for the transformation of white phosphorus (P_4) into useful monophosphorus compounds, as alternatives to the current wasteful and hazardous indirect processes, remains a significant challenge. Encouragingly, recent reports have shown that the reduction of P_4 with organotin hydrides and subsequent functionalisation with electrophiles allows for the efficient synthesis of an array of industrially relevant monophosphines in a 'one-pot' manner. However, despite the practical and conceptual simplicity, the appeal of this method is limited by the inherent toxicity of most organotin derivatives. Here, we address this problem through experimental and computational studies of the reactivity of lighter and less toxic hydrogermane and hydrosilane homologues of organotin hydrides (R_3EH, E = Ge or Si) towards P_4. These hydroelementation reactions can be employed to directly transform P_4 into useful monophosphorus compounds, in a simple 'one-pot' fashion similar to the original organotin-based systems.

Introduction

White phosphorus, P_4, is by far the most reactive and industrially relevant allotrope of the element. It serves as the synthetic precursor for all commercially valuable and academically important organophosphorus compounds (OPCs).[1–4] Current industrial routes for converting P_4 into these useful OPCs involve indirect multi-step processes such as (oxy)chlorination reactions with chlorine gas (Cl_2) to produce phosphorus chloride intermediates (PCl_3/PCl_5/$POCl_3$), or disproportionation reactions under acidic or basic conditions to generate phosphine gas (PH_3). The desired OPCs are then obtained by functionalisation of these intermediates with nucleophiles or by hydrophosphination reactions of unsaturated organic compounds, respectively (Scheme 1a).[1–6] As a result, significant efforts have been made to develop alternative strategies for the functionalisation of P_4 that avoid the use of such hazardous reactants and intermediates.[7–11]

Notably, in recent years various strategies have been reported for converting P_4 *directly* into one or more P_1 products.[12–14] These remain at early stages of development, but include the degradation of P_4 by divalent silicon species,[15] photocatalytic reactions,[16,17] electrochemical degradation,[18]



Scheme 1 (a) Current state-of-the-art routes for the transformation of P_4 into P_1 products. (b) Previously reported hydrostannylation of P_4 and subsequent treatment with electrophiles to afford P_1 compounds directly from P_4. (c) Hydroelemention of P_4 with lighter main group hydrides, reported herein. E^+ represents a generic electrophile.

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and oxidative 'onioation' of P_4.[19] Among these new approaches, our group recently reported a simple method that can convert both white and red phosphorus (P_{red}) into stannyl phosphines $(Bu_3Sn)_xPH_{3-x}$ (x = 0–3) using the 'classical' radical reagent Bu_3SnH and initiation by light or a chemical radical initiator such as azobis(isobutyronitrile) (AIBN).[20,21] The resulting stannylphosphine mixture serves as a P^{3-} source, affording industrially relevant monophosphorus compounds upon treatment with various electrophiles in a 'one-pot' protocol (Scheme 1b). Moreover, simple procedures have been developed for the closed-loop recycling of the tin hydride reagent, thus minimising organotin waste.[20,21]

Unfortunately, the use of most common organotin compounds raises fundamental concerns around toxicity that cannot be fully mitigated, even by these recycling strategies (although some much less toxic organotin derivatives are known, albeit typically at the cost of significantly higher molecular weight).[22] The replacement of R_3SnH with more benign options has long been an important goal for synthetic free-radical chemistry, and many alternative reagents have been proposed for a variety of other chemical transformations.[23–26] Particularly appealing in the context of P_4 reduction are lighter group 14 hydrides, which in other contexts are known to undergo reactions analogous to those of R_3SnH, although they display an intrinsically lower propensity for homolysis of the element-hydrogen bonds.[27]

Here, we present the first examples of hydrogermylation and hydrosilylation of P_4. Utilizing LED light irradiation, these reactions produce mixtures of germanyl- and silylphosphanes that can be transformed into valuable P_1 products *via* simple one-pot procedures (see Scheme 1c). Our findings significantly expand the application of hydroelementation as a general method for synthesizing useful organophosphorus compounds in a single reaction step from white phosphorus.

Results and discussion

Inspired by the practical and conceptual simplicity of the hydrostannylation of P_4, we anticipated that this radical-based activation of P_4 could be extended to the use of lighter R_3EH (E = Ge or Si). To evaluate the viability of such a process, we performed a computational investigation at the outset of this project. DFT studies at the PBE-D3(BJ)/def2-TZVP level of theory were focused on the first P–P bond cleavage step of the reaction of P_4 with truncated model radicals $Me_3E^\bullet$ (E = Ge, Si, Sn) and the subsequent hydrogen atom abstraction (HAT) step (Fig. 1a). The HAT step was found to be rate limiting for Me_3SnH.[28] Notably, while the addition of $Me_3Sn^\bullet$ to P_4 is energetically uphill (2.2 kcal mol^{-1}), the same process is barrierless and downhill for both other $Me_3E^\bullet$ (E = Ge, Si), forming the 'butterfly' P_4 radical intermediates $(Me_3E)P_4^\bullet$. The subsequent HAT step to $(Me_3E)P_4^\bullet$ from another equivalent of Me_3EH then proceeds over activation barriers that are significantly higher for Si and Ge than for the heavier analogue Sn (23.4, 18.7 and 10.8 kcal mol^{-1}, respectively) consistent with expected differences in the E–H bond strengths (Fig. 1b, for calculated bond dissociation energies see ESI, Table S1†).[24,27,29,30] Nevertheless, all of these barriers should be easily accessible even at room temperature, suggesting that the desired hydroelementation should be feasible. An analysis of the influence of the substituents in hydrides R_3EH (E = Si, R = $SiMe_3$, Ph, Me; E = Ge, R = Ph, Me) revealed the expected trend. The lowest barrier for the hydroelementation of the first P–P bond was observed for $(Me_3Si)_3SiH$. The barriers for Me_3EH are generally higher than for Ph_3EH (see Fig. S2, ESI†).

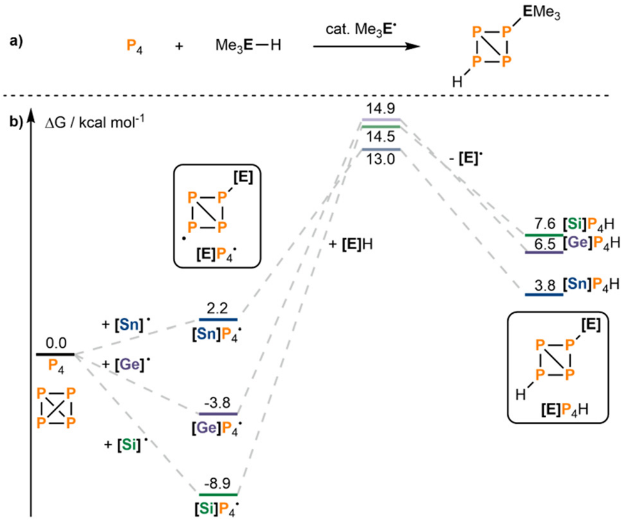
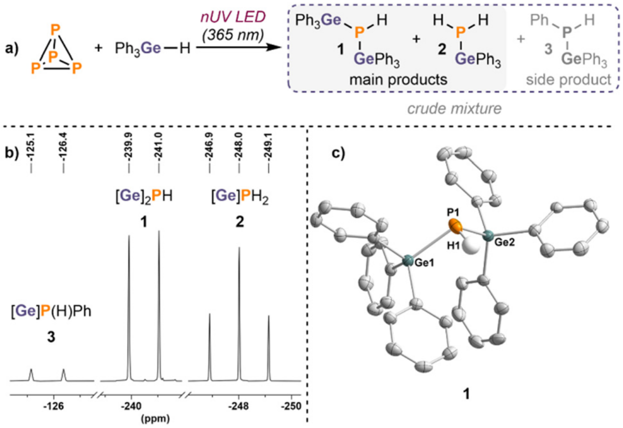


Fig. 1 (a) Model hydroelementation of the first P–P bond in P_4. (b) Calculated mechanism, *via* attack of **[E]**$^\bullet$ and subsequent HAT (relative free energies in kcal mol^{-1}). **[E]** = Me_3Si, Me_3Ge or Me_3Sn. For simplicity, stereochemistry is not shown.

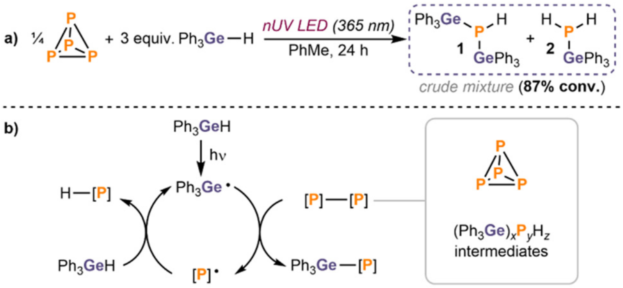
Hydrogermylation of P_4

Encouraged by the computational results, we began experimentally with investigation of the hydrogermylation of P_4. Notably, despite the stronger Ge–H bond, the commercially available organogermanes Bu_3GeH and Ph_3GeH have both been used as alternatives to replace organotin compounds in various radical reactions.[23,25,31] We first tested the reactivity of Bu_3GeH towards P_4, under similar conditions to those used for Bu_3SnH.[20] Unfortunately, in sharp contrast to the efficient reaction of P_4 with R_3SnH, the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures mainly showed unconsumed P_4 at −521 ppm (for full details see ESI, Section 3.1†). However, when Ph_3GeH, which has a weaker Ge–H bond (see ESI, Table S1†),[29] was used instead, additional minor resonances were detected at −240.5 and −248.0 ppm. Markedly, significant amounts of orange precipitate had formed at the end of the reactions with both Bu_3GeH and Ph_3GeH, suggesting the formation of red phosphorus or other insoluble polyphosphorus compounds (presumably $(R_3Ge)_xP_yH_z$; more detailed characterisation is hampered by the insolubility of these species).

Further investigations revealed that longer reaction times and irradiation with near UV LED light (365 nm) favoured the



Scheme 2 (a) Hydrogermylation of P_4 with Ph_3GeH promoted by near-UV LED irradiation (365 nm). (b) Insets of the ^{31}P NMR spectrum for the reaction of P_4 (0.01 mmol) with Ph_3GeH (3 equiv. per P atom) driven by 365 nm LED irradiation. (c) Single-crystal XRD structure of $[Ge]_2PH$ (**1**). [Ge] = Ph_3Ge. Thermal ellipsoids are shown at 50%. H atoms, except for the one bound directly to P, are omitted for clarity. C atoms are shown in grey, H is white, P in orange, and Ge in dark green.



Scheme 3 (a) Optimised conditions for the hydrogermylation of P_4 promoted by near-UV irradiation (365 nm). (b) Proposed radical chain mechanism for P_4 hydrogermylation, where [P]–[P] represents a generic P–P bond.

conversion of P_4 into the new species (Scheme 2a).‡ These can be assigned as $(Ph_3Ge)_2PH$ (**1**; −240.5 ppm) and Ph_3GePH_2 (**2**; −248.0 ppm), both by analogy to the major products observed in the previous hydrostannylation reactions and by comparison with the chemical shifts reported for related Ge-substituted phosphines.[20,32] This assignment is further supported by ^1H-coupled ^{31}P NMR spectra, where these resonances appear as a doublet ($^1J(^{31}P–^1H)$ = 185 Hz) and a triplet ($^1J(^{31}P–^1H)$ = 181 Hz), respectively (Scheme 2b). Corresponding doublets arising from coupling between ^1H and ^{31}P nuclei could also be observed in the ^1H NMR spectra (see ESI, Fig. S7†). A single-crystal X-ray diffraction study confirmed the identity of **1**, whose structure is analogous to the recently reported $(TerMe_2Sn)_2PH$, which is similarly a product of P_4 hydroelementation (Ter = 2,6-$Mes_2C_6H_3$).[28] An additional, minor resonance was always also observed during these investigations, appearing as a small singlet at −125.8 ppm in the $^{31}P\{^1H\}$ NMR spectra. This signal splits into a doublet in the ^1H-coupled ^{31}P NMR spectrum ($^1J(^{31}P–^1H)$ = 199 Hz) and is attributed to $Ph_3GeP(H)Ph$ (**3**) forming as a minor side product (Scheme 2b).§[33] Note that unlike with Bu_3SnH, no significant tertiary phosphine (*i.e.* $(Ph_3Ge)_3P$) or PH_3 products were observed.

Under these reaction conditions, the conversion to the main products (**1** and **2**) was still relatively limited (<54%), likely due to the continuing formation of the insoluble $(Ph_3Ge)_xP_yH_z$ compounds noted above. Gratifyingly, however, using an excess of Ph_3GeH and more concentrated reaction mixtures resulted in significantly improved reaction outcomes with conversions up to 87% (for **1** and **2**; 95% including **3**), reaction times reduced to 24 hours (see Scheme 3a and ESI, Table S2†), and clear yellowish solutions with no observable precipitates at the end of the reaction. Orange precipitates still form at the beginning of these reactions but later disappear,¶ which may suggest that the initially formed $(Ph_3Ge)_xP_yH_z$ compounds are in fact still available during the overall reaction course, serving as a source of P atoms in the formation of the final products. A similar degradation process has been described for the reaction of P_{red} with Bu_3SnH.[21] Consistent with this suggestion, reactions of P_{red} with Ph_3GeH gave the same hydrogermanylphosphines **1** and **2**, albeit with reduced conversion (39%, see ESI, Section 3.4†). Nevertheless, this provides a proof-of-principle confirmation that bench-stable P_{red} can also be functionalised using germanium hydrides.

We propose that the hydrogermylation of P_4 follows a radical chain mechanism analogous to the hydrostannylation of P_4 and P_{red} (Scheme 3b).‖ This is also consistent with the calculations noted above. Nevertheless, the observation of significant formation of insoluble $(R_3E)_xP_yH_z$ is a clear point of contrast between R_3GeH and R_3SnH.

To understand why this difference might occur, we considered the aggregation of P_4 to form larger $(R_3E)_xP_yH_z$ moieties computationally. For simplicity, calculations were limited to a single representative step: addition of further P_4 to the initial radical intermediate $(Me_3E)P_4^{\bullet}$, which was calculated for all three model systems, E = Sn/Ge/Si. This step would result initially in a P_8 "double butterfly" radical intermediate

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‡ Analogous resonances were also observed in the reaction with Bu_3GeH under these conditions, although with lower conversions. For full details see ESI, Section S3.1.†

§ Similar side/decomposition products have been observed in our previous study of the P_4 hydrostannylation system, in the form of $R_3SnP(H)R$, though in much smaller amounts. The fate of the remaining "Ph_2Ge" fragment whose formation is implied by the presence of the P-bound Ph group is currently unclear.

¶ During the optimisation of the reaction, no signals corresponding to soluble polyphosphorus intermediates were observed in the $^{31}P\{^1H\}$ NMR spectra.

‖ Irradiation with LED light is proposed to induce the formation of an initial $R_3Ge^{\bullet}$ or $R_3Si^{\bullet}$ radical which initiates the chain reaction. However, the precise details of this initiation are currently unclear and remain under investigation. Proof-of-concept results have also been achieved using chemical radical initators such as AIBN instead of LED irradiation. However, for these systems we have thus far only been able to achieve low conversions (<28% **1** and **2**). For full details see ESI, Section S3.5 and S4.7†.

($(Me_3E)P_8^{\bullet}$), *en route* to further aggregation and rearrangement steps (Fig. 2). Notably, for all three systems, this step was found to be *less* energetically demanding than the calculated HAT step that would lead to hydroelementation (*cf.* Fig. 1b), confirming that aggregation to larger $(R_3E)_xP_yH_z$ fragments is likely to be mechanistically relevant. However, for $Me_3Sn^{\bullet}$ the difference in activation barriers is relatively modest (2.2 kcal mol^{-1}; *cf.* Fig. 1b and 2 or see ESI, Fig. S1†), whereas for $Me_3Ge^{\bullet}$ and especially $Me_3Si^{\bullet}$ it is much greater (10.6 kcal mol^{-1} and 13.0 kcal mol^{-1}, respectively). This is mostly due to differences in the HAT step, which is sensitive to changes in the E–H bond strength. In comparison, the identity of the Me_3E substituent has relatively little impact on the barrier to further P_4 addition since it is distant from the active radical site. The results are consistent with the idea that for R_3SnH the desired hydrostannylation is sufficiently kinetically competitive with aggregation to prevent significant formation of large, insoluble $(R_3E)_xP_yH_z$ fragments. In contrast, for R_3GeH and R_3SiH there is a much stronger kinetic preference for aggregation, suggesting that large, insoluble $(R_3E)_xP_yH_z$ aggregates should be more prevalent and that their precipitation should limit the overall reaction rate, consistent with experimental observations. This problem should become more severe as E–H bond strength increases, consistent with the relative performance of Bu_3GeH and Ph_3GeH.

Functionalization of Ph_3GePH_2 and $(Ph_3Ge)_2PH$

After optimising the hydrogermylation of P_4, we next focused on the synthetic utilization of the newly formed Ge-substituted phosphines **1** and **2** in a 'one-pot' fashion. Notably, simple acidification of the crude mixture with HCl (in 1,4-dioxane) prompted the cleavage of the P–Ge bonds, resulting in the formation of PH_3 (**4**, Scheme 4, top) with similar efficiency to that achieved using Bu_3SnH (≥50% conversion, *cf.* ≥56% *via* Bu_3SnH). Furthermore, treatment of the crude mixture with benzyl bromide (BnBr) or bromoethane (EtBr) in the presence of base yielded the phosphonium salts $[Bn_4P]Br$ (**5**) and $[Et_4P]Br$ (**6**), with the former being isolated at preparative scale in 77% yield (Scheme 4, *cf.* 80% *via* Bu_3SnH). These results confirm that the P–Ge bonds in the new P_1 intermediate mixture are sufficiently reactive to allow functionalisation into desirable P_1 compounds although they require longer reaction times and higher temperatures than with $(Bu_3Sn)_xPH_{3-x}$.[20] Reactions of the crude mixture of **1** and **2** with other representative electrophiles that reacted successfully with $(Bu_3Sn)_xPH_{3-x}$, such as paraformaldehyde or acyl chlorides, have so far only resulted in low conversions and/or incomplete reactions (see ESI, Section 3.7†), indicating that this equivalence is not universal.

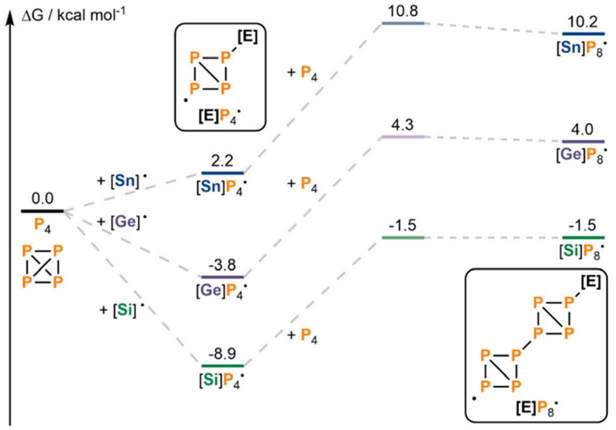
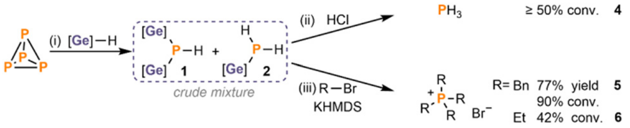


Fig. 2 Calculated aggregation between P_4 and the initial intermediate $[E]P_4^{\bullet}$ (relative free energies in kcal mol^{-1}). **[E]** = Me_3Si, Me_3Ge or Me_3Sn. For simplicity, stereochemistry is not shown.

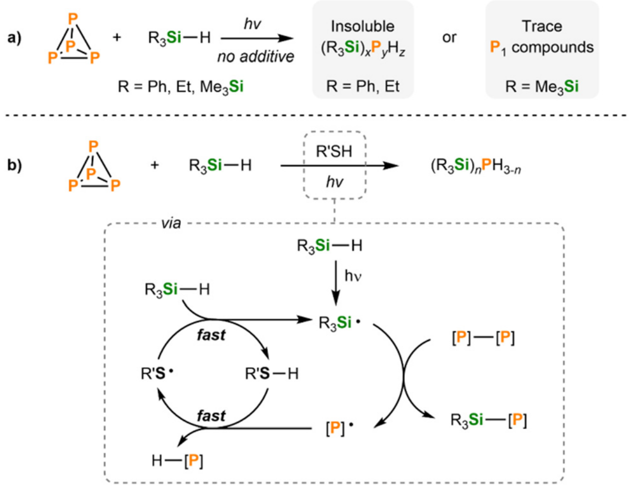


Scheme 4 Functionalisation of the crude mixture of **1** and **2** derived from P_4 directly into useful P_1 products. Equivalents are defined per P atom. (i) P_4 (0.25 equiv.), Ph_3GeH (3 equiv.), PhMe, 365 nm LEDs, RT, 24 h. (ii) Transformation of P_4 into PH_3 from crude mixture (**1** and **2**): 10 equiv. HCl (4.0 M in 1,4-dioxane) RT, 1 (h). (iii) Preparation of phosphonium salts $[R_4P]Br$ from crude mixture (**1** and **2**): 10 equiv. RBr (R = Bn or Et), 2.5 equiv. KHMDS, 100 °C, 3d. [Ge] = Ph_3Ge.

Hydrosilylation of P_4

Having established successful hydrogermylation of P_4, focus was then shifted to the generally cheaper and more readily available hydrosilanes, R_3SiH (*cf.* the more specialised R_3GeH). Hydrosilanes, however, are known to be poor radical chain reagents due to their relatively strong Si–H bonds.[30,34] Moreover, the calculations discussed above imply that formation of insoluble $(R_3Si)_xP_yH_z$ is likely to be an even greater problem for R_3SiH than for R_3GeH. Indeed, initial reactivity studies confirmed that the combination of R_3SiH (R = Ph, Et) with P_4 under the same conditions previously established for either R_3SnH or R_3GeH leads to either no reaction (see ESI, Section 4.1†) or formation of insoluble $(R_3Si)_xP_yH_z$ compounds only. Even when the hypersilane $(Me_3Si)_3SiH$, known for its higher reactivity as a radical reagent due to the hyperconjugation effect of the Me_3Si groups,[26,30,35] was used, only trace new resonances (and unreacted P_4) were observed in the $^{31}P\{^1H\}$ NMR spectra when it was reacted with P_4 (Scheme 5a).

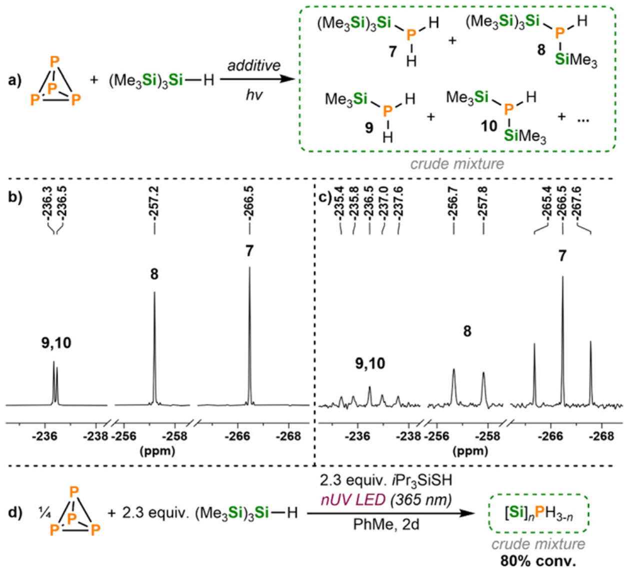
To overcome similar problems in the radical hydrosilylation of unsaturated C═C bonds, organic chemists have developed the use of simple thiols as hydrosilylation catalysts.[36,37] The origin of this catalysis lies in the poor electronic compatibility between the hydrosilane and C-centred radical (both nucleophilic), and much better electronic match between these species and the sulfanyl radical and thiol (both electrophilic), respectively.[38] Given the well-known, broad chemical similarity between P and C, and the fact that P is even slightly more electropositive than C, we speculated that a similar thiol-assisted reaction could facilitate the key HAT process and enable the



Scheme 5 (a) Reactivity studies of silanes R_3SiH towards P_4 driven by LED irradiation (456 nm or 365 nm). (b) Proposed thiol-assisted hydrosilylation of P_4, where [P]–[P] represents a generic P–P bond.

direct hydrosilylation of P_4 to $(R_3Si)_nPH_{3-n}$, as outlined in Scheme 5b.

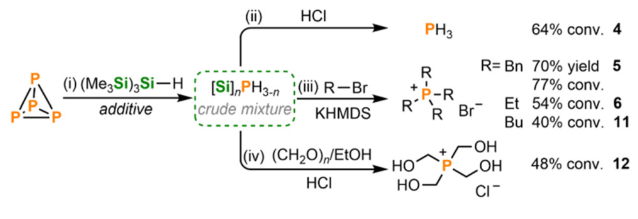
Gratifyingly, the reaction of $(Me_3Si)_3SiH$ and P_4 in the presence of an excess of a thiol such as *i*Pr_3SiSH led to the full consumption of P_4 and the formation of a mixture of Si/H-substituted monophosphorus products (Scheme 6), which appeared as singlets between *ca.* −210 and −280 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The main species formed were identified based on the $^{31}P\{^1H\}$ and ^{31}P NMR spectra (Scheme 6b and c, also see ESI, Fig. S30 and S31†).[39,40] The major product was the primary phosphine $[(Me_3Si)_3Si]PH_2$ (**7**, −266.5 ppm), followed by $[(Me_3Si)_3Si]P(H)SiMe_3$ (**8**, −257.2 ppm), Me_3SiPH_2 (**9**, −236.5 ppm) and $(Me_3Si)_2PH$ (**10**, −236.3 ppm), which contain Me_3Si groups directly bound to the phosphorus atom, indicating Si–Si bond cleavage within the hypersilane motif. Whether this cleavage occurs primarily before or after the hydrosilylation is presently unclear.[41] Satisfyingly, upon optimisation, hydrosilylation *via* this procedure yielded the major reduced P_1 products in almost 80% combined yield (Scheme 6d, also see ESI, Table S6†). The hydrosilylation of P_4 was also achieved with other thiol derivatives, RSH (R = Cy, Ad, Ph, 4-MePh), and even with 1,4-cyclohexadiene (1,4-CHD; see ESI, Table S7 and Fig. S32–37†).[42,43] Optimisation studies revealed that the use of substoichiometric amounts of the hydrogen atom donor was detrimental to overall conversions. Additionally, other, less activated silanes R_3SiH (R = Ph, Et, Me_3SiO) were found to be ineffective, even when an excess of additive was used (see ESI, Table S8†).



Scheme 6 (a) Hydrosilylation of P_4 with $(Me_3Si)_3SiH$ in the presence of a hydrogen atom transfer donor, promoted by LED irradiation. Insets of the $^{31}P\{^1H\}$ (b) and ^{31}P (c) NMR spectra for the reaction of P_4 with $(Me_3Si)_3SiH$ (3.5 equiv. per P atom) and *i*Pr_3SiSH (3.5 equiv. per P atom) in hexane and driven by 365 nm LED irradiation, for the full version of the spectra see ESI, Fig. S30 and S31.† (d) Optimised conditions for the hydrosilylation of P_4 in the presence of *i*Pr_3SiSH, promoted by near-UV irradiation.

Functionalization of crude $[Si]_nPH_{3-n}$ mixture

Finally, we examined the reactivity of the crude phosphine mixture obtained from the hydrosilylation of P_4 in the presence of a HAT donor to access monophosphosphorus compounds in 'one-pot' transformations. Simple acidification with HCl (in 1,4-dioxane) resulted in the efficient cleavage of the P–Si bonds and the selective formation of PH_3 (**4**) with good conversion (≥64%; Scheme 7, top). Additionally, various phosphonium salts including $[Bn_4P]Br$ (**5**, isolated in 70% yield), $[Et_4P]Br$ (**6**, 54% conversion), and $[Bu_4P]Br$ (**11**, 40% conversion, marketed commercially as CYPHOS 442W) were also accessible directly from P_4 after reaction of the $[Si]_nPH_{3-n}$ mixture with the corresponding alkyl bromides and base (Scheme 7, middle). Furthermore, treatment of the hydrosilylphosphine mixture with paraformaldehyde in EtOH resulted in exclusive formation of the industrially relevant phosphonium salt THPC (tetrakis(hydroxymethyl)phosphonium chloride, **12**, 48% conversion) after quenching with HCl



Scheme 7 Functionalisation of crude $[Si]_nPH_{3-n}$ mixture into useful P_1 products directly from P_4. Equivalents are defined per P atom. (i) P_4 (0.25 equiv.), $(Me_3Si)_3SiH$ (2.25 equiv.), *i*Pr_3SiSH or 1,4-CHD (2.25 equiv.), PhMe, 365 nm LEDs, RT, 2d. (ii) One-pot, selective transformation of P_4 into PH_3 from crude $[Si]_nPH_{3-n}$: 10 equiv. HCl (4.0 M in 1,4-dioxane) RT, 1 (h). (iii) Preparation of phosphonium salts $[R_4P]Br$ from crude $[Si]_nPH_{3-n}$: 10 equiv. RBr (R = Bn, Et or Bu), 2.5 equiv. KHMDS, 100 °C, 3d. (iv) preparation of THPC from crude $[Si]_nPH_{3-n}$: EtOH, 12.5 equiv. paraformaldehyde, 50 °C, 2d, then 10 equiv. HCl (4.0 M in 1,4-dioxane), RT, 2h. [Si] = $(Me_3Si)_3Si$ or Me_3Si.

(Scheme 7, bottom). Although these new reactions generally require more forcing conditions than when starting from $(Bu_3Sn)_xPH_{3-x}$, they demonstrate that the $[Si]_nPH_{3-n}$ mixture has a similar potential to act as an efficient P_1 precursor and P^{3-} synthon.

Conclusions

We have described herein our studies into the fundamental reactivity of hydrogermanes and hydrosilanes towards P_4, as part of our mission to overcome safety concerns associated with the use of tributyltin compounds. Satisfyingly, the hydroelementation of P_4 is successful with both families of lighter homologues R_3EH. While our computational and experimental studies both reveal relevant differences in reactivity (which are related to the differing E–H bond strengths), these can be overcome through rational optimisation of the reaction conditions. Furthermore, these hydroelementation reactions yield similarly functionalisable $[E]_nPH_{3-n}$ mixtures which can serve as P_1 precursors for useful organophosphorus compounds in a 'one-pot' reaction. These results clearly show that the desired P_4 functionalisation is not limited to organotin derivatives and is in fact generalisable. Extrapolation from these results implies that extension to other known R_3SnH alternatives should be possible, many of which are known to compete well with R_3SnH in other contexts. Efforts in this direction are currently ongoing in our laboratories. Of particular interest to us is the extension of these results to more robust R_3SnH surrogates, to facilitate their recycling and reuse and/or catalytic application (*cf.* Bu_3SnH).[20] Besides the obvious efficiency benefits, such (pseudo)catalytic approaches would also remove the need for stoichiometric, 'upstream' Cl_2 use.**

Author contributions

JC and DJS developed the hydrosilylation and hydrogermylation procedures. MS performed preliminary experiments with different R_3GeH. JC performed the mechanistic calculations, developed the functionalisation of the crude $[R_3E]_nPH_{3-n}$ mixtures (E = Si, Ge) and the procedures for product isolation and characterisation. DJS and RW conceived, oversaw, and directed the project. JC and DJS prepared the manuscript, with input from all authors.

Data availability

The data supporting the findings of this study are available within the article and its ESI.† Crystallographic information for **1** has been deposited at the CCDC under 2408662.

Conflicts of interest

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

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